

# p- and n-type Fe-doped SnO<sub>2</sub> gas sensors fabricated by the mechanochemical processing technique

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## Abstract

Fe-doped SnO<sub>2</sub> sensors were fabricated using micromechanical synthesis technique. The Fe-doped sensor was compared to pure SnO<sub>2</sub>. Fe-doped SnO<sub>2</sub> responded as a p-type semiconductor to oxygen concentrations of up to 10% at 300 °C. As the temperature increased to 400 °C, the material responded as an n-type semiconductor. Furthermore, a higher surface area and smaller grains size diameters were achieved when doping SnO<sub>2</sub> with Fe. This translated into improved dynamic gas sensing properties and also improved responses to gases such as ethanol.

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## 1. Introduction

The use of electronic noses and sensor arrays are expanding in various fields such as human breath quality, wine quality, food oil, and coffee quality. For pattern recognition purposes, it is necessary to incorporate a span of different gas sensors (n- and p-type) in the electronic nose. By doping metal oxides, n- or p-type semiconductors can be formed and may be used as the sensitive material in chemical gas sensors. The type of semiconductor (p- or n-type) is not only a function of doping and material extrinsic properties, but is also dependent on the concentration of oxygen exposed to the semiconductor [1]. This effect is important when metal oxide gas sensors are used as “lambda sensors” for oxygen measurements in exhausts. In the preceding study, mechanochemical processing is used to synthesize pure SnO<sub>2</sub>, which is used as a “reference gas sensor” and Fe-doped SnO<sub>2</sub>. This study focuses on the materials gas sensing properties particularly to gases such as oxygen (O<sub>2</sub>), carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>) and ethanol vapour.

## 2. Experimental

The Fe-doped SnO<sub>2</sub> sensors were fabricated using the novel mechanochemical processing technique [2]. The reactant mixtures contained SnCl<sub>2</sub>, FeCl<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, with NaCl added as a diluent. The precursor concentrations were varied accordingly to give a final dopant concentration of 5 mol% Fe<sub>2</sub>O<sub>3</sub>. Following milling, the as-milled mixtures were subsequently heat treated at 600 °C in an air atmosphere, and finally washed in DI water.

The structure of the powders was examined using a Siemens D5000 X-ray diffractometer (XRD) with Cu K $\alpha$  radiation. Microstructural examination was performed using a JOEL 6300F field emission scanning electron microscope (FESEM). The surface area of the dried powders was measured using a Micromeritics Gemini 2360 BET surface area analyser.

The films were deposited using the spin coating technique onto alumina substrate transducers. The as-deposited films were annealed at 500 °C for 1 h. The sensor response to O<sub>2</sub>, CO, NO<sub>2</sub> and ethanol vapour was examined using a four-channel gas calibration system with a computerised picoammeter unit [3,4]. The flow was set at 0.3 LPM, the ambient temperature was 20 °C and RH 30%. The operating temperature was varied between 200 and 500 °C.

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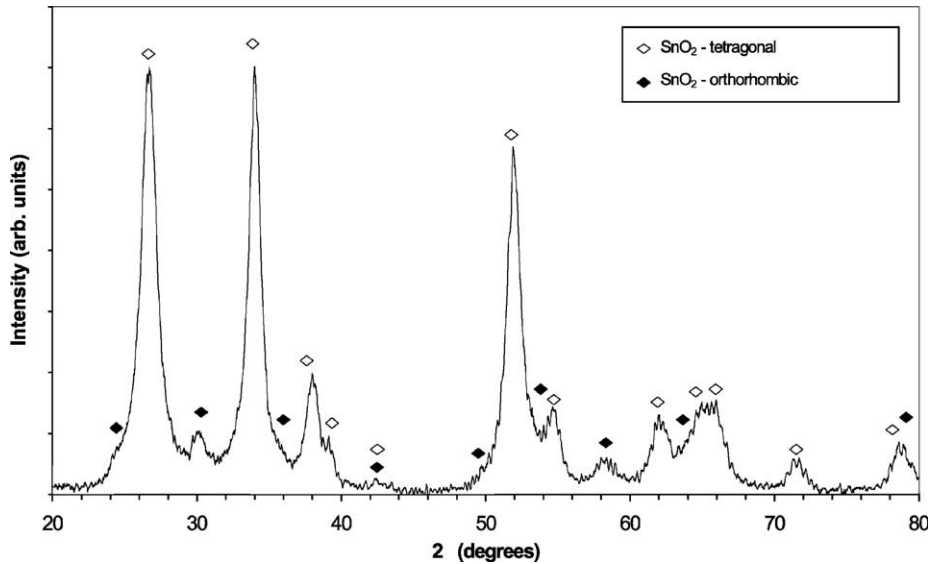


Fig. 1. XRD pattern of the SnO<sub>2</sub> powder doped with 5% Fe<sub>2</sub>O<sub>3</sub>, after heat treatment at 600 °C and washed.

### 3. Results and discussion

#### 3.1. Nanopowder analysis

The XRD pattern of the Fe-doped SnO<sub>2</sub> powder is shown in Fig. 1. Due to the low dopant concentration and to the solid solution formed, Fe<sub>2</sub>O<sub>3</sub> is not detected. Two phases of SnO<sub>2</sub> are present. The most dominant is the stable tetragonal phase, whilst the high-pressure orthorhombic phase is present to a lesser extent. The presence of both phases in ultrafine particles and thin films has been reported previously [3,4]. Fig. 2 shows a FESEM micrograph of the doped SnO<sub>2</sub> thin film. The film shows a uniform topography with even coverage of particles, but some small agglomerates also present. The Fe-doped SnO<sub>2</sub> powder has a surface area of 74.6 m<sup>2</sup>/g, which equates to an equivalent spherical diameter of 11.6 nm. However, calculating the crystallite size using Scherer equation [5] on the (1 1 0) tetragonal peak, the grain size was found to be 5.3 nm. Such a discrepancy could be explained by the presence of the agglomerates within the dried powder, as shown by the FESEM micrograph.

#### 3.2. O<sub>2</sub> gas sensing

Gas bottles with O<sub>2</sub> ranging from 100 ppm to 10% balanced with N<sub>2</sub> were used to test the sensors response ( $S = R_{\text{gas}}/R_{\text{baseline}}$ ) to O<sub>2</sub>. A total of 100 ppm of O<sub>2</sub> was used as baseline while the sensors were operated from 300 to 450 °C. From first measurements, it was shown that the Fe-doped films had a much higher resistance than that of the pure SnO<sub>2</sub> sensors. The baseline resistance at 300 °C was 2 GΩ for the Fe-doped sensor while the un-doped SnO<sub>2</sub> sensor had a resistance of only 5 kΩ. This complicated measurements since a large noise component was introduced into the Fe-doped sensor due this high impedance. Doping

SnO<sub>2</sub> with lower valency cations, such as Fe<sup>3+</sup>, increases the Debye length through a reduction in the carrier concentration, which increases the films resistivity. Since trivalent Fe<sup>3+</sup> acts as an acceptor type impurity, this could be expressed as:



where Sn<sub>Fe</sub> is Fe substitution in Sn sites, O<sub>0</sub> represents a lattice oxygen, V<sub>0</sub> represents lattice oxygen vacancies and O<sub>i</sub> represents interstitial oxygen. Therefore, the disappearance of electrons (increase in resistivity) can be expressed as:



From the results obtained, at an operating temperature of 300 °C, the Fe-doped SnO<sub>2</sub> sensor responded in a p-type fashion at O<sub>2</sub> concentrations up to 10%. Therefore, holes

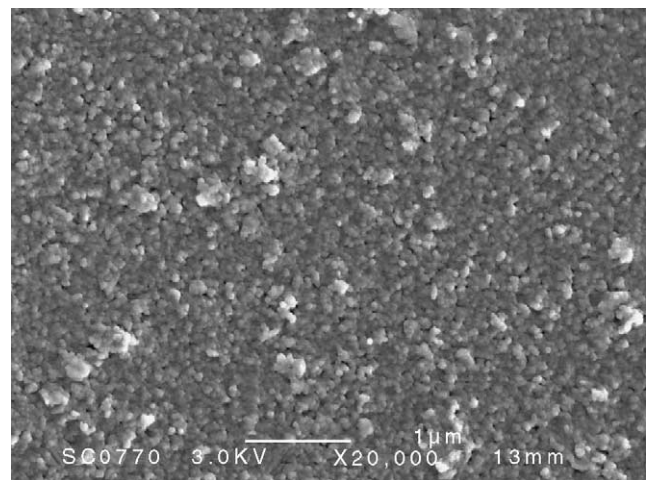
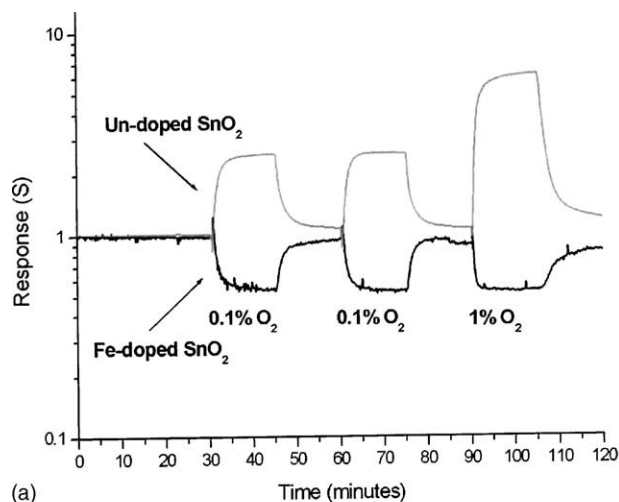
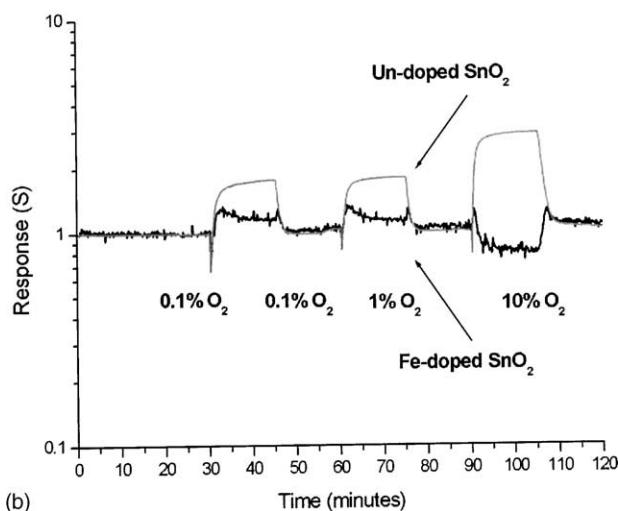


Fig. 2. An FESEM image of the doped SnO<sub>2</sub> spin coated films annealed at 500 °C.



(a)



(b)

Fig. 3. Sensors response to oxygen (100 ppm baseline) at (a) 350 °C and (b) 400 °C. The Fe-doped SnO<sub>2</sub> sensors remain responds with p-type behavior at 350 °C, however switches from p- to n-type between 0.1 and 1% of O<sub>2</sub> at 400 °C.

[h<sup>+</sup>] are indeed the majority charge carriers within the film. This behaviour was also apparent at 350 °C, as shown in Fig. 3a. Nevertheless, both sensors had repeatable gas sensing characteristics and consistently come back to baseline. The pure SnO<sub>2</sub> sensor had a response of 2.5 towards 1000 ppm of O<sub>2</sub>, while the Fe-doped sensor had a response of 1.8. However, as the operating temperature increases, a greater number of electrons jump into the conduction band from the valence band. This behavior is interestingly shown by the Fe-doped sensor operating at 400 °C, as shown in Fig. 3b. The Fe-doped sensor switches from p- (hole dominated) to n-type (electron dominated). This induces the two likely adsorption methods [6,7]:



However, as is highlighted in Fig. 3b, the film can switch back to p-type if there is enough oxygen molecules to adsorb

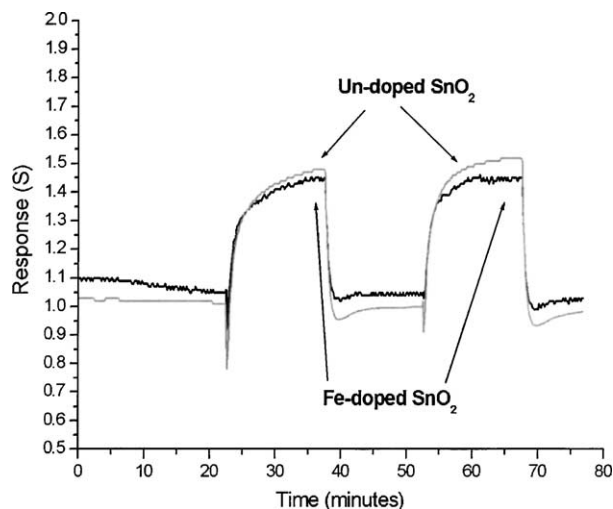


Fig. 4. Sensors response to 1000 ppm of oxygen (100 ppm baseline) at 450 °C. Both doped and un-doped SnO<sub>2</sub> sensors possess identical characteristics at 450 °C.

all the electrons in the conduction band, and hence, leave the film with holes as the majority carrier.

As the Fe-doped sensor is further increased in operational temperature, the film responds as a pure n-type semiconductor up to a concentration of O<sub>2</sub> of 10%. At this stage, as shown in Fig. 4, the gas sensing characteristics of both the doped and un-doped sensors are surprisingly identical.

### 3.3. CO, ethanol vapour and NO<sub>2</sub> gas sensing

The sensors were next exposed to CO, ethanol vapour and NO<sub>2</sub> balanced with synthetic air. The sensors were tested from 300 to 500 °C. Figs. 5a and 6a show the un-doped and Fe-doped sensors response at 300 °C, respectively. With respect to 500 ppm of CO gas, the un-doped sensor has a higher response of 2.2 compared to 1.6 for the Fe-doped sensor. However, the dynamic properties of the Fe-doped sensor is superior. For instance, the un-doped sensor has a response time of 280 s towards 500 ppm of CO while the Fe-doped sensor has only 49 s. Such an improvement in dynamic properties is related to the increased surface area (BET surface area, un-doped = 45.3 m<sup>2</sup>/g and doped = 74.6 m<sup>2</sup>/g) achieved by doping the SnO<sub>2</sub> with Fe which resulted in a smaller grain size (un-doped = 9.5 nm, Fe-doped = 5.3 nm).

Furthermore, the other major highlight is the response towards ethanol vapour. Towards 500 ppm of ethanol, the un-doped sensor has a response of 18 with a response time of 98 s, while the Fe-doped sensor is nearly one order more sensitive with a response of 109 and a response time of 42 s.

Such a dramatic increase in response shows the advantage of doping SnO<sub>2</sub> with Fe to be used as a gas sensor. However, the gas response of the un-doped film was indeed more sensitive towards NO<sub>2</sub> as shown. Figs. 5b and 6b also show the results of the sensors when operated at 500 °C. Similar outcomes prevailed as those reported at a temperature of 300 °C.

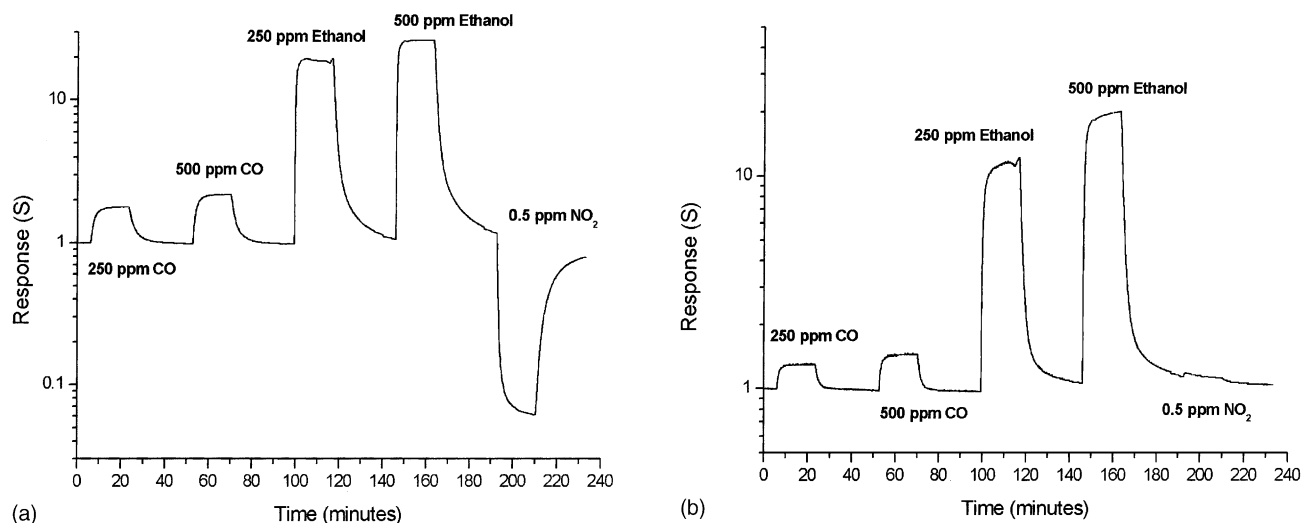


Fig. 5. Un-doped  $\text{SnO}_2$  sensor response to CO, ethanol vapour and  $\text{NO}_2$  at (a) 300 °C and (b) 500 °C.

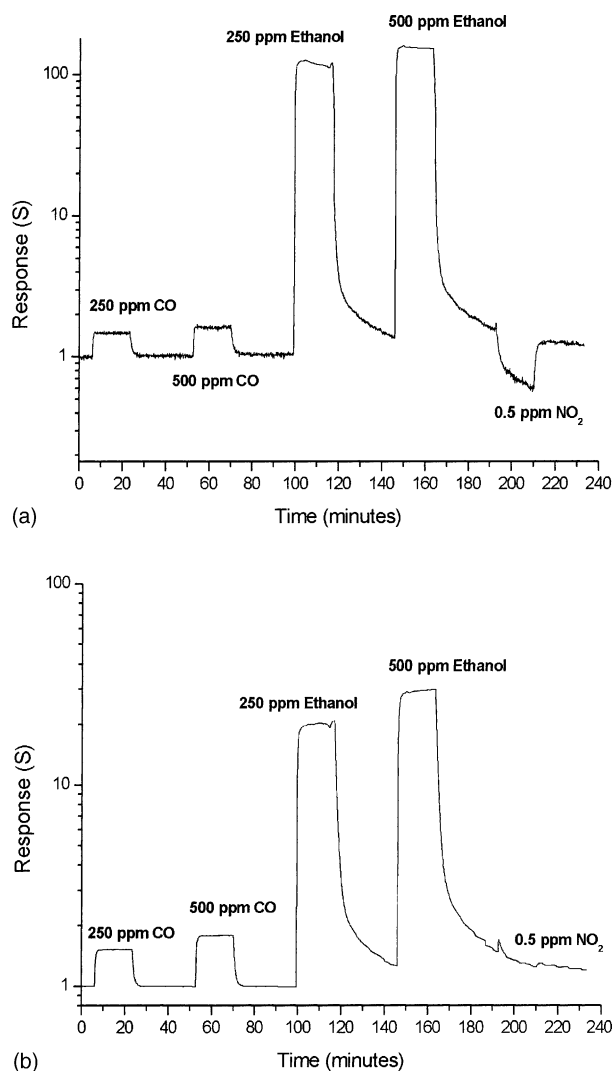


Fig. 6. Fe-doped  $\text{SnO}_2$  sensor response to CO, ethanol vapour and  $\text{NO}_2$  at (a) 300 °C and (b) 500 °C.

#### 4. Conclusions

The variation from un-doped  $\text{SnO}_2$  to Fe-doped  $\text{SnO}_2$  shows the potential in obtaining different semiconductor types (n- and p-type). The resistance of the sensor also changes, in this case increased to a high impedance in the  $\text{G}\Omega$  range which also introduced an unwanted noise component. Nevertheless, the p-type response to oxygen was clearly observed at various concentrations and operating temperatures. Furthermore, a higher surface area and smaller grains size diameters were obtained when doping  $\text{SnO}_2$  with Fe. This was successfully achieved via the mechanochemical synthesis approach employed. This translated into improved dynamic gas sensing properties related to the increased surface area (BET surface area, un-doped =  $45.3 \text{ m}^2/\text{g}$  and doped =  $74.6 \text{ m}^2/\text{g}$ ) achieved by doping the  $\text{SnO}_2$  with Fe, which resulted in a smaller grain size (un-doped = 9.5 nm, Fe-doped = 5.3 nm).

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