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Hydrogen sensors on the basis of SnO_2-TiO_2 systems

D. Shaposhnik[a]*, R. Pavelko[b], E. Llobet[a], F. Gispert-Guirado[a], X. Vilanova[a]

a Minos-EMAS, Department of Electronic Engineering, University Rovira i Virgili, Tarragona, Spain
b Institute of Physical Chemistry. University of Tübingen, Tübingen, Germany

Abstract

In this study we compare sensor responses to H_2 in air using two types of sensing materials: SnO_2 bulk doped with TiO_2 and mechanical mixtures of SnO_2 and TiO_2. The materials were analyzed in the broad range of working temperatures and H_2 concentrations. Thermal stability of SnO_2 bulk doped with TiO_2 was studied by in-situ XRD at 700°C.

Keywords: semiconductor gas sensor; hydrogen; tin oxide; titanium oxide; crystallite growth model

1. Introduction

Fast development of hydrogen-based technologies, including promising reports on hydrogen vehicles and fuel cells, give rise to a need for inexpensive and sensitive detectors of hydrogen leakages. Importance of hydrogen sensors was also sadly proved in atomic industry: both Chernobyl and Fukushima accidents were aggravated by hydrogen explosions. Another application of hydrogen detectors is early fire detection [1].

MOX sensors, being robust, compact and low-cost, are good candidates for H_2 detection. The promising sensing material for this purpose is SnO_2 bulk doped with TiO_2 [2]. It was shown in our previous study that SnO_2-TiO_2 oxide system manifest the highest sensitivity to H_2 in the presence of water vapors [3].

* Corresponding author. Tel.: +34-977-25-65-71; fax: +34 977-55-96-05.
E-mail address: dmitry.shaposhnik@urv.cat.

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2. Material preparation and characterization

Co-precipitation method, reported in [4], was used after modification to synthesize SnO_2 bulk doped with TiO_2. Tin(IV) hydroxide acetate and titanium (IV) isopropoxide were dissolved in glacial acetic acid in the molar ratio 9:1 (denoted as SnO_2-TiO_2). NH_3H_2O was used to cause hydrolytic precipitation of the oxides. Mechanical mixtures of blank oxides were prepared in the mortar using following SnO_2:TiO_2 molar ratios: 9:1, 4:1 and 2:1 (denoted as SnO_2:TiO_2).

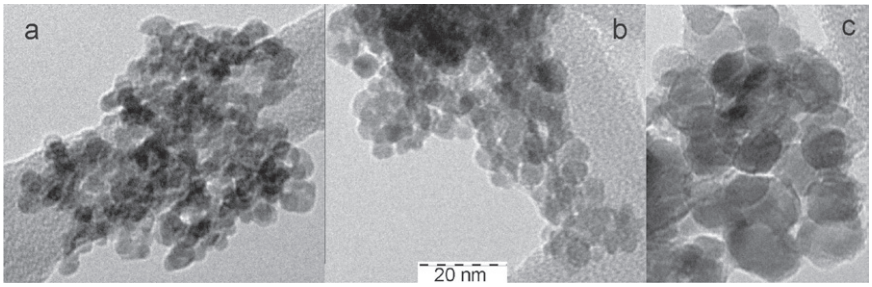

Fig. 1. TEM images of blank tin oxide (a), SnO_2-TiO_2 9:1 (b) and TiO_2 (c)

Figure 1 shows TEM images of some synthesized materials (performed on Jeol JEM 1011 at 100 kV). Mean particle size for blank SnO_2 was found to be close to 4 nm, while mean crystallite size for this material amounts to 2 nm. Both values are lower by ca. 1.5 times compared to SnO_2 bulk doped with TiO_2. In the case of blank TiO_2 the particles are notably larger, with size between 5 and 18 nm, and mean crystallite size about 6 nm.

Some of the synthesized materials were analyzed by means of FTIR spectroscopy (JASCO 680 Plus, KBr discs). As it can be seen, blank SnO_2 demonstrate the highest hydroxylation degree (Fig. 2). The later decreases remarkably for co-precipitated oxides and the lowest value was found for blank TiO_2. Preferential acidity of surface OH groups can be estimated from position of the peak maximum of ν_{OH} at ca. 3400 cm^{-1}. The latter shifts towards lower frequencies upon doping with TiO_2, suggesting that OH groups become more acidic. The same tendency is observed for molecular water at 1636-1624 cm^{-1}. As was established by XRD, co-precipitated SnO_2 and TiO_2 oxides are crystallized in cassiterite structure, as well as blank SnO_2 (Fig. 3).

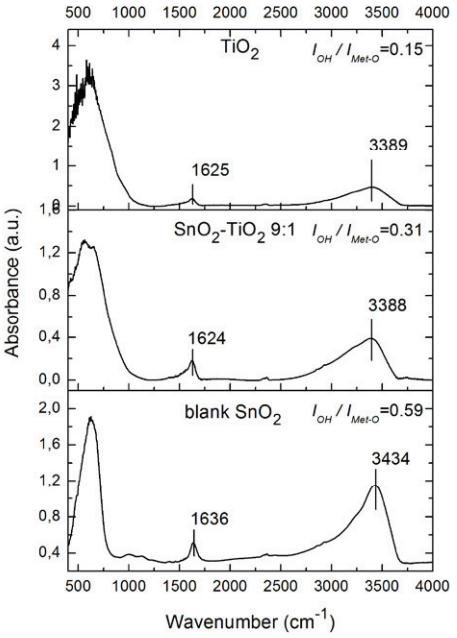

Fig. 2. FTIR spectra of some synthesized materials

Thermal stability of the co-precipitated oxides was compared with the one of blank oxide using TXRD technique (BRUKER D8 Discover). The patterns were recorded during 32 h of isothermal annealing at 700 ^oC in static air (Fig.3). Crystallite sizes were calculated with Scherrer formula and the TOPAS 4.2 software by fitting the entire profile (20-96º 2θ). The calculated values were plotted as a function of annealing time and analysed by grain growth model with size dependent impediment (Fig. 4, see ref. [4] and [5] for details related with the model).

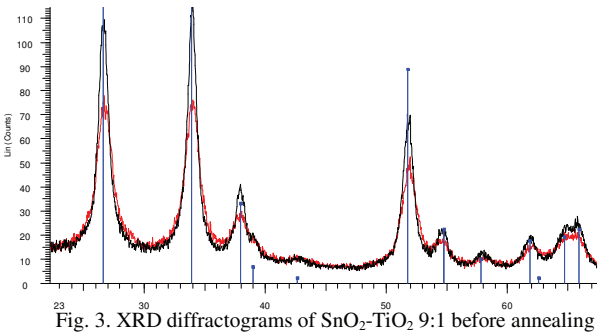

Fig. 3. XRD diffractograms of SnO_2-TiO_2 9:1 before annealing (red line), and after 32 hours heating at 700°C (black line). Marked peaks indicate cassiterite Bragg reflections.

As it was found in our previous studies [3], the doped material manifests lower thermal stability compared to the blank SnO_2. The growth rate constant is ca. 3 times higher for the former (4.4 against 12.1 nm^2/h). However, limiting crystallite sizes for both materials are rather close. The bulk doping with TiO_2 does not lead to abnormal crystallite growth, which was found for SnO_2 bulk doped with Pd.

The synthesized materials were mixed with organic vehicle and printed on ceramic sensor substrate with Pt electrodes and heather. The signals towards 20 ppm H_2 in

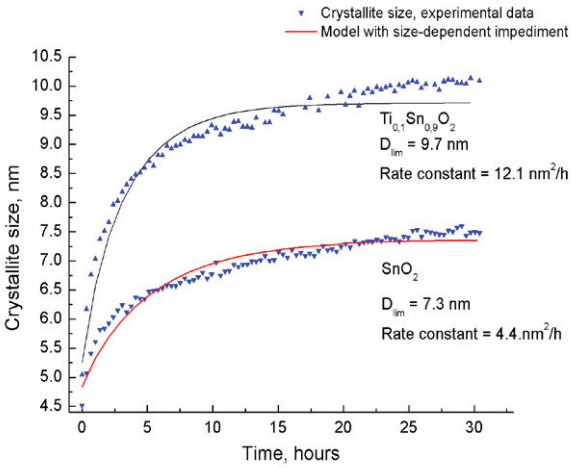

Fig. 4. Crystallite size evolution at 700°C calculated for SnO2-TiO2 9:1 and blank SnO_2. Experimental data (triangles) and model approximation (line)

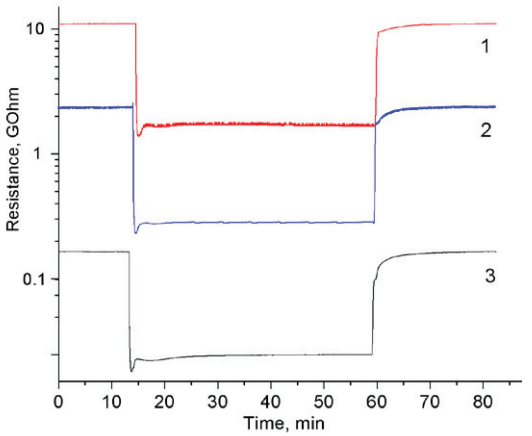

Fig. 5. Signals towards 20 ppm H_2 in air (400°C): 1 – SnO_2:TiO_2 4:1; 2 – SnO_2-TiO_2 9:1; 3 – blank SnO_2

dry air were measured at 300, 350, 400, 450 and 500°C. Some of the sensing materials were tested also to 1, 3, 10, 50, 200 and 500 ppm H_2 in air at operation temperature 400°C.

Figure 5 gives typical sensor responses to 20 ppm H_2 in air at working temperature 400°C. The sensors manifest rather similar response and recovery times, suggesting similar kinetics for the materials in question. The response time for all the sensors ranged from 12 to 14 seconds, while recovery time was between 4.5 and 5 minutes.

Signal values were calculated as resistance ratio: $(R_{air}\text{-}R_{gas})/R_{gas}$, where R_{air} is the resistance in pure air, and R_{gas} is the one in the presence of the target gas. Obtained results for the synthesized materials, operating at different temperatures, are summarized in Figure 6.

All sensing materials manifest signal maximum close to 400°C. The highest signal at 400°C was observed for SnO_2:TiO_2 4:1 and SnO_2-TiO_2 9:1. If we compare sensing signals of the latter with those of SnO_2:TiO_2 9:1 it becomes clear that co-precipitated oxides remarkably differ from their mechanical mixture with the same Sn:Ti ratio. Co-precipitation remarkably increases sensor signal, while mechanical addition of the same amount of TiO_2 decreases sensor signal. On the other hand, higher amount of TiO_2 (4:1) mechanically added to SnO_2 results in the highest sensor signal. This suggests that interphase

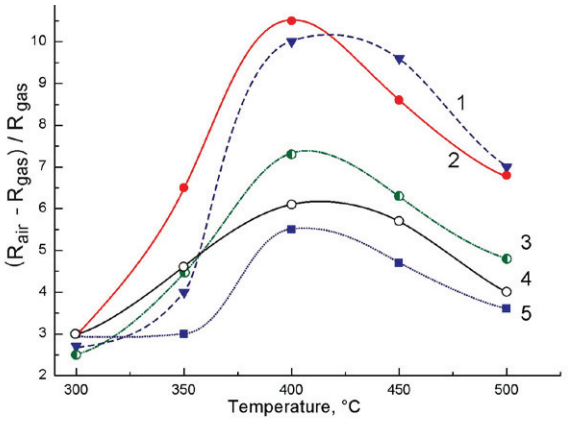

Fig. 6. Sensors responses to 20 ppm H_2 at various working temperatures: 1 - SnO_2-TiO_2 9:1; 2 – SnO_2:TiO_2 4:1; 3 – SnO_2:TiO_2 2:1; 4 – blank SnO_2; 5 – SnO_2:TiO_2 9:1

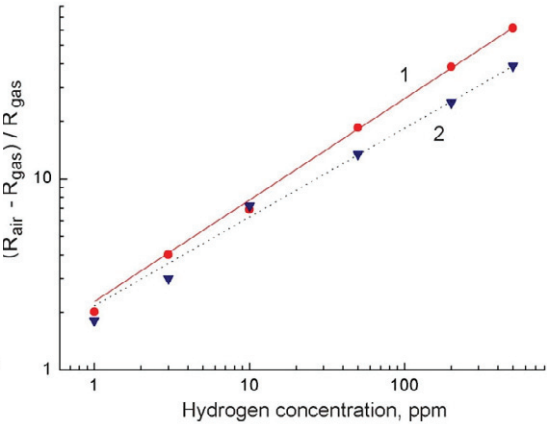

Fig. 7. Calibration curves: SnO_2-TiO_2 9:1 sensor (1) and SnO_2:TiO_2 4:1 sensor (2)

interaction between SnO_2 and TiO_2 oxides plays crucial role in the gas detection and seems to occur in both types of materials: co-precipitated and mechanically mixed.

Calibration curves were obtained for the materials with the highest signals towards 20 ppm H_2 (Fig. 7). Both materials manifest sensitivity with concentration exponents equal to 0.53 and 0.46 for SnO_2-TiO_2 9:1 and SnO_2:TiO_2 4:1, respectively. The close values again indicate similarity in the sensing mechanism, suggesting that sensing role is most probably played by the contacts between two phases.

3. Conclusions

Doping with TiO_2 seems to be efficient way to increase sensitivity of SnO_2 based materials towards H_2. Both co-precipitation and mechanical mixture of blank oxides results in increase of sensor signal towards 20 ppm H_2. However, for co-precipitated materials the increase is observed at lower quantity of TiO_2 (ca. 10 mol.%), compared to the mechanical mixtures (ca. 20 mol. % TiO_2 is needed). The obtained results indicate that sensing properties of the two-component systems are mostly determined by the interphase interaction. However, it is not still clear why small amounts of TiO_2 mechanically mixed with SnO_2 decrease the signal towards H_2. Thermal stability of the co-precipitated material was found lower, compared with blank SnO_2 oxide.

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