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Sensing mechanism of hydrogen sensors based on Pd loaded tungsten oxide (Pd-WO_3)

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Abstract

This paper presents a study on hydrogen sensing mechanism of Pd-loaded tungsten oxide nanocomposites (Pd-WO_3). The Pd-WO_3 nanocomposites were prepared and characterized by SEM, TEM, XRD and XPS analyses. The responses to 25-200 ppm hydrogen were measured at 50% relative humidity. The changes in the optical properties and crystal phases of Pd-WO_3 in contact with hydrogen were investigated by UV-Vis-IR spectroscopy and XRD. In-situ characterization were carried out at different conditions, 3% H_2 diluted in synthetic air/or nitrogen at temperatures ranging from 25 to 200°C. The changes in the crystal phases (formation of hydrogen tungsten bronze) in the surface or in bulk were correlated with the electrical responses. More experimental results and explanations will be presented and discussed.

Key words: WO_3, Pd-WO_3, hydrogen sensors, sensing mechanism.

Introduction

The sensing mechanism of gas sensors based on modified metal oxides by noble catalyst (NM-MO) is reported in the literature by several authors [1,2]. It is accepted that the mechanism is associated to the change of the resistance in contact with the chemisorbed oxygen and gases species on the surface of the metal oxide. In NM-MO such as (Pd-SnO_2), the catalyst on the surface of the metal oxide promote the oxygen species (O^-, O_2^-, O^{2-}) presented on the surface, resulting in an electrons depletion region on the surface of the sensor material. When the surface of gas sensor is exposed to reducing gases (CO, ethanol, methanol…ext.), the oxygen species react with the gases and electrons are feed back to the semiconductor, which increases the sensor conductivity.

For hydrogen, in addition to the reaction on the surface of the sensor between oxygen species and hydrogen, the catalyst dissociates H_2 which reacts with WO_3 to form blue tungsten bronze [1,2]. The formation of the tungsten bronze can be limited at the surface of the sensitive materials or in the bulk depending on the atmospheric conditions. In this work, Pd-WO_3 nanocomposites were prepared, the changes in the optical properties on the surface and crystal phases of Pd-WO_3 in contact with hydrogen were demonstrated in the surface and in the bulk of WO_3 depending on the atmospheric conditions. The effects of the temperature (from 27°C to 200°C), the catalyst (pure and modified Pd-WO_3) and the oxygen (in the air or in nitrogen atmospheres) on the electrical and optical properties were also studied.

Experimental

Pd-WO_3 nanocomposites were prepared and characterized [3], WO_3 nanoparticles were obtained by direct precipitation of 0.5 M Na_2WO_4 at 80°C in hydrochloric acid (3M). The resulting product was washed several times, dried and annealed in air at 400°C for 4 hours.

To prepare Pd-doped WO_3 coatings, palladium chloride salt was dissolved and dispersed in organic solvent (terpineol) with WO_3 nanopowder using sonication. The resultant dispersion with 2 wt% Pd loading was screen-printed on alumina substrates fitted with gold electrodes and platinum heating element [3].

WO_3 and Pd-WO_3 sensors were annealed at 400°C for 12 hours.

For gas sensing tests, the Pd-doped WO_3 coatings are heated at 200°C for 24 hours in ambient air before their exposition to the gases into a Teflon chamber (the setup is reported in reference [4]).

The response of the senor to 25-200 ppm hydrogen in air was measured at various relative humidities as reported previously [3]. Vis-NIR spectra in reflection of the same powders were also measured at room temperature and at 200°C in contact with 4000 ppm of hydrogen diluted in synthetic air. XRD using CuK_α radiation were carried out on the same powder from 27 to 200°C in contact with hydrogen as following: condition (I): 3 % hydrogen diluted in nitrogen and condition (II): 3% hydrogen diluted in synthetic air. XRD of pure WO_3 were also performed from 27 to 200°C in contact with 3% of hydrogen diluted in synthetic air or in nitrogen (conditions (I) and (II)).

Results and discussions

The electrical response to 25-200 ppm hydrogen is presented in Fig.1. It is well observed that the resistance of the sensors decreases once in contact with hydrogen. The changes in the resistance in contact with hydrogen can be attributed to two phenomena (I): the oxygen species chemisorbed on the surface of WO_3 reacts with hydrogen to form water vapor, the electrons trapped by oxygen feed back to the conductance band and (II): the dissociated hydrogen on the catalyst reacts with WO_3 to form hydrogen tungsten bronze. Both mechanisms result in an increase of the sensor conductivity. In this work, the mechanism (II) was observed on the surface of Pd-WO_3 in contact with hydrogen (4000 ppm of H_2 diluted in synthetic air). As shown on Fig. 3, the reflectance of Pd-WO_3 surface decreased from 40 % to 25 % at λ = 2000 nm. This color change is due to the reduction of W^{+6} to W^{+5} or W^{+4} on the surface. In the bulk, the XRD data showed that the diffusion of hydrogen and its insertion into WO_3 lattice is governed essentially by the presence of oxygen as explained afterwards. The XRD data presented in Fig.4 showed that Pd-WO_3 is transformed to H_xWO_{3-y} after 60 min of contact with 3% diluted hydrogen in nitrogen, no change is observed if Pd is not added. In the presence of oxygen (3% H_2 diluted in air), no change in the crystal phase is observed, the monoclinic WO_3 phase remains even after 16 hours at 200°C. Tab. 1 summarizes the change in the crystal phase of monoclinic WO_3 under different operating conditions. The tetragonal hydrogen tungsten bronze phase was observed only for NM-WO_3 in condition (I): temperature ranging from 27 to 200°C in contact with diluted hydrogen in nitrogen atmosphere. The modification of the optical spectra and no change of XRD mean that the formation of the bronze is limited to the surface when oxygen is present. It should be noted that no change in the crystal phase is observed of pure WO_3 for the two conditions (I) and (II).

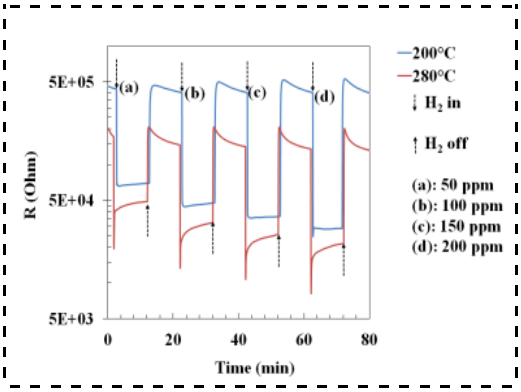

Fig. 1. Resistance changes of Pd-WO_3 films in contact with H_2 versus hydrogen concentration at 200 and 280°C (RH = 50%).

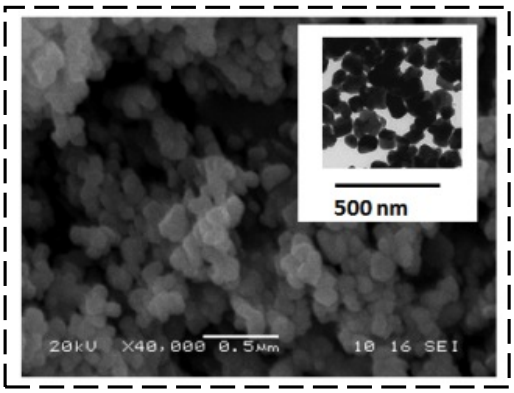

Fig. 2. SEM and TEM images of WO_3 nanoparticles annealed in air at 400°C for 4 hours.

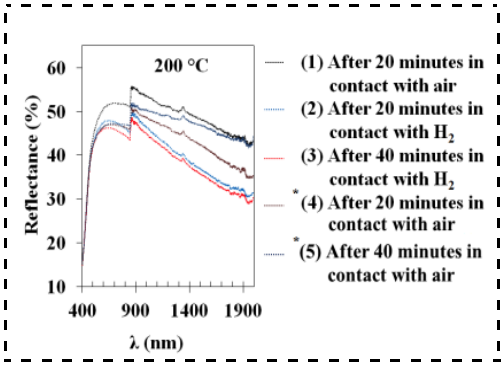

Fig. 3. Evolution of the reflectance of the Pd-WO_3 coatings in contact with H_2 in air at 200°C, (*) the tests were recorded after 60 minutes of contact with hydrogen.

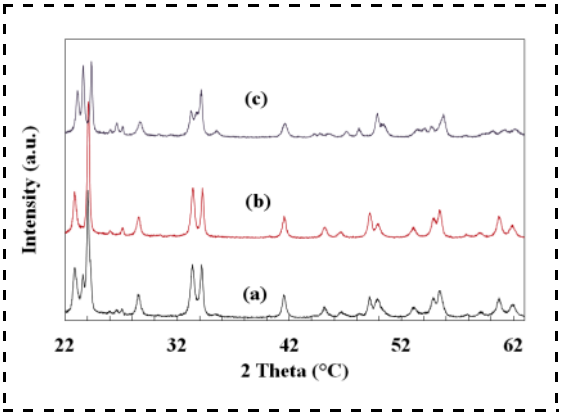

Fig. 4. XRD patterns of (a) monoclinic phase of pure WO_3 after 16 hours in contact with 3% diluted hydrogen in N_2; (b) formation of tetragonal hydrogen tungsten bronze in Pd-WO_3 after 60 minutes in contact with 3% diluted hydrogen in N_2 and (c) monoclinic phase of WO_3 in Pd-loaded WO_3 after 16 hours in contact with 3% hydrogen diluted in O_2.

Tab. 1: Summary of the change in the crystal phases obtained by XRD analysis of pure WO_3 and Pd-loaded WO_3 in contact with hydrogen (3% diluted hydrogen in synthetic air/or diluted in nitrogen).

T / °C	Sample	Atmospheres	Crystal phase
200	Pure WO_3	3 % of H_2 diluted in air	Monoclinic WO_3
27-200	Pure WO_3	3 % of H_2 diluted in N_2	Monoclinic WO_3
27-200	Pd-WO_3	3 % of H_2 diluted in air	Monoclinic WO_3
200	Pd-WO_3	3 % of H_2 diluted in N_2	Tetragonal H_xWO_3

Conclusions

Pd-loaded WO_3 nanocomposites were prepared and characterized. Thick films based on the prepared nanocomposites were fabricated and their sensing properties to hydrogen in the ppm level were measured under various conditions (temperatures and humidities). The sensors showed high performances (response, response time and recovery times) to hydrogen in the ppm level (50-200 ppm).

Hydrogen sensing mechanism of Pd-WO_3 was studied. In-situ characterizations of the changes in the crystal phases and the surface coloration (formation of hydrogen tungsten bronze) for different operating conditions were performed indicting the formation of a bronze with hydrogen in the surface but not in the bulk in presence of oxygen. These observations are attributed to the competition between reduction of W^{+6} to W^{+5} (formation of hydrogen tungsten bronze) and its oxidation (W^{+5} to W^{+6}). In the presence of oxygen, the oxidation is predominated. The sensing mechanism can be modeled. More experimental results and explanations will be presented and discussed.

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