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Use of zeolite films to improve the selectivity of reactive gas sensors

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Abstract

Semiconductor (Pd-doped SnO_2) gas sensors covered with zeolitic films (MFI or LTA) have been developed and used for gas phase sensing of different species (methane, propane, and ethanol) at different humidity levels. The dynamic responses obtained with these sensors were compared with the response of a reference sensor without a zeolitic layer. The results clearly indicate that a suitable zeolite layer strongly reduces, and in some cases suppresses, the response of the sensor to paraffins, thereby increasing the sensor selectivity to the alcohol, while the reference sensor could not discriminate between these molecules. This clearly shows the potential of zeolite-based sensors to achieve a higher selectivity/sensitivity in gas sensing applications.

Keywords: Semiconductor gas sensors; Pd-doped SnO_2; MFI and LTA zeolites; Hydrocarbons; Ethanol

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1. Introduction

Zeolites have pores of molecular size, which gives rise to strong molecule–pore wall interactions. These interactions are responsible for interesting applications of zeolites when they are prepared as films and membranes [1]. Thus for instance, zeolite membranes (including MFI, MOR, LTA, and FAU zeolites) are useful for separating mixtures of isomers and azeotropes [2]; as zeolite membrane reactors, they can increase the reaction yield by preferentially removal of an intermediate [3] or of a final [4] product. Also, zeolites (mostly LTA and FAU zeolites) have been employed to modify the surface of conventional chemical electrodes in order to increase their electroanalytical performance [5].

Zeolites have attracted increasing attention in the field of chemical sensor applications. Ten years ago, Yan and Bein [6] reported the coupling of silicalite crystals to the surface of quartz crystal microbalances (QCM); in this case, the regular micropores of the zeolitic material were found to effectively control molecular access to the device. Based on QCM technology, Yan and Bein [7] and Mintova et al. [8] have developed devices to sense ethanol (using zeolite MFI) and humidity (using zeolite LTA), respectively.

On the other hand, semiconductor gas sensors are widely used in domestic and industrial applications due to their characteristics as low-cost and robust devices. The sensor material usually contains SnO_2 as a base material, often doped with Pd, although many other metal oxides have also been advocated for this purpose. The working principle of these sensors is based on the change of conductivity that takes place after exposure to certain reducing gases,

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which react with chemisorbed oxygen. With n-type semiconductors such as SnO_2, adsorbed oxygen immobilizes the electrons near the surface of the SnO_2 particles. If a gas, such as a hydrocarbon, reacts with adsorbed oxygen, these electrons are released and the electrical conductivity increases (electrical resistance decreases). The main problem for state-of-the-art semiconductor gas sensors relates to the interference from other molecules, such as water or organic compounds, which are frequently present in the mixtures to be tested and contribute to the sensor response. This gives rise to a lack of selectivity, producing false alarms and errors in the concentrations measured by the detector. Recently, zeolites have been advocated as a means of increasing the selectivity of SnO_2 gas sensors: for example, layers of previously synthesized crystals of zeolites FAU and FER were formed to cover the sensing layer of La_2O_3–Au/SnO_2 sensors giving rise to ethanol filtering effects that increased CO selectivity [9]. On the other hand, it has also been reported that modified sensors prepared by mechanical mixing of SnO_2 with MCM-41 powder showed enhanced sensitivity to H_2 [10].

The aim of this work is to develop an improved sensor that can be used for a variety of gas phase species. To this end, a barrier containing zeolitic material will be deployed between the sensing element (Pd-doped SnO_2) and the gas atmosphere to be sensed. Ideally, depending on their specific interaction with the zeolite pores and on the operating conditions used, the passage of undesired molecules may be hindered and/or the concentration of the target species in the vicinity of the sensitive layer may be increased.

2. Experimental

2.1. Basic sensor (Pd-doped SnO_2) preparation

Fig. 1 shows a scheme of the sensors prepared, where the zeolite film can be seen covering a 2 mm × 3 mm Pd/SnO_2 layer that had been previously deposited on top of the measuring electrodes using a screen printing technique. SnO_2 nanocrystalline powders were first obtained by using a microwave energy source to heat a saturated $SnCl_4{\cdot}5H_2O$ solution in methanol. The Pd dopant was added in situ by introduction of $PdCl_2$ in the solution. The amount of Pd on SnO_2 was 1% (nominal, Pd/Sn). For this process, a specially modified microwave oven was used with a wavelength of 2.45 GHz and a power up to 1 kW. Maximum irradiation time was 10 min. Further stabilization treatment with conventional thermal annealing was applied for 2 h at 450 °C. To obtain sensor devices, the Pd-doped SnO_2 powders were coated on alumina substrates with printed Pt electrodes. After this, a short thermal treatment (700 °C for 1 h) was necessary to stabilize the mechanical properties of the layer. Additional details are given elsewhere [11,12].

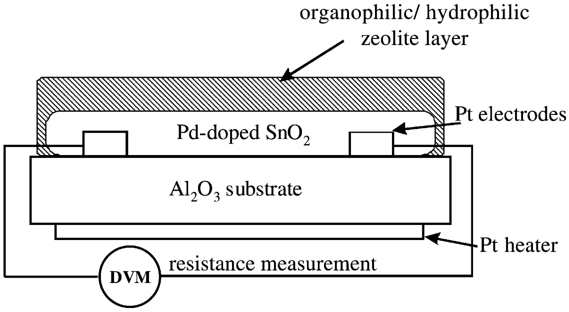

Fig. 1. Modified Pd-doped SnO_2 sensor scheme, where DVM is the digital voltmeter.

2.2. Synthesis of zeolite layers on Pd-doped sensors

MFI (silicalite) films were synthesized on Pd-doped SnO_2 sensors. Firstly, in situ seeding was carried out by placing the sensors in a Teflon-lined stainless steel autoclave at 130 °C for 2 h with a mixture of the following composition: 10 SiO_2:2.4 TPAOH:1 NaOH:110 H_2O [13], where TPAOH, the structurant agent, is tetrapropylammonium hydroxide. This first synthesis originated a homogeneous coating of nanocrystals (ca. 150 nm) of silicalite, covering the whole surface of the Pd-doped SnO_2 surface, as will be shown later. Secondly, the seeds were grown into a continuous crystal layer by in-situ hydrothermal treatment at 175 °C for 18 h in a synthesis gel of composition: 1 TPABr:4.5 TEOS:1 KOH:1000 H_2O [14], where TPABr is tetrapropylammonium bromide and TEOS tetraethylorthosilicate. In both cases the autoclave was heated in a convection stove. After the synthesis, the samples were washed with deionized water, then dried and calcined at 480 °C for 8 h to remove the structurant agent. The heating and cooling rates of the calcination process were 0.5 and 1 °C/min, respectively.

LTA (zeolite NaA) films were synthesized on Pd-doped SnO_2 sensors. Sensors were first seeded by rubbing with commercial NaA zeolite crystals with an average particle size close to 1 μm. Hydrothermal synthesis was then carried out at 80 °C for 5 h in a Teflon-lined autoclave filled with a clear solution of molar composition: 80 Na_2O:1 Al_2O_3:9 SiO_2:5000 H_2O [15]. After crystallization, the sensor was removed from the solution, washed with deionized water until neutral pH, and dried at 50 °C. The hydrothermal synthesis was repeated three times in order to obtain continuous films.

The samples obtained were characterized by SEM (JEOL, JSM-6400 operating at 20 kV) and XRD (Rygaku/Max System, Cu Kα $\lambda = 1.5418$ Å, 2θ).

2.3. Sensor testing system

The sensor responses were measured in an experimental setup similar to that described in Ref.[12]. A mass-flow controlled air stream (200 cm^3 (STP)/min) containing a certain concentration of the desired organic compound was fed to a measuring chamber capable of holding up four sensors. The organic gases tested were methane (500 and 2500 ppm), propane (250 to 2500 ppm) and ethanol (10 and 50 ppm) with sensor exposures of 30 min at each new concentration. In the same way, the desired degree of humidity in the measurements could be achieved by passing part of the feed stream through a saturator filled with deionized water.

The sensors were stabilized for 12 h at the experimental conditions prior to sensor response measurements. The nominal sensor temperature (always 350 °C in this work) was kept at the desired value by means of a Pt heater printed on the sensor back side. A thin thermocouple was fixed very close to the active layer by means of a ceramic glue, allowing a direct monitoring and control of the sensor temperature. Resistance measurements were made by a multimeter (Fluke 8840A) connected to the Pt electrodes printed at the base of the Pd-doped SnO_2 layer (see Fig. 1). The flow rates of the different gases, the measuring point temperatures and the sensor responses were continuously monitored by a computer-controlled data acquisition system.

3. Results and discussion

3.1. Synthesis of zeolite layers

XRD characterization (see Fig. 2) of the zeolite films prepared onto the Pd-doped SnO_2 layers (supported on alumina) confirmed that pure silicalite and zeolite NaA layers were synthesized for the MFI and LTA-modified gas sensors, respectively.

Fig. 3a shows a top view of the surface of the Pd-doped SnO_2 before coverage with a zeolite layer. Cirera et al. [12] have found by TEM analysis that the particle size of the undoped material, after treatment at 1000 °C (i.e., a higher temperature than that used in this work), is about 60 nm, although some increase is expected upon doping. Fig. 3b shows the same sensor surface after deposition of silicalite seeds. It can be seen that the silicalite particles have a homogeneous size of approximately 150 nm and look like those prepared in similar conditions and coated on alumina [14] and stainless steel substrates [16].

Growth of the zeolite seeds gives rise to a silicalite polycrystalline layer with a columnar structure that exhibits preferential c-orientation (see Fig. 3c and d corresponding to the top and cross-section views, respectively), in agreement with the results of Xomeritakis et al. [14]. In the present study, the continuous

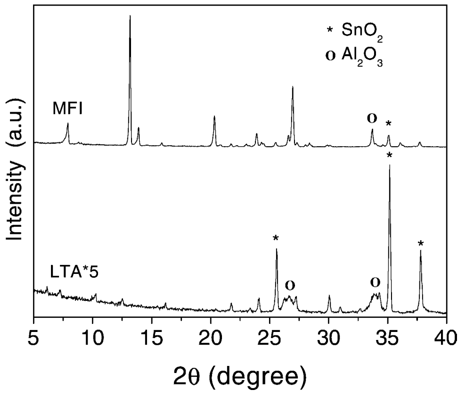

Fig. 2. XRD patterns of zeolite films grown on alumina substrates with Pd/SnO_2 layers.

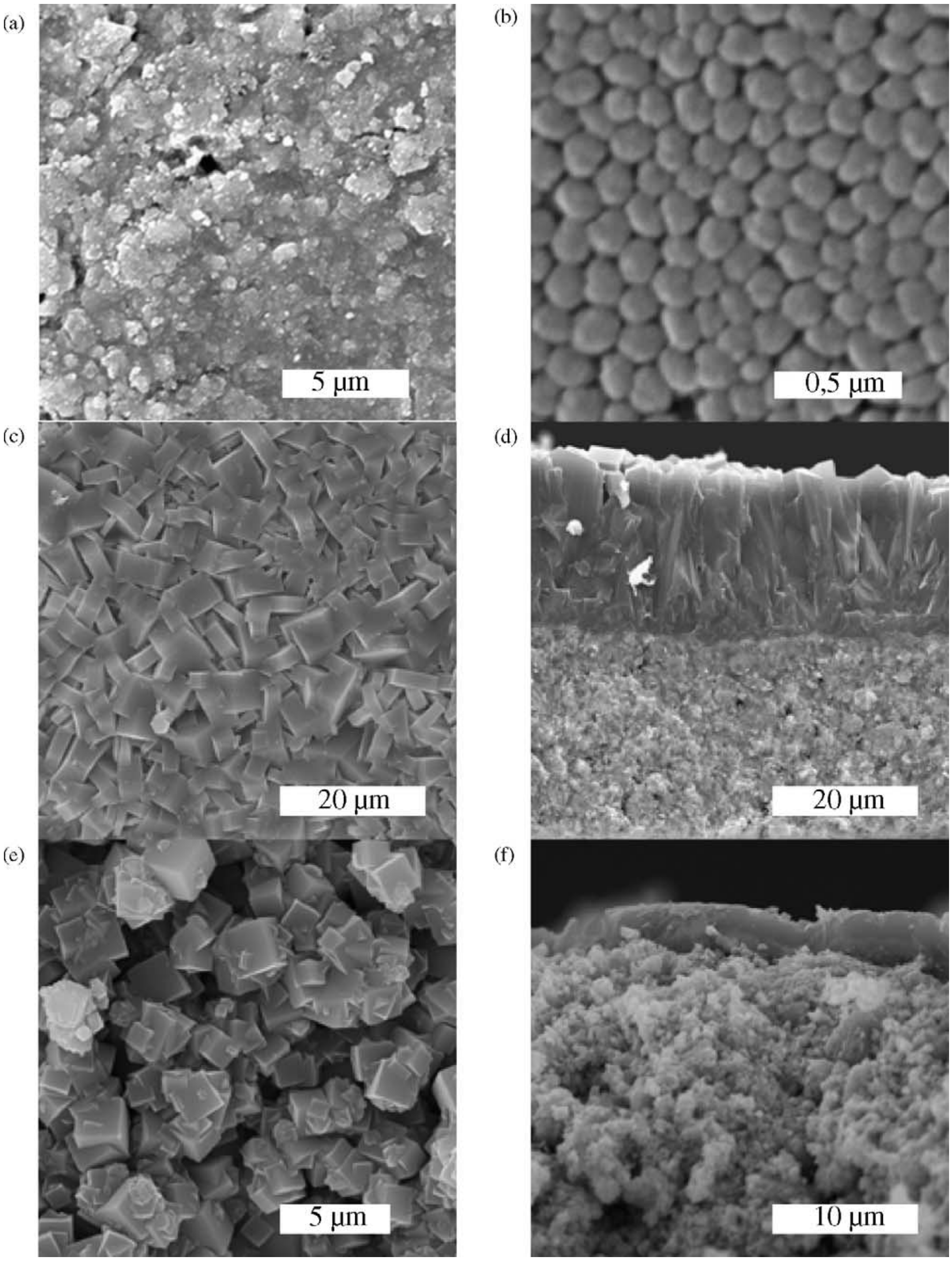

Fig. 3. SEM images: (a) top view of a Pd-doped SnO_2 sensor, (b) top view of a sensor surface after seeding with silicalite crystals, (c) top view of a silicalite film grown on a Pd-doped SnO_2 layer, (d) cross-section of a silicalite film on a Pd-doped SnO_2 layer, (e) top view of a zeolite NaA film on a Pd-doped SnO_2 layer, and (f) cross-section of a zeolite NaA film on a Pd-doped SnO_2 layer.

MFI (silicalite) layer on the Pd/SnO_2 surface is approximately 20–25 μm thick. In the case of the sensors modified with zeolite A films (Fig. 3e and d), although the SEM micrographs of the cross-section show the existence of a 2–3 μm thick layer of zeolitic material, its quality, in terms of intergrowth (see the top view) and continuity, seems to be clearly lower than that of the silicalite layer.

3.2. Comparison between sensors

Fig. 4a shows the response of three different sensors to different concentrations of methane and ethanol at 0% of relative humidity in the feed. The nomenclature used is as follows: reference for the "as made" Pd-doped SnO_2 sensor; MFI, for the Pd-doped SnO_2 sensor after deposition of a silicalite film on the top surface; LTA, for the Pd-doped SnO_2 modified with a film of zeolite NaA. The sensor sensitivity is defined as the ratio between decrease of electrical resistance in the presence of the testing compound and the resistance corresponding to pure air. Thus, in the presence of a hydrocarbon, highly sensitive sensors will display a large drop of resistance with respect to the baseline signal in air. With the reference sensor, it can be seen that for methane a sensitive response is obtained, that depends on the methane concentration. Therefore this reference sensor could be used to measure methane concentrations in binary mixtures with air. However, the response of the reference sensor also shows sensitivity to other organic molecules. Thus, it can be seen that the signal obtained in the presence of 10 ppm of ethanol is similar to that of 500 ppm of methane. Therefore, the sensor cannot be used to measure methane if other organic molecules may be present, even at trace concentration levels.

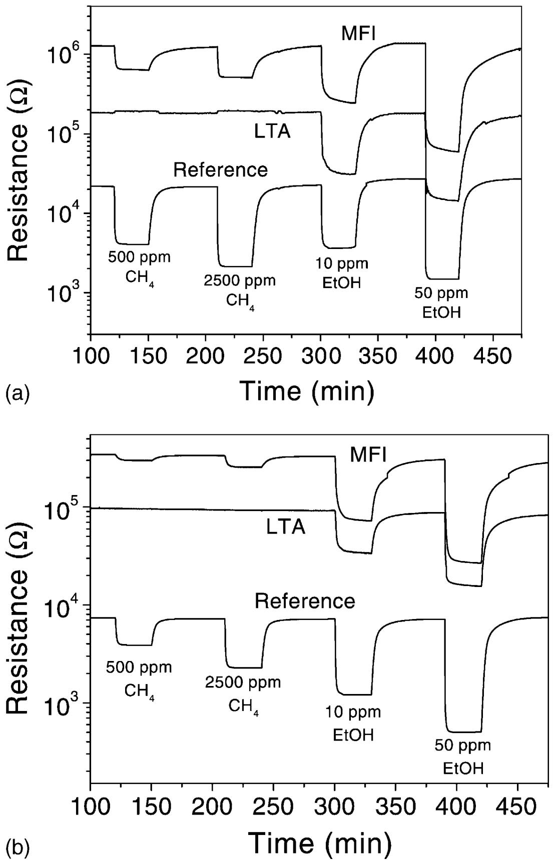

Fig. 4. (a) Sensor resistance as a function of the nature (methane or ethanol) and concentration of the organic compound. Testing at 350 °C with (a) 0% and (b) 50% of relative humidity in the feed, for the reference (unmodified) sensor and for sensors modified with silicalite and zeolite A layers.

The response of the sensors modified with MFI and LTA films is significantly different. For the MFI sensor it can be seen that the sensor sensitivity with respect to methane is roughly halved, while there is little effect on the response to ethanol. This can be explained as a result of the increase in the diffusion resistance for methane caused by the MFI layer, hindering the access of methane to the sensing region. Although the increased diffusion resistance also works for ethanol, the interaction of the alcohol with the MFI membrane is considerably stronger, and the surface flux contribution is able to compensate the diffusion resistance. This is not possible for methane, a molecule with a much weaker adsorption on MFI membranes. As can be seen in Fig. 4a, the best results were obtained with the LTA-modified sensor. In this case, the response of the LTA sensor to methane is practically suppressed, while the response to ethanol is approximately maintained. This could be explained as a direct consequence of the hydrophilic character of the zeolite NaA. During sensor operation, organic compounds react on the Pd-doped SnO_2 catalyst, producing water that adsorbs on the LTA layer. Adsorption certainly decreases with temperature, but would nevertheless be present even at the operating conditions used in this work. This adsorbed water would hinder the path of methane towards the sensing plane, strongly decreasing the sensor response to methane. Ethanol, a polar organic compound would be able to compete with water under the conditions used and still reach the sensing plane, giving rise to the resistance drop observed in Fig. 4a. At lower temperatures the access of ethanol would also probably be blocked, (in fact zeolite NaA membranes, are industrially used to dehydrate water/ethanol mixtures [17]). However, at the temperatures used (near 350 °C) a steady flow of ethanol would still be able to reach the sensing surface. When the same experiment was repeated in the presence of a higher concentration of water in the gas phase (50% relative humidity, Fig. 4b), the response to methane was still null, but the response to ethanol decreased. This would be in agreement with the above hypothesis, since under these conditions the surface flux of ethanol would decrease (water would displace ethanol from adsorption sites) and its access to the sensor would be reduced.

Fig. 5 compares the response of the three sensors to propane and ethanol. The same trends as with methane can be observed, although with propane the effect of introducing the MFI layer is smaller, in keeping with the fact that propane is capable of adsorbing much more strongly than methane on MFI zeolites. For the LTA sensor it can again be observed that the introduction of the zeolite A layer completely suppresses the sensor response to propane. The results found for the LTA sensor are very encouraging, as they suggest that the signal suppression with zeolite NaA films observed for methane and propane can probably be extended to a wide variety of hydrocarbons.

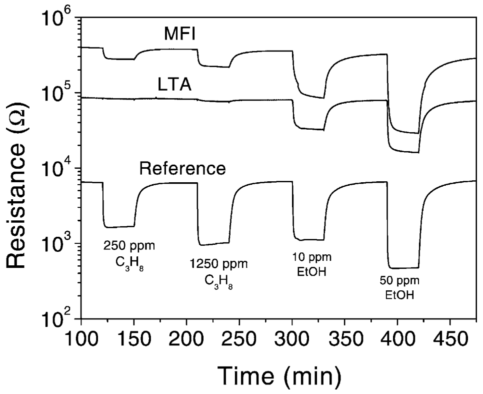

Fig. 5. Sensor resistance as a function of the nature (propane or ethanol) and concentration of the organic compound. Testing at 350 °C with 50% relative humidity in the feed for the reference (unmodified) sensor and for the sensors modified with silicalite and zeolite A layers.

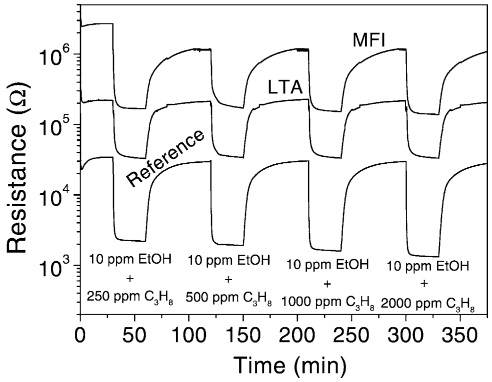

Fig. 6. Responses of the different sensors in the presence of propane/ethanol mixtures. Testing at 350 °C without humidity in the feed.

Finally, some of the results obtained with mixtures are shown in Fig. 6. In this case the concentration of ethanol was kept constant (10 ppm), while that of propane was progressively increased. It can be seen that the signal obtained with the reference sensor clearly reflects the contribution from both species, with a drop of electrical resistance related to the concentration of propane. With the MFI-modified sensor, the sensitivity of the sensor to propane is decreased, although some contribution can still be ascertained. However, the objective of eliminating the interference of propane is fully achieved with the LTA-modified sensor, even at propane concentrations that are 200 times greater than that of ethanol.

4. Conclusions

The use of zeolite films allows the preparation of semiconductor (SnO_2-based) sensors with improved sensitivity. The addition of zeolite layers reduced (MFI) or even eliminated (LTA) the sensor response to hydrocarbons (methane and propane). Based on these results, sensors could be designed to detect ethanol, and possibly other low molecular weight polar organic compounds (such as methanol, propanol, formaldehyde, acetaldehyde, acetone, acetic acid, etc.) in the presence of hydrocarbons. However, more experimental work is needed in order to fully elucidate the sensing mechanism of zeolite modified gas sensors.

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