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# Gas detection with $SnO_2$ sensors modified by zeolite films

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**Abstract**

Zeolite films have been grown on top of $SnO_2$ sensors to modify their response to gas phase molecules with the aim of improving their selectivity. To this end $SnO_2$ sensors were first prepared using conventional procedures, and then zeolite layers (silicalite and zeolite A) were grown on the outer $SnO_2$ surface, using different synthesis procedures. The zeolite-modified sensors were tested in the analysis of single gases ($H_2O$, $H_2$, CO, $CH_4$, $C_3H_8$, and $C_2H_5OH$, at concentrations from 20 to 10,000 ppm) and mixtures, and their response was compared with that of uncoated $SnO_2$ sensors. The zeolite-coated sensors were able to suppress the response towards certain analytes, while maintaining or even improving the sensitivity towards others. The differences in sensor behaviour and the improvement of sensor selectivity increased with the quality of the zeolite layer. The best zeolite films were obtained on $SnO_2$ layers pretreated at 450 °C, in which the external surface had a lower roughness.

*Keywords:* Silicalite; Zeolite A; Zeolite films; Tin oxide sensors; Gas sensor selectivity

## 1. Introduction

Semiconductor gas sensors are widely used in domestic and industrial applications due to favourable characteristics such as low cost and robustness. For $SnO_2$, one of the most widely used sensor materials [1,2], the working principle is based on the change of conductivity that takes place after exposure to gases capable of reacting with chemisorbed oxygen. Since adsorbed oxygen immobilizes electrons near the surface of n-type semiconductors such as $SnO_2$, when a gas (e.g., a hydrocarbon) reacts with and removes adsorbed oxygen, these electrons are released and the electrical conductivity increases [3,4]. These reactions generally take place at temperatures in the range 150–600 °C and therefore the sensor must be heated to obtain a suitable response.

The main problem of these sensors is their inherent lack of selectivity. Many gas phase compounds, such as steam and a variety of organic molecules, can contribute with different intensities to the sensor response, thus posing serious challenges for the analysis of mixtures. The analysis of specific gases in air is thus possible only when the interfering molecules are present in sufficiently low amounts. To overcome the lack of selectivity in semiconductor sensors, several strategies have been proposed:

(i) Use of different working temperatures: since for a given sensor the maximum sensitivity to different gases generally occurs at different temperatures [5], it is reasonable to devise a strategy based on a battery of sensors that operate at different temperatures. Thus, $SnO_2$ gas sensors working at low temperatures (250 °C) can be used to detect CO, while detection of methane requires higher temperatures (450 °C) [6,7].
(ii) Use of additives (e.g., Pt, Pd, Au, Al and other metals) that increase the sensitivity to some gases and decrease the detection temperature. Pd or Pt doping of $SnO_2$ gives a higher sensitivity to CO [8], while Ru can be used to improve $NO_2$ detection [9].
(iii) Use of filters: adsorbent barriers can be placed between the sensor surface and the atmosphere to be analyzed, with the aim of selectively retaining some analytes and/or interfering compounds. The commonest filter is a bed of active carbon where, depending on the temperature, selective

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adsorption of some molecules becomes possible. However, this procedure has to face the problems of a limited applicability (the adsorbent material must be selective towards the desired molecules) and the need for periodic regeneration or replacement [10].

The present work deals with the last group of strategies (filters as a means to increase sensor selectivity), and uses zeolites as the filter material in view of their specific properties. Zeolites are crystalline microporous materials with pores of molecular size that give rise to strong molecule–pore wall interactions. When prepared as films or membranes, these interactions are responsible for remarkable results in separation and reaction applications [11,12]. From the point of view of their use in gas sensors it is also interesting to note that zeolite films and membranes can give rise to selective separations even when the target gas phase species are present at trace concentration levels [13,14].

In view of their favourable characteristics, the use of zeolites in conjunction with analytical devices (electrodes and sensors) has been proposed in the past as a method to improve the sensitivity or selectivity of analysis. Thus, zeolite-modified electrodes (ZME) have been used in a variety of electrochemical detection procedures which are generally applied in the liquid phase (e.g., Refs. [15,16]). While application of zeolites to gas sensing is less frequent, a number of zeolite-modified gas sensors can be found in the literature. Zeolite crystals have been deployed as a barrier between the sensor and the gas mixture to remove interfering species in different processes. Thus, Hugon et al. [17] used high-Al mordenite crystals as a filter that adsorbed interfering ethanol, allowing the detection of methane or *n*-hexane, and Kaneyasu et al. [18] used a bed of zeolite NaY to minimize the interference of CO and ethanol in the detection of $CO_2$ with a solid electrolyte sensor. In a different approach, Fukui and Nishida [19] eliminated the interference of ethanol by using zeolites as a catalyst rather than as an adsorption barrier, thus avoiding the need for adsorbent regeneration. These authors deployed ferrierite crystals on the sensor surface that, at the sensor working temperature (300 °C), acted as a catalyst to convert ethanol to ethylene, which was not detected. Similarly, Szabo and Dutta [20] used a filter made of Pt/zeolite Y powder to equilibrate $NO + N_2O$ mixtures and fully oxidize CO, thus minimizing interferences in the analysis of $NO_x$ with YSZ sensors. Muller and Lange [21] used a gas detection system based on a set of MOS sensors coated with layers made of zeolite particles precipitated from solution which would act as gas filters, then proposed an operational algorithm to differentiate among the patterns obtained from different gases. Rauch and Liu [22] synthesized zeolite membranes in an attempt to impart selectivity to mixed-conducting amperometric sensors. While the effectiveness of the membrane was limited by the formation of cracks, they were able to maintain a good sensitivity to oxygen while limiting the response of the sensor to carbon dioxide.

On the other hand, instead of removing interfering compounds, the intrinsic selectivity of zeolite crystals can also be used to provide sensitivity towards the target molecules in a mixture. This is the case of zeolite-loaded mass sensors (surface acoustic wave (SAW), quartz crystal microbalance (QCM) and cantilevers) that detect a mass change when the desired molecules adsorb in a suitable zeolite (e.g., Refs. [23–26]), and of capacitive sensors (e.g., Refs. [27,28]) where zeolites are placed between the electrodes to facilitate sensing based on the changes of sensor impedance that take place upon adsorption of the target gas phase species.

In a previous work [29], we proposed for the first time the use of continuous zeolite films as low-inertia filters in $SnO_2$ sensors. To this end, relatively thin (5–30 μm) films of zeolite were grown directly on the $SnO_2$ surface. The initial results indicated that zeolite layers could be used effectively to increase the selectivity of $SnO_2$ sensors. Additionally, these zeolite-coated sensors were able to operate continuously, without the need for a regeneration step. In this work, we have continued the study of zeolite-modified $SnO_2$ sensors in an attempt to gain further insight into the mechanisms leading to the observed increase of selectivity. Two types of zeolitic coatings have been investigated, namely, silicalite (MFI-type structure), a siliceous zeolite with a two-dimensional pore network (0.51 nm × 0.53 nm and 0.53 nm × 0.56 nm channels), and zeolite A (LTA-type structure), an aluminosilicate zeolite with a low Si/Al ratio and a three-dimensional network with circular channels of ca. 0.4 nm diameter. Here, we present the preparation procedures for both types of zeolitic films on top of the $SnO_2$ layers, study their characteristics and attempt to relate them to the behaviour of the modified sensors.

## 2. Experimental

### 2.1. Sensor preparation and characterization

The basic (i.e., uncoated) sensor was prepared as described previously [1]. Briefly, nanometric $SnO_2$ powder was obtained by microwave synthesis starting from a saturated tin chloride solution in methanol. The Pd dopant was added *in situ* by introducing the required amount of $PdCl_2$ in the solution to give the desired Pd concentration (nominally a Pd/Sn atomic ratio of 0.01). After synthesis, the powders were subjected to a stabilization thermal treatment in air for a period of 6 h, at temperatures ranging from 450 to 800 °C. The support of the sensor was an alumina slab (4 mm × 19 mm), on both sides of which Pt-wire circuits had been printed. The circuit at the top side was meant as an electrode, while the one at the back acted as the sensor heater. A 2.5 mm × 4 mm layer made of the Pd-doped $SnO_2$ powder was then screen-printed on top of the Pt electrode. Fig. 1 shows the general appearance of the basic sensor after depositing the $Pd/SnO_2$ layer on one side.

Once the basic sensor had been prepared, a zeolite layer was grown on top of the $Pd/SnO_2$ layer by means of a secondary (seeded) synthesis method. The composition of the gels used and the synthesis conditions employed for the different preparations are given in Tables 1 and 2, respectively. The synthesis was carried out once the $Pd/SnO_2$ surface had been covered with the zeolite seeds in a previous seeding step. For silicalite films, the seeding process was carried out either by dip-coating of previously synthesized zeolite seeds, or by carrying out a short preliminary synthesis, using a gel with a composition adjusted