

# Simplified models for SnO<sub>2</sub> sensors during chemical and thermal transients in mixtures of inert, oxidizing and reducing gases

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## Abstract

In this work, a set of models able to predict the behavior of tin oxide (SnO<sub>2</sub>) sensors during chemical and thermal transients is presented. These models are obtained through simplification of more complex physicochemical ones, taking into account both the intrinsic behavior of the sensors, observable during the exposure to an inert gas, and the extrinsic one, responsible for the sensor response in the presence of oxidizing and reducing gases. In particular, three simple models were developed, one for the intrinsic behavior, one for operation in oxygen (O<sub>2</sub>), and one for operation in the presence of carbon monoxide (CO) and an inert gas. Finally, a complete model for operations in mixtures of CO and O<sub>2</sub> was derived from these latter. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Electronic nose; Metal oxide sensors; Tin oxide sensors; Carbon monoxide; Temperature modulation; Parametric model

## 1. Introduction

The development of a simple dynamic model for tin oxide (SnO<sub>2</sub>) sensors is surely an interesting issue. This, in fact, would help in designing experiments, and also in deeply understanding the behavior of such sensors. In recent years, many studies have been carried out with the aim of understanding the surface reactions of SnO<sub>2</sub> sensors, or more in general of metal oxide sensors, with special attention to simple cases, i.e. interaction with mixtures of oxygen (O<sub>2</sub>), carbon monoxide (CO) and water vapor [1–10]. Many papers have discussed this subject, and some simplified models were developed and applied by different researchers [4–6].

The authors of this paper proposed, in previous works [11–13], a simplified model which, starting from a physical-chemical description of the surface reactions, provides a compact description of the sensor behavior in dry O<sub>2</sub>, and in the presence of both O<sub>2</sub> and CO. Under these conditions, the authors explained the sensor dynamics by means of oxygen adsorption

and ionization processes, and of CO reactions with the ionized adsorbed oxygen, as suggested also by many other researchers [1,3]. The model applies to large grained thick film sensors.

In this work, the authors extend and modify the previously proposed model in order to describe the dynamic behavior of SnO<sub>2</sub> conductance sensors, also in the presence of gas mixtures composed only by inert gases and CO.

The starting point of this work was a measurement campaign carried on in a period of more than one year with commercial sensors. The same sensor array, composed of eight sensors, was tested in environments composed of dry nitrogen (N<sub>2</sub>), O<sub>2</sub>, CO and mixtures of these three gases. In particular, the analysis of data obtained in mixtures of an inert gas and CO led the authors to modify the previously proposed models.

In detail, two important modifications of the previously presented models are proposed and discussed in this paper.

The first modification is based on the following observations: first of all a large response of the sensors was observed in the presence of the reducing gas (CO) even after having kept the sensors at high temperature in an inert environment (N<sub>2</sub>) for a long time (hours), thus cleaning the surface from all adsorbed oxygen species. A very good reproducibility (if compared with data usually obtained with sensors of this kind) was observed: the baseline obtained in N<sub>2</sub> was recovered after the exposure

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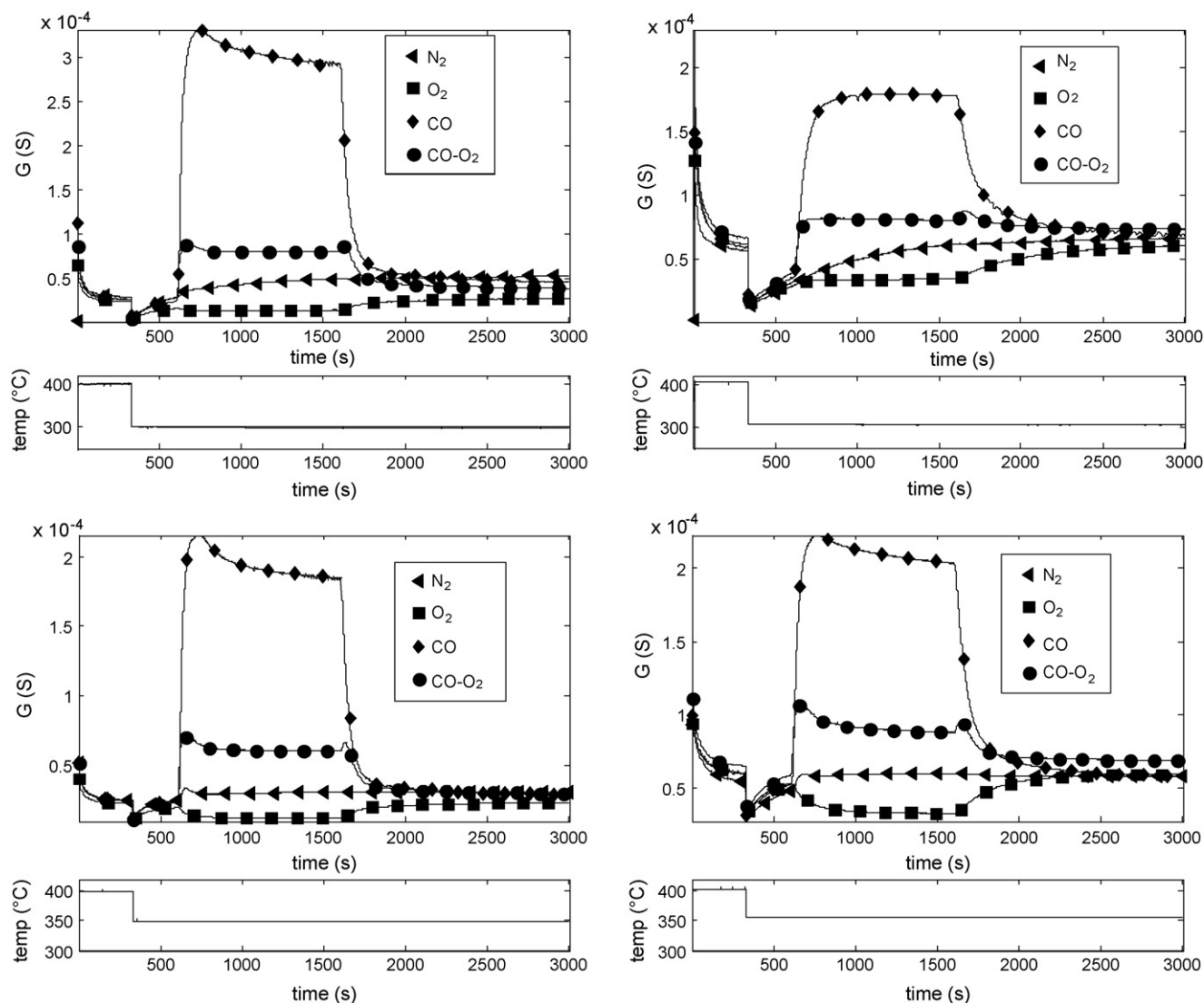


Fig. 1. Thermal and chemical transient responses of two different sensors (left: TGS2620, right: TGS2610). Total flow 200 ml/min. Carrier gas  $N_2$ . Gas pulses:  $O_2 = N_2 + 4\% O_2$ ;  $CO = N_2 + 0.02\% CO$ ;  $CO-O_2 = N_2 + 4\% O_2 + 0.02\% CO$ .

to CO. On the other hand, when the sensors were exposed to  $CO-O_2$  mixtures with high concentration of  $O_2$  (i.e. 0.02% CO and 4%  $O_2$ ), the sensor response was smaller but the dominant contribution was still observed to be the one of the reducing gas (Fig. 1).

All the mentioned observations could be explained by assuming a direct reaction surface-reducing gas as the dominant effect. The most reasonable hypothesis seems to indicate an adsorption of CO with subsequent ionization to form  $CO^+$  as the dominant phenomenon, whereas the formation of  $CO_2$ , which was the only one accounted for in the previous model, can be viewed as a side effect that, in any case, has to be taken into account when the  $O_2$  concentration is high, as suggested by literature [3,9,10].

The second model modification is based on the following fact: observing the experimental data it can be seen that the contribution of the oxygen species to the conductivity variation is not very relevant. As it was already pointed out in the previous work, the dynamic behavior of the sensors in  $N_2$  is not so different from the behavior in a mixture with a high concentration

of  $O_2$  (21% as in synthetic air). For this reason, in the previous work [11], the same model was successfully applied (validation r.m.s. errors below 10%) both for measurements in synthetic air and in  $N_2$ . This was justified through the hypothesis of a very slow desorption of oxygen, so that during measurements in  $N_2$  the dynamic behavior was attributed to the ionization and de-ionization of the residual adsorbed oxygen. This assumption was derived from the analysis of data obtained by flowing  $N_2$  for relatively short time periods (some tens of minutes). But different experiments consisting of a long exposition of the sensors to  $N_2$  during which both a temperature pulse, and subsequently a gas mixture pulse with 4% of  $O_2$  concentration was delivered to the measurement chamber, show that the previous hypothesis could not be correct. In fact, the response of the sensors, once the  $O_2$  pulse has finished, recovered in a relatively short time (tens of minutes at 400 °C), and assumed again the baseline found in  $N_2$  (Fig. 1). This behavior seems to point out that the rate limiting phenomenon could not be the desorption or adsorption of oxygen, that on the contrary can be considered fast thermodynamic

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