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# CO sensing with $SnO_2$-based thick film sensors: Surface state model for conductance responses during thermal-modulation

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**Abstract**

There exists a strong interest in developing simplified models able to predict the $SnO_2$ sensor response and aiming at a better comprehension of the mechanisms involved with sensing operation. In this paper, a simple grey-box model is proposed for predicting, with a good approximation (r.m.s. error < 10%), the behavior of some commercial $SnO_2$-based sensors in presence of oxygen and a reducing gas (CO) during fast temperature variations. Auger electron spectroscopy (AES) permitted to highlight differences in the surface composition of the sensors after extended operation time.


*Keywords:* Electronic nose; Metal oxide sensors; Temperature modulation; Grey-box model; CO

## 1. Introduction

It is well recognised that the ability of metal oxide-based gas sensors (MOS) to detect chemicals relies on the interaction between the analyte molecules and the surface of the sensing material. It is widely accepted that adsorbed oxygen ions ($O^{2-}$, $O^-$ and $O_2^-$) have a decisive influence on the response of the semiconductor to a reducing/oxidising gas. Adsorbed oxygen species act as surface acceptors binding electrons from the conduction band of the material, then giving rise to Schottky potential barriers at grain boundaries. It is considered that reducing gases like CO decrease the surface oxygen concentration (CO combustion) and thus decrease the sensor resistance. Measurement techniques characterized by a variable sensor temperature have been applied to discriminate among different gas mixtures [1–3]. Recent works demonstrated that these techniques can improve the selectivity of MOS based systems. Nevertheless, since the shape of the 'optimum' temperature profile must be tailored to the specific application, its selection for a given chemical mixture is often a time-consuming phase, involving long measurement processes [2]. In this context, there exists a strong interest in developing simplified models able to predict the sensor response during temperature modulations.

Various attempts have been made to yield insight into the mechanisms that affect the dynamic response of these materials. Until now, the transient behavior of tin oxide sensors was mainly treated by curve fitting methods or by black-box models [4,5]. Some theoretical models have been already proposed [6–8], but they are very complex and dependent on many physical parameters whose estimation is critical.

In the present work, a simplified response model based on a grey-box approach is proposed. This model is able to satisfactorily predict the $SnO_2$ sensor response in presence of dry synthetic air and a reducing gas (CO) during sensor temperature modulations.

## 2. Experimental

Measurements were performed with a laboratory computer-driven electronic nose described in detail elsewhere [2]. The

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electronic nose is provided with a flexible sensor temperature control system based on a micro-controller (H8S2345), able to individually control, by feedback loops, the temperature of up to eight sensors. In particular, the micro-controller generates a voltage value ($V$) which is applied to a voltage divider comprising the sensor heater ($R$) and a reference precision resistor ($R_f$). The voltage across the precision resistor ($V_f$) is amplified and then A/D converted by the micro. The knowledge of $V$ and $V_f$, at a given time instant, allows to obtain an indirect measurement of the heater resistance, of its actual temperature $T$ and of the temperature error $\Delta T_{err}$, exploiting the following equations:

$$R = \left(\frac{V}{V_f} - 1\right) R_f \tag{1a}$$

$$R = R_0(1 + \alpha T - \beta T^2) \tag{1b}$$

$$\Delta T_{err} = T - T_D \tag{1c}$$

where $\alpha$ and $\beta$ are experimentally determined constants ($1.45 \times 10^{-3}$ [1/°C] and $4.03 \times 10^{-7}$ [1/°C$^2$], respectively, for ruthenium oxide films used in Taguchi sensors), $R_0$ is the resistance of the heater at 0 °C, while $T_D$ is the desired temperature value. Once obtained $\Delta T_{err}$, the voltage across the heater is adjusted in order to zero this error (integral control).

The voltage $V$ is generated in the range (0–10 V), with an accuracy of 2 mV, whereas $V_f$ is measured with an accuracy of about 0.4 mV. This implies a worst case error for a typical Taguchi sensor ($R_0 = 50\,\Omega$) at the lower end of the temperature range (250 °C) within ±2 °C. This accuracy was reached by individually calibrating each channel in terms of gain and offset.

To obtain the measurement results presented in this paper, the sensors were exposed either to dry synthetic air (21% $O_2$ + 79% $N_2$, purity 99.999%) or to a controlled mixture of CO (200 ppm (v/v)) and dry synthetic air with a total flow of 200 ml/min. All measurements start with a period of 300 s at high temperature (about 450 °C) to lead the sensor response to a steady-state independent from the initial conditions. Subsequently, the temperature of the sensors is modulated with different profiles. The gas-sampling unit is a digitally controlled system providing the possibility of injecting the desired gas or gas mixture into the measurement chamber, and of controlling the gas flow (up to 500 ml/min) by means of three mass flow controllers (Model F-201C–22V, Bronkhorst [13]). The measurement chamber is kept inside an incubator for precise temperature control (Model 200, Memmert [14]). Three different commercially available Taguchi screen-printed sensors were used (TGS2610, TGS2620 and TGS2442, Figaro Engineering Inc. [15]), with the latter two indicated for CO detection by the manufacturer. Charcoal filters packaged with TGS2442 sensors were removed. TGS2442 sensors are designed for pulsed temperature operations and they can be classified as 'fast' sensors, referring to their quick thermal response (in the range of ms), while the TGS26XX sensors are larger and have a thermal response in the range of seconds.

The morphology of the tested sensors was characterized using a scanning electron microscopy (SEM, PHILIPS XL-30). Moreover, preliminary surface composition studies were conducted: a Cylindrical Mirror Analyser (Varian spectrometer) was used to obtain the Auger electron spectra (AES). The energy of the primary electron beam was 3 keV. The spectra were recorded in the first derivative mode using a lock-in amplifier and a modulation amplitude of 5 V peak-to-peak. An imaging system (based on the detection of secondary electrons) allowed to choose the points of the surface to be analyzed.

## 3. Proposed model

For a porous layer, in the case of large grains with small contact regions, the free conduction electrons have to overcome the surface barrier ($V_s$) when hopping from one grain to another [9,10], and the conductance of the sensing layer can be expressed by:

$$G(T, V_s) = G_0 \exp\left(\frac{-qV_s}{kT}\right) + G_c \tag{2}$$

where $k$ is the Boltzmann's constant, and $T$ is the absolute temperature, while $q$ is the electron charge.

The pre-exponential factor in the left term is:

$$G_0 = gq\mu_s N_D \tag{3}$$

where $N_D$ is the density of the ionized donors, $g$ a constant determined by the semiconductor geometry, $\mu_s$ the mobility of the electrons. $G_0$ is a temperature-dependent parameter which varies with $T^{-3/2}$ as $\mu_s$, and $G_c$ is a constant introduced to account for different conductivity phenomena.

Eq. (2) describes the changes in the sensor conductance, caused by the modulation of the depletion region thickness at the surface according to the thermoelectronic emission theory [10]. An alternative expression for conductance in large grain films can be obtained by applying the diffusion theory. The expression is of the same form of that in Eq. (2) but for the dependence of the pre-exponential factor $G_0$ on $V_s^{1/2}$ that can be neglected when compared to its strong dependence on $V_s$ expressed in the exponential term.

Eq. (2), with a potential barrier $V_s = qN_s^2/2\varepsilon_r\varepsilon_0 N_D$, where $N_s$ is the density of occupied surface states, can be used in the case of layers whose grains are much larger than the Debye length, $\lambda_D$ (typically of the order of tens to hundreds of nanometers) [10]. The SEM images recorded for the different sensors showed that the films are essentially inhomogeneous and formed by grains with a mean diameter of about 1 μm in the case of TGS26XX (Fig. 1(a)), and of less than 0.5 μm for TGS2442 (Fig. 1(b)). Hence, to model the TGS26XX conductance, Eq. (2) seems a reasonable choice. This model might be expected to be less suitable for representing the behavior of TGS2442, whose grain dimensions are smaller, and for which the contact region between grains seems to be larger. However, experimental results (data not shown) proved that Eq. (2) can also be used for the TGS2442 sensors at temperatures over 250 °C.

### 3.1. Response model for oxygen

Assuming that in the considered temperature range (temperature over 250 °C) the ionized oxygen $O^-$ is the dominant species