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# Metal-oxide nanowire sensors for CO detection: Characterization and modeling

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ABSTRACT

This paper concerns characterization and modeling of single crystalline tin oxide nanowires used as CO sensors. In this work we analyze the performance of these devices when they are used with variable operating temperatures. The aim is reducing the power consumption and establishing a model suitable for the development of sensing systems working with programmed temperature protocols. In particular we developed and tested a model for the dynamic behavior of the sensor able to predict the sensor response during thermal or chemical transients. This model can be therefore exploited for the selection of optimum temperature profiles targeted to specific applications.



## 1. Introduction

Among the different metal-oxide nanostructures proposed to develop gas sensors, nanowires have attracted a large interest. These materials are single crystals growing according to well-defined crystalline directions, featuring nanosized diameter [1]. Thanks to the reduced lateral dimensions, these materials exhibit high sensitivity to surface phenomena involved in gas sensing, whereas their quasi one-dimensional structure is suitable for the development of innovative devices, such as, for example, gas sensors based on a single nanowire exploiting the self-heating effect to obtain an ultra-low power consumption (a few μWs to warm the device to 300–400 °C) [2,3]. Several works report that nanowires exhibit good sensitivity to different gases such as, for example, ethanol, CO, hydrogen [2–5]. Despite the promising structure and the results obtained till now, a large work is still needed to understand and exploit the potentialities of these materials.

In this paper characterization and modeling of sensor consisting of bundles of single crystal metal-oxide (MOX) nanowires, to be used as CO sensors, are presented. In particular, the performance of these devices used with a variable operating temperature is considered, with the aim of both further reducing the power consumption and establishing a model suitable for the development of sensing systems working with programmed temperature protocols. In fact, modulation of MOX temperature can promote specific gas-semiconductor reactions, and the selection of a proper operating temperature profile can be therefore effective in increasing the selectivity of metal-oxide gas sensors [6,7].

To select the optimum temperature profile for a target application by experimental trials is a time wasting approach: it is much more efficient to use, for this purpose, a model able to predict the dynamic behavior of the sensor. The main result of this work is the identification of a simplified model based on the surface reaction kinetics that was developed starting from a model described by the authors in previous works [8]. The model can predict with a satisfactory accuracy the conduction in the sensing films consisting of a bundle of mono-dimensional (1D) wires, both in dry air and in CO. The developed model can also give some inputs to better understand the behavior of such structures.

## 2. Sensor preparation

Metal-oxide nano-crystals were prepared by means of the evaporation-condensation (EC) process, with vapour–liquid–solid (VLS) growth mechanism promoted by the use of Pt nanoparticles as catalyst. The method has been detailed in [5]. Briefly, it consists in the following steps. First, Pt nanoparticles are deposited by sputtering on 2 mm × 2 mm alumina substrates, while tin oxide powders are placed in an alumina tube furnace. The source temperature is raised to 1370 °C to evaporate it, vapors are transported by means of a constant Ar flow of 75 sccm, working at a constant pressure of $10^4$ Pa. Furnace heating from room temperature to 1370 °C takes 1.5 h approximately. During furnace heating and cooling a reverse Ar gas flow (from the substrates to the powder) is applied, to avoid uncontrolled mass deposition in inappropriate conditions. Nanowires grow in a colder zone of the furnace, at a temperature of 390 °C.

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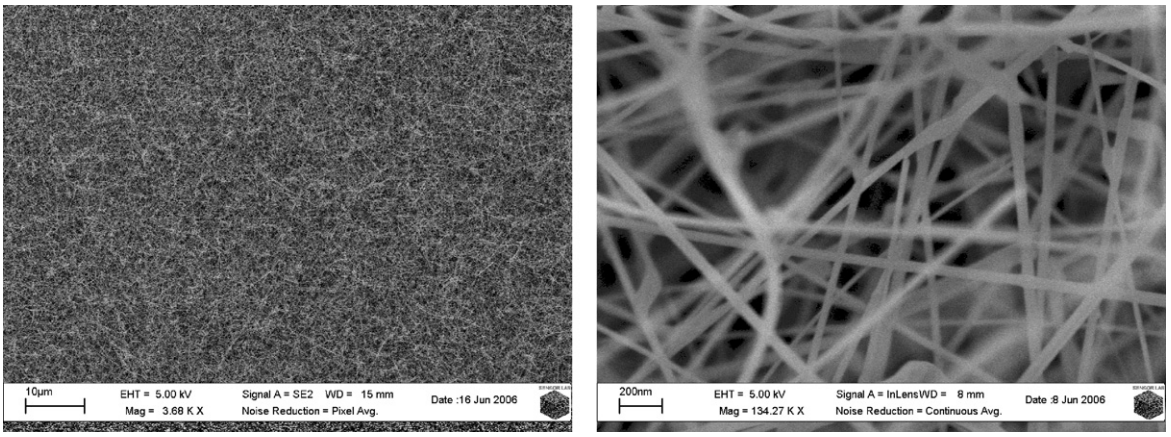


**Fig. 1.** Low- and high-resolution SEM images of tin oxide nanowires deposited with Pt catalyst at a deposition temperature of 390 °C. The SEM analysis shows the homogeneous distribution of nanowires over the substrate as well as their nanosized (less than 100 nm) lateral dimensions.

Morphological investigation of the obtained nanowires was carried out by means of a LEO 1525 scanning electron microscope (SEM) equipped with a field-emission source. The observation of uncoated nanowires over the insulating alumina substrate indicates that nanowires are homogenous in size with diameters smaller than 100 nm (Fig. 1).

The single crystalline arrangement of the prepared materials and their crystalline structure was analyzed in a previous work [5] by means of transmission electron microscopy. The $SnO_2$ nanowire symmetry agrees with the cassiterite tetragonal phase (P42/mnm-SG136), with the wire growing along to the [1 0 0] direction.

The developed sensors are completed by sputtering platinum electrodes with interdigitated structure, spaced by 250 μm, and a Pt meander that acts both as heater and temperature sensor.

## 3. Sensor behavior model

### 3.1. Surface chemical reactions

The film behavior in presence of dry gas mixtures containing CO and $O_2$ is described assuming the following reactions at the sensor surface [8,9]:

$$CO + S_{CO} \underset{k_{-CO}}{\overset{k_{CO}}{\rightleftarrows}} (CO\text{–}S_{CO}) \quad (CO\ \text{adsorpion}) \tag{1a}$$

$$(CO\text{–}S_{CO}) \underset{k_{-CO^+}}{\overset{k_{CO^+}}{\rightleftarrows}} (CO^+\text{–}S_{CO}) + e^- \quad (CO\ \text{ionization}) \tag{1b}$$

$$\frac{1}{2}O_2 + S_O \underset{k_{-O}}{\overset{k_O}{\rightleftarrows}} (O\text{–}S_O) \quad (O\ \text{adsorption}) \tag{1c}$$

$$(O\text{–}S_O) + e^- \underset{k_{-O^-}}{\overset{k_{O^-}}{\rightleftarrows}} (O^-\text{–}S_O) \quad (O\ \text{ionization}) \tag{1d}$$

$$(O^- - S_O) + CO \xrightarrow{k_{CO_2}} CO_2 + S_O + e^- \quad (CO\ \text{oxidation}) \tag{1e}$$

where $S_X$ indicates the surface adsorbing site for the specie X (e.g. oxygen or Sn atoms), whereas (X–$S_X$) indicates the adsorbed species X (X = O, $O^-$, CO, $CO^+$), and $k_X$ the rate reaction constants.

The conductivity of the sensor is changed by the reactions that implies electronic exchange, i.e. it depends on the total charged surface-state density, hereafter named $N_s$. This latter is given by the charged species that are formed at the surface from the adsorbed gases, but also by the density of ionized intrinsic surface states (defects), hereafter named $N_{si}$, whose density can vary depending on the temperature. In particular, on the basis of Eq. (1), the following Eq. (2) can be written:

$$N_s = N_{si} + [O^-\text{–}S_O] - [CO^+\text{–}S_{CO}] \tag{2}$$

In accordance with what found in some previous works [8] it can be assumed that only the reactions involving charged species ((1b), (1d), and (1e)) are relevant for the dynamic behavior, and that the adsorption reactions are fast phenomena, so that, in practice, the adsorption reactions ((1a) and (1c)) can be always considered at the equilibrium. Under this hypothesis, and assuming first order kinetics, the dynamics of the surface states $N_s$ as a function of temperature and chemical condition variations can be described by three first order differential equations as follows [8]:

$$\begin{aligned}
\frac{dN_{si}}{dt} &= k_i n_s (N_i - N_{si}) - k_{-i} N_{si} \\
\frac{d[CO^+\text{–}S_{CO}]}{dt} &= k_{CO^+}[CO\text{–}S_{CO}]_0 - k_{-CO^+}[CO^+ - S_{CO}]n_s \\
\frac{d[O^- - S_O]}{dt} &= k_{O^-}[O\text{–}S_O]_0 n_s - k_{-O^-}[O^- - S_O] - k_{CO_2}[CO][O^- - S_O]
\end{aligned} \tag{3}$$

The first equation describes the intrinsic sensor behavior, e.g. the intrinsic surface states ionization and neutralization: in other words it describes the dynamics of the sensor in an inert environment where no adsorption is possible. $N_i$ is the total density of intrinsic surface states, and $n_s$ is the density of surface electrons. The charged surface states are responsible for the modulation of the width of a depleted region at the surface of the nanowires, for a surface electric field and for a potential barrier at the nanowire boundary contacts whose height is hereafter named $V_s$.

### 3.2. Sensor conductance

To complete the sensor model, the relationship must be found between $N_s$ and the measured quantity, that is the film conductance, $G$.

The sensor is a bundle of nanowires (as in Fig. 2) so the current path consists of many nanowires, that have small contact surfaces.

In the case of wires with diameter larger than the Debye length $\lambda_D$, the potential barrier at the wire surface, $V_s$, can be expressed as a function of the occupied surface states $N_s$ as follows [8,10]

$$V_s = \frac{qN_s^2}{2\varepsilon N_d} \tag{4}$$

where $\varepsilon$ is the electrical permittivity of the semiconductor, $N_d$ is the ionized bulk donor density, and $q$ is the electron charge.

This results stems from the assumption of a depletion region confined near the surface of the grain or crystallite, hence it is valid