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# Coupled microstructural and transport effects in n-type sensor response modeling for thin layers[☆]

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ABSTRACT

The chemical gas sensor system of CO detection in a $SnO_2$ matrix was considered. A model was formulated which incorporated the coupled processes of gases diffusing into a porous ceramic and then participating in surface chemical reactions of adsorption, ionization and desorption. Microstructural properties of the sensor matrix were coupled with the diffusion and surface chemistry processes. The consequent surface chemical state served to partition bulk and grain boundary contributions to the n-type material conductance. Conductivity levels determined both with and without the presence of the target gas, CO, allowed sensor response to be determined as a function of film thickness.

This simulation represents a modeling advance as it is the first to couple spatial variation of microstructural properties with diffusing gas species and the attendant surface chemistry and electroceramic properties, to predict sensor response as a function of film thickness. This will serve to be a useful design tool for ensuing materials research work towards improved sensor device development.

## 1. Introduction

Tin dioxide ($SnO_2$) is presently a leading material for sensing CO gas because it is relatively inexpensive, chemically stable and has high electron mobility [1]. Material properties of $SnO_2$ are such that its electroceramic response to CO gas is significant under normal atmospheric conditions.

$SnO_2$ based sensors have been the most studied type of oxide-based gas sensors [2]. Despite this, the commercial development of $SnO_2$ sensors for various specific applications has been somewhat limited by inadequate control of both sensitivity and selectivity. Better comprehension of the mechanistic functioning of these devices would lead to enhanced microstructural control, and thus improved products, and more widespread use.

It is well known that sensor selectivity is a coupled function of $SnO_2$ microstructure and mode of operation, together with the surface chemistry which drives the electroceramic response. The present study aims to formulate and implement a numerical model comprising all of the above elements, namely resolving the surface chemistry in view of the prevailing microstructure and device operating conditions. The output of such a simulation would aid in a more thorough approach for specific designs for $SnO_2$ sensors operating in real environments.

## 2. Model formulation

### 2.1. Analytical basis

A point of departure for this work was the paper by Sakai et al. [3] where an analytical model was formulated which demonstrated a number of results and effects related to the equilibrium target gas concentrations established inside a sensing film of 300 nm thickness.

In order to do this, the steady state diffusion equation was treated

$$D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A = 0 \qquad (1)$$

where $D_K$ is the Knudsen diffusion coefficient, $C_A$ is the local concentration of the target gas, $x$ is the linear dimension and $k$ is a first-order rate constant for capture of the target gas by the sensor.

Applying boundary conditions of $C_A = C_{A,s}$ at $x = 0$ (i.e.; the sensor–air interface), and a zero gradient condition at an internal depth $L$ of 300 nm, that is, $\partial C_A/\partial x = 0$ at $x = L$, the following solution

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was obtained,

$$C_A = C_{A,s}\frac{\cosh((L-x)\sqrt{k/D_K})}{\cosh(L\sqrt{k/D_K})} \tag{2}$$

### 2.2. Numerical approach

The problem introduced here was treated by a numerical approach, whose starting point was the general convection diffusion transport equation,

$$\frac{\partial}{\partial t}(\rho C_A) = -\nabla\cdot(\rho\vec{v}C_A) - \nabla\cdot\vec{J}_A + S_A \tag{3}$$

The above equation has a concentration rate term and a convective transport term for species $A$ which is a function of the velocity vector $\vec{v}$, on the right-hand side, as well as the diffusive flux term $\vec{J}_A = -\rho D_K \nabla C_A$ and the term $S_A$ which is a source term for creation or elimination of target species $A$.

The solution of a numerical problem requires a discretization scheme. Eq. (1) is a one-dimensional expression. The commercial CFD software FLUENT® was used to treat the problem. Eq. (3) was implemented in two dimensions on a 500 × 2 mesh, representing a solution domain 1000 nm long and 1 nm wide. The cell density was graded to provide increased density and resolution near the air interface.

### 2.3. Model scheme

The present project aims to incorporate and couple microstructural effects into the simulation of sensor function.

To define species diffusivity through the film, Knudsen diffusion is used. The Knudsen numbers ($\mathrm{Kn} = (k_B T)/(\sqrt{2}\pi d_{\mathrm{gas}}^2 PL)$, here, $k_B$ is Boltzmann's constant, $T$ temperature, $d_{\mathrm{gas}}$ is the diameter of the gaseous species in question, $P$ the pressure and $L$ a length scale, in this case a pore diameter) for these microstructures for the gases under consideration, even with pore diameters 20 times the particle diameters would be above 20, putting the diffusion well within the Knudsen regime [4].

The following expression is used to calculate the Knudsen diffusivity for all gases in each cell of the meshed domain:

$$D_K = \frac{\varepsilon}{\tau}\frac{4r}{3}\sqrt{\frac{2RT}{\pi M}} \quad (\mathrm{m^2\,s^{-1}}) \tag{4}$$

In Eq. (4), $\varepsilon$ refers to porosity and $\tau$ is the tortuosity.

The expression for tortuosity, ($\tau = 1 + 0.78333(1-\varepsilon)$) is taken from [5]. Above, $T$ is temperature, $M$ the molecular weight, $r$ the pore radius and $R$ is the gas constant. In the present model, spatial variation in the microstructure can be imposed on the $SnO_2$ matrix. Given that a $SnO_2$ material formed by pulsed laser deposition is being considered, the density was set to 90% theoretical over the 1000 nm depth of the sample, with grain diameters set to 20 nm [6–8]. The sensor operating temperature was set at 573 K. The way that a $SnO_2$ matrix functions as a gas sensor is as follows: In any baseline situation, gases from the neighbouring air diffuse into the porous structure and interact with the ceramic surface. The presence of oxygen gives rise to some surface chemical activity, namely, its adsorption and subsequent ionization on the tin oxide matrix surface. The differing rates of diffusion and chemical activity produce equilibrium concentration profiles of gas species and surface species inside the sensor matrix. The electrical conductivity of $SnO_2$ is a function highly dependent on the surface concentration of oxygen ions. Next, when a target gas (CO in our study) appears in a small concentration in the air at the sensor–gas interface, it also diffuses into the ceramic matrix and participates in further chemical reactions which alter the gas and adsorbed species equilibrium profiles. The quantitative nature of how the electrical properties of tin oxide are modulated as a function of target gas concentration is, in essence, what defines the system as a chemical sensor.

The mechanism of $O_2$ adsorption onto a surface site (S), is described by the following reactions [9]. Here they describe the mechanism in two steps:

$$\text{Chemisorption}: \quad \frac{1}{2}O_2 + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} O{-}S$$

$$\text{Ionization}: \quad O{-}S + e^- \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} O^-{-}S$$

Then the reaction with CO is given by:

$$O^-{-}S + CO \overset{k_3}{\rightarrow} CO_2 + S + e^-$$

where $e^-$ represents a free surface electron. The kinetic parameters for the various reactions are summarized in Table 1, for the generic reaction rate with the functional form $k_i = k_{i0}\exp(E_i/RT)$, where $k_{i0}$ is the Arrhenius pre-exponential term for species $i$. Kinetic parameters are taken from [9,10].

The $O - S$ and $O^-{-}S$ surface concentrations were modeled by adding the formation rate of the species to the previous concentration of the species on an iterative basis, as,

$$[S]_{j,i+1} = [S]_{j,i} + \mathrm{rate}_{j,i+1} \quad (\mu\mathrm{mol/m^2})$$

where the indices $j$ and $i$, respectively refer to species and iteration number. Variables used to represent the surface concentrations of the reacting species are: adsorbed oxygen $[O{-}S]{=}N_O$, adsorbed oxygen ions $[O^-S]{=}N_S$, and surface electrons $[e^-] = n_S$. The number of possible adsorption sites = $S_0 = 8.7 \times 10^{19}$ (molec/m$^2$) [10], which is based on the specific surface area.

Kinetic rates for the surface species were given by [11],

$$\begin{aligned}\frac{d[O{-}S]}{dt} &= k_1(S_0 - N_O - N_S)\sqrt{[O_2]} - k_{-1}N_O - k_2 n_S N_O \\ &\quad + k_{-2}N_S + k_3[CO]N_S\end{aligned} \tag{5}$$

$$\frac{d[O^-{-}S]}{dt} = k_2 n_S N_O - k_{-2}N_S - k_3[CO]N_S \tag{6}$$

$$n_S = N_d \exp\left(\frac{-q^2 N_S^2}{2k_B\epsilon_0\epsilon_r N_d T}\right) \tag{7}$$

Above in the expression for $n_S$, some of the parameters are: $N_d = 9.6\times10^{24}$ (m$^{-3}$), $q$ is the elementary charge constant ($1.6 \times 10^{-19}$ C), $k_B$ is Boltzmann's constant ($1.380 \times 10^{-23}$ (J/K)), $\epsilon_0$ is the permittivity in a vaccum ($8.854 \times 10^{-12}$ (F/m)), $\epsilon_r$ is the dielectric constant of $SnO_2$ (13.50).

The above rate expressions for the surface species can be seen to be functions of the concentrations of the diffusing gas species. Likewise, for the diffusing gas species, (referring back to the diffusion equation, Eq. (4)), their rate expressions or source terms are:

$$\frac{d[O_2]}{dt} = -k_1(S_0 - N_O - N_S)\sqrt{[O_2]} + k_{-1}N_O \tag{8}$$

$$\frac{d[CO]}{dt} = -k_3[CO]N_S \tag{9}$$

$$\frac{d[CO_2]}{dt} = k_3[CO]N_S \tag{10}$$

The number of available adsorption sites S is given by $S = S_0 - N_O - N_S$. Note that the gas phase source terms must be converted to units of kg/m$^3$/s for use in Eq. (3), so the factor $A_{\mathrm{spec}} \cdot M_W/(Av \cdot 10^3 \cdot \varepsilon)$ must be applied to the rate constants. Above, $A_{\mathrm{spec}}$ is the specific surface area and $Av$ is Avogadro's number.