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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.sna.2008.06.007>

Sensors and Actuators A, 147, pp. 378-386, 2008

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

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ARTICLE INFO

Article history:

Received 30 October 2007

Received in revised form 17 April 2008

Accepted 7 June 2008

Available online 19 June 2008

Keywords:

Transport modeling

Spatial resolution

Coupled simulation

Ceramic microstructure

ABSTRACT

The chemical gas sensor system of CO detection in a SnO₂ 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 conductivity. 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.

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1. Introduction

Tin dioxide (SnO₂) 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 SnO₂ are such that its electroceramic response to CO gas is significant under normal atmospheric conditions.

SnO₂ based sensors have been the most studied type of oxide-based gas sensors [2]. Despite this, the commercial development of SnO₂ 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 SnO₂ 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 SnO₂ 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

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

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,

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

2.2. Numerical approach

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

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

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 ($Kn = (k_B T) / (\sqrt{2} \pi d_{\text{gas}}^2 P L)$), here, k_B is Boltzmann's constant, T temperature, d_{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:

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

In Eq. (4), ε refers to porosity and τ is the tortuosity.

The expression for tortuosity, ($\tau = 1 + 0.7833(1 - \varepsilon)$) 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:

Then the reaction with CO is given by:

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

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

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 $[\text{O}-S] = N_0$, adsorbed oxygen ions $[\text{O}^- - S] = N_S$, 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],

$$\frac{d[\text{O}-S]}{dt} = k_1(S_0 - N_0 - N_S)\sqrt{[\text{O}_2]} - k_{-1}N_0 - k_2n_SN_0 + k_{-2}N_S + k_3[\text{CO}]N_S \quad (5)$$

$$\frac{d[\text{O}^- - S]}{dt} = k_2n_SN_0 - k_{-2}N_S - k_3[\text{CO}]N_S \quad (6)$$

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

Above in the expression for n_S , some of the parameters are: $N_d = 9.6 \times 10^{24}$ (m^{-3}), q is the elementary charge constant (1.6×10^{-19} C), k_B is Boltzmann's constant (1.380×10^{-23} (J/K)), ϵ_0 is the permittivity in a vacuum (8.854×10^{-12} (F/m)), ϵ_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:

$$\frac{d[\text{O}_2]}{dt} = -k_1(S_0 - N_0 - N_S)\sqrt{[\text{O}_2]} + k_{-1}N_0 \quad (8)$$

$$\frac{d[\text{CO}]}{dt} = -k_3[\text{CO}]N_S \quad (9)$$

$$\frac{d[\text{CO}_2]}{dt} = k_3[\text{CO}]N_S \quad (10)$$

The number of available adsorption sites S is given by $S = S_0 - N_0 - N_S$. Note that the gas phase source terms must be converted to units of $\text{kg}/\text{m}^3/\text{s}$ for use in Eq. (3), so the factor $A_{\text{spec}} \cdot M_W / (Av \cdot 10^3 \cdot \varepsilon)$ must be applied to the rate constants. Above, A_{spec} is the specific surface area and Av is Avogadro's number.

Table 1
Kinetic parameters for the reactions occurring in the CO—SnO₂ system

k_1	k_{-1}	k_2	k_{-2}	k_3
$k_{10} = 1.2 \times 10^{-5}$	$k_{-10} = 0.9 \times 10^{-3}$	$k_{20} = 3.2 \times 10^{-19}$	$k_{-20} = 1.1 \times 10^{-4}$	$k_{30} = 1.8 \times 10^{-5}$
$E_1 = 0.3 \times 10^5$	$E_{-1} = 0.9 \times 10^2$	$E_2 = 5.84 \times 10^{-9}$	$E_{-2} = 7.57 \times 10^2$	$E_3 = 7.0 \times 10^3$

For a porous material undergoing surface chemical activity, the conductivity is also a function of the microstructure as described in [12]. Fig. 1 schematically depicts the boundary between two grains, which contributes to the overall connectivity of a contiguous structure, influencing its electrical conductivity. Resolving such a system requires a number of microstructural parameters which are derived from some original theoretical work presented by McLachlan et al. [13] The following system of volume fractions can be solved to provide parameters to determine a net conductivity value based on the combined contributions of bulk and grain boundary conductivities.

$$\begin{aligned} f_{np} &= 1 - \varepsilon \\ f_{gb} &= f_{np} \frac{N_d}{N_i} \\ f_g &= 1 - \varepsilon - f_{gb} \\ f_{pgb} &= 1 - (f_g + f_{gb}) \\ f_c &= f_{pg} + f_g \end{aligned}$$

Above, f_{np} is the non-porous volume fraction, f_{gb} the grain boundary volume fraction, f_{pgb} the pore volume fraction at grain boundary, f_g the grain volume fraction and f_{pg} is the grain pore volume fraction. The assumption of no porosity inside the grains sets $f_{pg} = 0$. A configuration to give physical meaning to the above list of volume fractions is shown in the inset of Fig. 1.

The conductivities are renormalized as follows [12]:

$$\begin{aligned} \sigma_i &= \sigma_{gb} (1 - f_{pgb}^{2/3}) \\ \sigma_c &= \sigma_g (1 - f_{pg}^{2/3}) \quad (\text{because } f_{pg} = 0) \end{aligned}$$

Here, σ_i is the renormalized conductivity of insulating components, σ_c the renormalized conductivity of conducting components, σ_g

the grain conductivity and σ_{gb} the grain boundary-depletion layer conductivity.

The calculation of the effective medium conductivity is possible by solving an equation which combines the surface electrical partition coefficients with the renormalized component conductivities. In cases where f_c is greater than f_p (the percolation threshold; $f_p = 0.16$ [12]) it is appropriate to calculate the effective medium conductivity using the GEM (General Effective Media) equation:

$$\frac{f_c(\sigma_c^{1/t} - \sigma_{eff}^{1/t})}{\sigma_c^{1/t} + ((1 - f_p)/f_p)\sigma_{eff}^{1/t}} + \frac{(1 - f_c)(\sigma_i^{1/t} - \sigma_{eff}^{1/t})}{\sigma_i^{1/t} + ((1 - f_p)/f_p)\sigma_{eff}^{1/t}} = 0 \quad (11)$$

Above, $t = 1.7$ is a percolation exponent [12] suitable for the present conditions. With spatially resolved diffusing gas and surface chemical concentration profiles, the conductivity profile of σ_{eff} can be determined using Eq. (11). In the simulations conducted here, the maximum f_{gb} values observed were around 0.50, so that all cases were well within the GEM theory range of applicability.

3. Experimental

Samples of pure SnO₂ were prepared for the purpose of measuring their conductivity as a function of temperature. Microstructures of thin films of SnO₂ made by pulsed laser deposition (PLD) typically show theoretical densities upwards of 90% and grain sizes in the 10–30 nm diameter range [6–8].

3.1. Target preparation

Two grams of SnO₂ powder (Aldrich, 99.9%) was pressed into a pellet using a stainless steel form under approximately 2 tonnes of applied pressure. The pellet was further densified using a cold isostatic press (American Isostatic Presses, Inc. model CP360) that applies 200 MPa of pressure. The pellet was then sintered at 1400 °C for 6 h. The diameter and thickness of the sintered pellet were 1.25 and 0.38 cm, respectively. The calculated density of the pellet was 4.225 g/cm³ (62% of theoretical density of 6.85 [14]). Pellets produced in this manner have been examined by X-ray diffraction and show excellent correspondence with reference spectra for SnO₂. The pellet was used in the deposition of SnO₂ films by PLD.

3.2. Film deposition

The PLD process is carried out by subjecting the sintered pellet to laser pulses that produce a plume of ablated material that is deposited as a film onto a nearby substrate. The film formed during this process was used as the sensing material in subsequent tests.

Films were prepared by PLD using a Lambda Physik LPX305i, $\lambda = 248$ nm KrF excimer laser at an energy of 600 mJ/pulse (fluence 1.5 J/cm²) at a frequency of 8 Hz. The films were deposited onto single-crystal sapphire substrates (1 $\bar{1}$ 02) mounted onto a resistive heater. Shadow-masking of a test film allowed for calibration of the deposition rate using a Dektak IIA stylus profiler (ex situ). Using the determined rate of 29 nm/min, a 200 nm thick film of SnO₂ was prepared. The film was deposited under a background oxygen pressure of 100 mTorr at a temperature of 650 °C. Post-deposition, the film temperature was maintained at 650 °C for 30 min in an oxygen atmosphere of 400 Torr. Under this oxygen pressure the film was

Fig. 1. Schematic diagram demonstrating the morphological effects on conductivity, as incorporated in the General Effective Media theory. The dark blue regions represent the depletion layer, with low conductivity, σ_i , while the light yellow regions represent the higher conductivity, σ_c , bulk interior regions. Consider the following cases: (a) reference case; (b) the same depth of depletion layer as in (a), but sintered to a higher density, such that the neck region is sufficiently wide to connect the more highly conducting interiors, thereby reducing sensitivity; (c) the same depletion layer thickness on smaller particles shows that at an equivalent neck size ratio as case (b), (i.e.; equal density), the depletion layer remains intact and sensor sensitivity is enhanced. In the inset, the blue regions represent the grain boundary volume fraction f_{gb} (with σ_i), while the yellow regions represent the grain volume fraction f_g (with σ_c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 2. One-dimensional grid used for the simulation.

then cooled at approximately 10 K per minute back down to room temperature.

3.3. Film conductivity measurements

The conductivity of the pure SnO_2 film was measured using an in-house sensor test bed setup comprised of a 1 L stainless steel chamber that houses a resistive heating element and allows for electrical connection to the film and continuous computer-control of the film temperature. Gold pads, 300 nm thick, were evaporated onto the surface of the SnO_2 film to serve as electrical connections to the measurement electronics. The projected surface area of exposed SnO_2 was 0.12 cm^2 . Film conductivity was determined by a two-point (DC) method. The small bias voltage used to deter-

mine the conductivity was applied in both positive and negative polarities with respect to the sensor film to avoid any charge build up. Each data point represents the average value of the conductivity obtained from these two measurements. The conductivity tests were carried out under a 200 sccm/min flow of zero air scrubbed of water vapour and CO_2 (BOC gases gas grade AIR 0.1). The conductivity of the film was determined in the temperature range of 373–773 K in intervals of 20 K. At each temperature step, the film was allowed to equilibrate over a period of 60 min prior to measurement of the reported conductivity to ensure steady state conditions. The temperature ramp rate between measurement steps was 10°C per minute.

4. Numerical implementation and initial calculations

Spatial profiles of the diffusing gases were calculated as well as the consequent surface concentrations of N_{O} , N_{S} and n_{S} . The diffusion equation (Eq. (4)) was solved for each species using the computational fluid dynamics (CFD) software FLUENT®. A simple 500 cell grid was used. The lateral boundaries were set

Fig. 3. Concentration profiles of: (a) N_2 , (b) O_2 , (c) CO_2 , (d) CO , (e) $\text{O}-\text{S}$ and (f) O^--S in the SnO_2 matrix, at a temperature of 573 K and an interface CO mass fraction of 10^{-4} .

as symmetries. The left side boundary, the sensor–air interface, was set as a wall, while the right side boundary was also set as a symmetry. A diagram of the grid is shown in Fig. 2.

The procedure for extracting data was as follows: For a given microstructural case, the solution was first obtained without the presence of target gas. Resistivity values calculated in these cases were then stored as the R_0 values for each cell in the domain. The target gas concentration at the interface was then set to a finite value and the simulation was restarted. Convergence was subject to the condition that all residual values for the partial differential equations had to go below 10^{-7} .

The microstructural properties and the surface chemistry inside the ceramic matrix were coupled with the gas diffusion solutions. Initialization of the system entailed setting oxygen and nitrogen concentrations in the porous fraction of the sensor matrix equal to their proportional mass fractions in air, 0.2095 and 0.7808, respectively, the balance being CO_2 and Ar, which were excluded from the simulation. The temperature of the system was set to 573 K. Since the reaction zone extended over a very thin material layer, and typical sensor systems include external heat sources and controls, thermal effects arising from the chemical reactions in this thin zone were not considered in the present treatment. A number of concentration profile plots are given in Fig. 3, showing the behaviour of the diffusing and interdependent gas and surface species.

A number of comments can be offered on the results in Fig. 3. The O_2 and CO profiles level off at a certain depth, indicative of the equilibrium achieved between diffusion and their consumption due to surface reactions. Since the CO_2 is produced internally as a by-product, its profile is reversed in general character, and has its minimal value at the sensor–gas interface where it can also diffuse back out into the external gas. The adsorbed atomic oxygen (O^- -S) and the ionized oxygen (O^- -S) have linked profiles, but the magnitude of the adsorbed atomic species is much lower since the kinetics of ionization are extremely fast.

Part (e) of Fig. 3 shows slight increase in $[\text{O}^- \text{S}]$ when CO is present. This result is a numerical artefact linked to the transient solution method. The $\text{O}^- \text{S}$ is consumed by the oxidation reaction in a rate based step for producing $\text{O}^- \text{S}$. When the concentration of $\text{O}^- \text{S}$ decreases due to the presence of CO, the reverse reaction rates of both the oxidation and adsorption reactions are slightly slower, producing a slightly higher $\text{O}^- \text{S}$ concentration. In real terms, this has negligible impact on the results as the surface oxygen remains at a level where the reaction rates essentially consume it all in one step.

The diffusing gas concentration values are plausible in that they show spatial variations in line with other measurements and calculations from the literature. Further, for cases without CO, the surface species show surface coverage in the range of 0.001 for $\text{O}^- \text{S}$ and 1.7×10^{-5} for $\text{O}^- \text{S}$ (i.e.; normalized with respect to S_0), in agreement with respective values of 0.0008 and 1.5×10^{-5} from theoretical Monte Carlo calculations for these species presented by Pulkkinen et al. [15].

5. Sensor conductivity

Recall Eq. (11) which is used to calculate a value of effective conductivity in the presence of the diffusing gases for a given microstructure. It is an intractable non-linear expression and requires an iterative numerical solution for σ_{eff} .

A theoretical study of the general behaviour of Eq. (11) was done to assist its implementation in the simulation. From the gas sensing mechanisms, the essential factor in determining the functionality of the conductance was the parameter f_{gb} , which is a measure of the contribution of grain boundary conductance to the overall conduc-

Fig. 4. Plot comparing present numerical simulation output with analytical solutions of Sakai et al. The numerical tests were conducted using a value of 0.05 for $C_{A,s}$.

tance, also known as the depletion layer volume fraction. In more detail [12],

$$f_{\text{gb}} = f_{\text{np}} \left(\frac{N_d}{N_i} \right) = f_{\text{np}} \frac{N_s A_g}{2x \rho_M V_g} \quad (12)$$

Above, f_{np} is the non-porous volume fraction of the compact, and the ratio N_d/N_i is the fraction of surface sites occupied by ionic oxygen, calculated explicitly using A_g which is the surface area of one grain, x the oxygen defect concentration in SnO_2 , ρ_M the number of molecular units per volume, and V_g the grain volume. An x value of 0.15 ± 0.093 for nano-scale grains of SnO_2 against air was measured by Yoo et al. [16]. The value was adjusted to $x=0.135$ based on the functionality of defect concentration being inversely proportional to grain size [17].

6. Model validation

The model was first tested over a 300 nm depth and compared identically to generic results given by Sakai et al. [3], shown in Fig. 4.

The simple case of constant grain size and microstructural density with both zero and nonzero concentrations of CO at the sensor–air interface shows the effect of O_2 diffusion inside the sample in Fig. 3 b, e and f. Runs were done at 573 K, with 90% theoretical density and 20 nm grain diameters.

Referring back to Fig. 3 f, oxygen ion concentrations are plotted for two cases, the first in red with zero CO concentration, the second with an external CO mass fraction of 10^{-4} . This data shows that the introduction of CO into the system reduces the oxygen ion concentration across the range of its profile, and will accordingly make appreciable changes to the conduction, thereby driving the sensing phenomena.

The conductivity measurements described above were compared to some data generated by the sensor simulation, shown in Fig. 5. In the absence of CO, the peak in the conductance that is present around 530 K is attributed to the increase in charge carriers in the semiconductor material coupled with the eventual dominance of the oxygen chemisorption and ionization processes at higher temperatures. The simulation data consists of only five points, but the observed maximum at the 573 K point is qualitatively consistent with the measured data. Other results from the literature can be cited in connection to these data: Ivashchenko et al. [18] reported a conductivity maximum for SnO_2 around 560 K and Korotcenkov et al. [19] show this maximum around 540 K.

Fig. 5. Plot of conductivity vs. temperature comparing measured data from experimental samples and simulation output.

Response data, while they reflect the temperature functionality of conductivity but also depend on other factors, have been shown to exhibit maxima in the 550–630 K temperature range [20,21]. When conductivity measurements are made with SnO₂ in humid atmospheres, only a weak maximum is shown in the 550–575 K temperature range, owing to added complexity in the surface chemistry equilibria [22].

The simulation determined composite-type conductivities based on the grain compact morphology, using pure crystal data from Das et al. as a basis for the thermal functionality for σ_g [23]. Quantitatively, the data sets differ at temperatures below 650 K, which is attributable to the estimates made about the microstructure of the experimental samples, notably the grain growth which occurred under sintering. The numerical simulation is not accurate at higher temperatures since the effects of ion adsorption of the atomic O²⁻ species, which are not accounted for in the model, become significant [2].

Another area to compare is that of conductance models. Fig. 6 shows the conductivity calculated in the present simulation which was based on surface chemistry and microstructural features (i.e.; Eq. (11)) plotted in light blue, and conductivity values plotted in red and dark blue based on a model given by Ding et al. [11], and using parameters given by Ionescu et al. [10].

The GEM theory model was applied since it was designed to accommodate spatial microstructural variation. Adapting N_i and N_d

Fig. 6. Comparison of Ding conductance model with present simulation showing spatial variation within the conducting layer.

Fig. 7. Response vs. sensor depth for a range of CO concentrations.

values [9,10], the GEM model makes use of the potential barrier concept in determining the conductivity contribution from the grain boundary [12,13], which is where the potential barrier is assumed to be located in models such as Ding's. Microstructural features, as discussed in Fig. 1, which arise from density or grain size variation, can be locally treated with the GEM model, imparting spatial resolution of the conductivity field over the domain. In effect, the GEM model is a more sophisticated implementation of the potential barrier concept.

The present model predicts a value on the same order as one given by Ionescu et al. for the slightly lower CO mass fraction of 8.0×10^{-5} .

$$\sigma_{\text{eff-DING}} = \sigma_g \exp\left(\frac{-q^2 N_s^2}{2k\epsilon_0 \epsilon_r N_d T}\right) + \sigma_{gb} \quad (13)$$

The model used in Eq. (13) can be shown to be hyper-sensitive to the adjustable parameter N_d , which is the site density of donors. A two order of magnitude range is considered possible for this parameter [24]. With this wide range, the parameter can be adjusted to calculate an accurate single point value for the conductivity. Accurate agreement at one point along with variation in other parameters will cause the conductance to swing sharply between σ_{gb} and σ_g values as seen in Fig. 6. The value of $N_d = 9.6 \times 10^{24}$ was from [10], and $N_d = 2.3 \times 10^{24}$ was from [11]. These effects are liable to be consequences of not considering morphological elements connected to conductivity, so that variations in oxygen ion concentration end up having an unrealistic and exaggerated impact on the electroceramic properties.

Sensor response is often expressed as the ratio R/R_0 , which gives the ratio of material electrical resistance with the target gas present vs. a base state in pure air. For a device of a real thickness x_{lim} , this ratio is determined by,

$$\left(\frac{R}{R_0}\right)_{\text{DEVICE}} = \frac{R(x)}{R_0(x)} = \frac{\int_0^{x_{\text{lim}}} \sigma_0(x) dx}{\int_0^{x_{\text{lim}}} \sigma(x) dx} \quad (14)$$

Ultimately, the R/R_0 plot for a CO mass fraction of 10^{-4} can be determined as shown in Fig. 7. When conductivity ratios are significantly different from unity, the response of the device improves. It can be seen that thinner devices are preferable. The R/R_0 values in Fig. 7 are in general agreement with some simplified calculations performed by Chwieroth et al. [12].

7. Parametric studies with the simulation

7.1. Effect of sensing layer depth and CO concentration

Given that the sensor electrical properties are driven by gas diffusion and reaction, it was shown that the surface chemical activity is greatest in the near interface region. As a consequence of this situation, the depth of the ceramic film employed as a sensing layer is a critical and important factor in designing and fabricating sensor devices.

To this end, Fig. 7 demonstrates these effects. Using a simulation run with an interfacial CO concentration of zero to provide R_0 values, then introducing CO at different concentrations, R profiles are obtained. Sensor response is seen to increase with target gas concentration. In Fig. 7, what are shown are local values of the R/R_0 ratio. In real sensors however, one overall value of this ratio is provided, and it comes from electrical measuring devices which obtain a value for an entire film or layer. That is, values of R and R_0 are separately determined over a prescribed film thickness, and their local ratio is then integrated, to give the value $(R/R_0)_{\text{DEVICE}}$ [3]. The prediction of this simulation compares well with a value reported by Ionescu et al. [10] for a CO mass fraction of 1.3×10^{-4} . The present simulation considered a CO fraction of 10^{-4} , so the slightly lower R/R_0 value reported by Ionescu corresponds to higher response for higher CO concentration. The Ionescu data was not resolved spatially, so the constant value shown on the plot simply is for comparison purposes.

Fig. 7 shows the effect of integrating to different x_{lim} values. The sensitivity of the device is clearly improved as the sensing layer thickness decreases. As the target gas concentration (mass fraction) at the interface decreases, so also does the sensor response. The simulations in Fig. 7 were run with $T = 573$ K, $\rho = 0.9$, and $d_p = 20$ nm.

7.2. Density variation

The main effect of matrix density on sensor performance is that for a given grain size, the ratio of surface area to volume increases, thereby augmenting the relative impact of the electroceramic surface chemical effects. A more porous matrix in general, produces a more sensitive sensor. The theoretical density range of 0.50–0.95 is considered in Fig. 8.

Some of the lower density microstructures considered here may be purely hypothetical, but are considered nonetheless to explore parametric functional tendencies. It should be noted that the particle size considered here was 20 nm. Laser deposition methods will

Fig. 8. Response vs. sensor depth for a range of theoretical densities.

Fig. 9. Conductivity as a function of temperature for a 1000 nm thick SnO_2 layer sensing CO at an interfacial mass fraction of 10^{-4} . Profile also shown for case with CO absent.

give quite dense films (~ 0.90 theoretical density) and small grain sizes. SnO_2 layers produced by other methods which may involve conventional types of sintering will have microstructures affected by much more grain growth and heat driven surface diffusion, such that the densities are much lower (~ 0.50 theoretical density) but the sensor performance may not be much improved since the grain sizes would be commensurately much larger. The simulations in Fig. 8 were run with $T = 573$ K, $d_p = 20$ nm and an interface CO mass fraction of 10^{-4} . Again, the use of Knudsen diffusion is made with the 50% porosity case for the purposes of exploring sensor response in a broad range of the parametric space, with the understanding that the results as shown are intended to be more qualitative than strictly quantitative.

7.3. Effect of temperature

As temperature increases, the kinetics of the reactions are accelerated, with the main effect of lessening the oxygen ion concentration in the diffusion zone. At ambient temperatures, the surface chemical reactions are too slow to produce any appreciable consumption of oxygen (O^-) ions, and thus the SnO_2 material does not exhibit sensor characteristics. Heated to 573 K, at a CO mass fraction of 10^{-4} , the conductance decreases somewhat for cases without CO. Temperature effects are linked to the oxygen ion profile without the presence of target gas, and thus induce an appreciable sensor response at 573 K and above, as seen in plot showing con-

Fig. 10. Response vs. sensor depth for a range of temperatures. For $d_p = 20$ nm and CO mass fraction of 10^{-4} .

Fig. 11. Response vs. sensor depth for a range of grain diameters in the sensor ceramic microstructure.

ductivity in Fig. 9. Simulation data showing R/R_0 values are plotted in Fig. 10. These cases were run with $\rho = 0.9$, $d_p = 20$ nm and an interface CO mass fraction of 10^{-4} .

7.4. Effect of grain diameter

The conductivity decreases markedly as the grain size increases, primarily from the change this causes in the surface to volume ratio. For the system and operating conditions under consideration here, a mean grain size under 50 nm would be required to provide adequate sensor performance. The simulations in Fig. 11 were run with $T = 573$ K, $\rho = 0.9$ and an interface CO mass fraction of 10^{-4} .

7.5. Effect of a graded density in the sensing layer

The density was shown previously in Fig. 8 to have a marked effect on conductivity. This was primarily through the increased surface to volume ratio obtained at a constant grain size. The effect of grading the density seems straightforward in the sense that it is tantamount to adding material of greater specific surface area to the sensing region and hence, increasing sensor sensitivity. The density effects, as presented in Fig. 12 are purely hypothetical, and hence notional in their application, as it may not be really possible to prepare a powder compact with density gradations without simultaneously having to incorporate grain size functionality as well. For example, the case 90–75% implies $\rho = 0.90$ at the gas interface, and

Fig. 12. The effect of a microstructural density gradient on sensor response.

$\rho = 0.75$ at the depth of 1000 nm inside the layer. Increasing porosity with depth serves to maintain the R/R_0 response closer to a constant value across a wider layer depth. Reversing the gradient takes advantage of the higher sensitivity of the less dense material in the region near the gas interface. The simulations in Fig. 12 were run with $T = 573$ K, $d_p = 20$ nm and an interface CO mass fraction of 10^{-4} .

8. Conclusions

A simulation based on physical fundamentals which coupled the diffusion of a mixture of gases into a porous ceramic matrix, with simultaneous interdependent surface chemical and electroceramic calculations, has been established.

Surface concentrations of adsorbed species have been shown to match ranges found in other studies, and the electroceramic trends demonstrated are all plausible and self consistent. The microstructure based General Effective Media conductance model of Eq. (11) was shown to give physically plausible results that were consistent with all the parametric variations imposed. Further, the R/R_0 ratios calculated were consistent with published values for SnO_2 devices for detecting CO. Thermodynamic parameters as well as microstructural parameters were investigated.

The simulation as it stands, 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 for predicting 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.

Acknowledgement

We thank Mr. Laurent Peigat of ENSCI Limoges for experimental measurements done in support of this project.

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