

Application of Surface Science to Preparation and Characterization of Solid-State Chemical Sensors

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Beyond the capabilities of detecting and discriminating chemical species, sensors are advantageous with respect to their stability, durability and response times. The aim of this study is to apply surface science to common problems found in the fabrication of chemical sensors, focusing on sensor stability. Models are proposed, which describe grain growth and intragrain defect diffusion, and optimal preparation procedures are elucidated for obtaining stable sensor materials.

1. Introduction

The greatest challenges in the fabrication of chemical sensors and all electronic devices are field durability and reliability. Weak stability leads to high maintenance costs in industrial environments, while the lack of dependable, long-lived sensors prevents their incorporation as safety devices for home and in environmental applications.

The durability of a chemical sensor is normally determined by the stability of its surface. This concern obviously goes far beyond the standard prerequisite of thermodynamic phase stability. Among others, three factors which may affect sensor operation are: (1) grain size changes, (2) drift in the surface defect concentration, and (3) irreversible gas adsorption.

The aim of this work is to review problems associated with stability, providing interpretations for commonly observed problems of sensors, and suggesting possible solutions to improve their performance. We will focus on the first two issues, and a study of irreversible gas (water) absorption will appear in forthcoming papers.

2. Grain Coalescence and Material Sintering

Grain coalescence is known to occur during sensor operation as a result of the relatively high operation temperature. Such a growth is expected to modify the electrical response of the sensor since it changes the grain surface area (and also the size of the intergrain contact area). A rather thorough study of long-term degradation was reported by Nakamura.⁽¹⁾ He showed that SnO₂-based commercial devices exhibit growth from an initial size of 5 – 15 nm up to elongated grains with sizes of about 20 – 40 nm after one year of usage. More detailed data were collected by Gautheron et al.⁽²⁾ on thin SnO₂ films deposited at different temperatures. Grain sizes were shown to increase from 12 nm to 29 nm when the deposition temperature increases from 460°C to 560°C.

The growth mechanism can be analyzed using the Lifshitz-Slezov model.^(3,4) For pellets, grain distribution is affected by the coalescence of voids inside the solid. The average grain size $\langle R \rangle$ is thereby predicted to depend on the processing temperature T and on the processing time t as

$$\langle R \rangle^3 = \frac{8}{9} D_v \frac{\Sigma}{kT} \mathcal{V}^2 c_{v_i} \quad (1)$$

$$= \frac{8}{9} D_v^0 \frac{\Sigma_0}{kT} \mathcal{V}^2 c_{v_i}^0 \exp\left(-\frac{\Delta G_{f,v} + E_D + E_\Sigma}{kT}\right). \quad (2)$$

Σ is the surface energy, \mathcal{V} is the atomic volume, c_v is the vacancy equilibrium concentration, D_v is the bulk vacancy diffusivity and k is the Boltzmann constant. We also expanded D_v , Σ and c_v as $D_v = D_v^0 \exp(-E_D / kT)$, $\Sigma = \Sigma_0 \exp(-E_\Sigma / kT)$, $c_v = c_v^0 \exp(-\Delta G_{f,v} / kT)$.

In films, void coalescence is shown⁽³⁾ to compete with a mechanism of void outdiffusion (expulsion). The former dominates the film region far from the outer surface, while the latter controls the remaining part. The boundary between the two regions is set at a depth ζ given by

$$\zeta^3 = 3^{5/2} \frac{D_v \Sigma \mathcal{V}^{1/2} c_{v_i}}{Q_0^{3/2} kT}, \quad (3)$$

where Q_0 is the initial vacancy supersaturation over the entire film (grains and voids). Two characteristic times can therefore be written: for coalescence,

$$\tau_c \equiv \frac{3}{4\pi} kT \frac{c_v^0}{c_v^0} \times \frac{1}{n_0 D_v^0 \Sigma_0 \mathcal{V} c_{v_i}^0} \exp\left(\frac{\Delta G_{f,v} + E_D + E_\Sigma}{kT}\right) \quad (4)$$

(where n_0 is the initial number of grains and c_0 is the initial concentration of grains and

vacancies); and for void outdiffusion,

$$\tau_s \equiv \frac{a^2}{D_V^0} \exp(E_D / kT) \quad (5)$$

(where a is the film thickness or ζ , whichever is smaller).

3. Defect Diffusion

Interface-related degradation has been observed and studied in ZnO and SnO₂-based semiconductor sensors. In a previous paper⁽⁵⁾ we showed that gas-solid equilibration induces different equilibrium densities of defects at the exposed surface with respect to the bulk. Therefore, another active degradation mechanism of the electrical response is the (slow) migration of defects throughout the grain.

Finite (and slow) defect diffusivity leads to a defect density gradient between the grain surface and the bulk. At the surface, defect density c_s is given by

$$c_s = K_s p^{-1/n}, \quad (6)$$

where K_s is the equilibrium constant of the defect-forming reaction, p is the analyte partial pressure and n is an appropriate integer depending on the reaction stoichiometry. In the bulk, however, defect concentration c_b can be expressed as

$$c_b = K_b^{1/n}. \quad (7)$$

Therefore, the defect profile throughout the grain can be written as

$$c(x, t) = c_s + (c_b - c_s) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right). \quad (8)$$

Note that the previous equation holds when $c_s > c_b$, which is usually the case for sensor applications. For $x/(2\sqrt{Dt}) \ll 1$ the error function can be expanded to the linear term. The resulting linearly graded junction can be analyzed by the depletion layer approximation. The potential barrier ϕ_B at the junction can be written as

$$\phi_B = \frac{e}{\epsilon_s} \left[\frac{1}{2} c_s x_d^2 - (c_b - c_s) \frac{x_d^3}{6\sqrt{Dt}} \right], \quad (9)$$

where x_d is the width of the depletion layer, e is the electron charge and ϵ_s is the material permittivity. Therefore, its differential capacitance in the absence of dc bias V_a computes as

$$\frac{c(t)}{A} = \frac{1}{A} \left. \frac{\partial Q_s}{\partial V_a} \right|_{V_a=0} = \sqrt{\frac{c_s \epsilon_s e}{2 \phi_B}} - \frac{\epsilon_s (c_b - c_s)}{c_s} \sqrt{2 \sqrt{Dt}}, \quad (10)$$

where A is the junction area. Its differential conductance is independent of time. Thus, in the low-signal limit the electrical transient equation reads

$$\mathcal{R} \frac{dQ_s}{dt} + \frac{Q_s}{\pi_0 - \pi_1 / \sqrt{t}} = V_0, \quad (11)$$

where \mathcal{R} is the junction resistance (per unit area), Q_s is the surface charge, V_0 is the applied voltage, and π_0 and π_1 are short-hand notations for the first and second terms of the right-hand side (r.h.s.) of eq. (10), respectively. Eq. (11) holds for $V_0 \ll \phi_B$ and $t \gg (\pi_1/\pi_0)^2$.

The solution of eq. (11) is rather cumbersome⁽⁵⁾ and can be written in finite terms only in the asymptotic case $t \rightarrow \infty$. The asymptotic expansion gives the following expression for the conductivity:

$$\sigma(t) = \sigma_1(t) - \sigma_2(t), \quad (12)$$

where

$$\sigma_1(t) \propto \frac{\pi_1^3 t^{3/2}}{\mathcal{R}^{1/2} \pi_0^3} \quad (13)$$

and

$$\sigma_2(t) \propto (\mathcal{R} \pi_0)^\beta t^{-\beta} e^{-t/R\pi_0} \quad (14)$$

with $\beta \equiv \pi_1^2 / R \pi_0^3$.

In spite of its mathematical complexity, the previous equations provide simple physical information. The current is controlled by two mechanisms, each independently contributing to its transient behavior. The (fast) exponential surge in the current (σ_2) results from the standard charging of the capacitor associated with the depletion layer. This is the mechanism responsible for the gas-sensing properties of the material. A much slower drift of the capacitance value adds to it, controlling the long term characteristics of the sensor. This is due to the diffusion of defects throughout the grain (σ_1), and can be held partially responsible for device degradation.

Moreover, in this case, a characteristic time must be written. However, the decay of $\sigma(t)$ is not exponential. Therefore, some adjustments are needed. Based on physical considerations, signal drifts are not expected either when diffusivity is high or negligibly small. In the former case, bulk-surface equilibration takes place immediately, while for $D \rightarrow 0$ adiabaticity is recovered. Accordingly, an effective characteristic time is written as

$$\tau_D \equiv \frac{(\tau_1 - \tau_2)^2}{\tau_1}, \quad (15)$$

where

$$\tau_1 \equiv \mathcal{R}^2 \frac{2Dc_s^{7/3}\epsilon_s e}{\phi_B(c_b - c_s)^2} \quad (16)$$

and

$$\tau_2 \equiv \mathcal{R} \sqrt{\frac{c_s \epsilon_s e}{2\phi_B}} \quad (17)$$

Note that, as expected, $\tau_D \rightarrow \infty$ both when $D \rightarrow \infty$ and when $D \rightarrow 0$.

4. Discussion

We can compare model consistencies from data collected on sensor materials. The Lifshitz-Slezov model proves to properly fit experimental data collected on SnO₂. Fitting

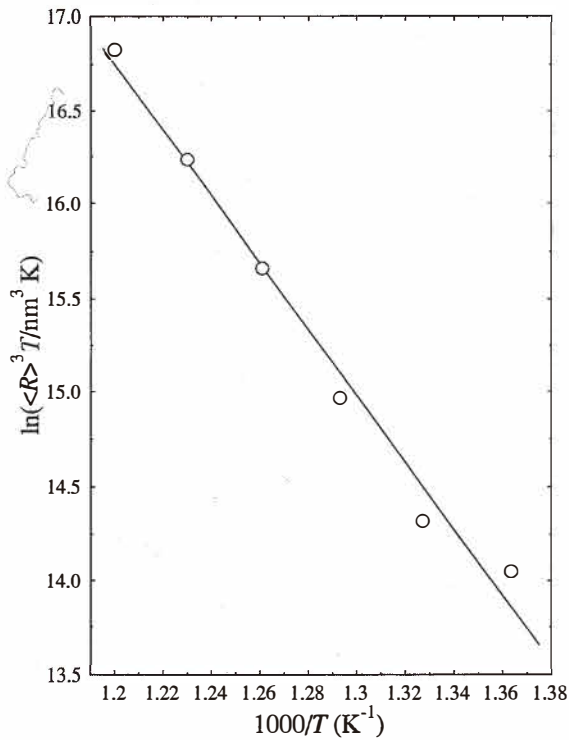


Fig. 1. Best fit of Lifshitz-Slezov equation to grain size data in tin dioxide.

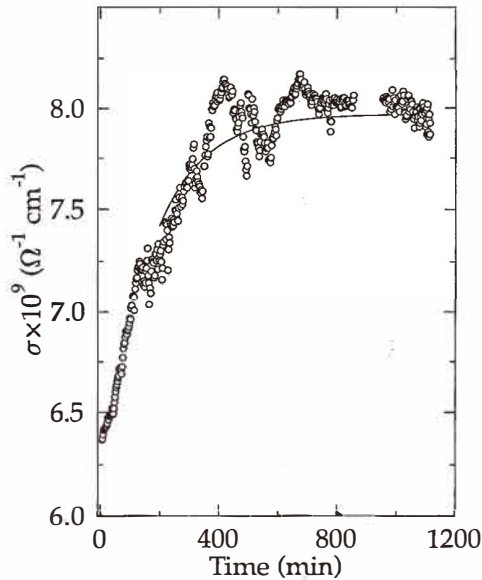


Fig. 2. Drift of the conductivity as a function of time in zinc oxide. Line shows the best fit to eqs. (12)–(14).

Labeau's data⁽²⁾ to eq. (2) yields $\Delta G_{f,v} + E_D + E_E = 1.52$ eV (Fig. 1), also providing an estimate for $\zeta Q_0^{1/2}$ of $2.85 \text{ nm}^{-1/2}$ at 500 K.

Resistivity drift due to intragrain diffusion in $\text{ZnO}^{(5)}$ was studied in detail. Figure 2 shows the fit of eq. (12) to typical transient conductivity data for thick ZnO films exposed to oxygen. Defect diffusivity (in the case Zn_i) computes to $(4.8 \pm 0.6) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \exp[-(0.60 \pm 0.07) \text{ eV}/kT]$, which is in good agreement with Thomas' measurements,⁽⁶⁾ of $5.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \exp(-0.55 \text{ eV}/kT)$.

Based on eqs. (4)–(15), some conclusions can be drawn regarding nonthermodynamic phase stability. Two diffusivities enter the characteristic times, namely the diffusivity of vacancies (D_v) and the diffusivity of mobile defects (D). When vacancies are neither fast nor very slow diffusers, we may quite obviously predict that grain growth-related instabilities will not be observed when D_v is low (i.e., at low temperatures, for a given material). Furthermore, low vacancy (and void) concentrations contribute to material stability. More interesting is the case of slow-diffusing vacancies. In this case, eq. (4) determines the highest operative temperature T_c (for a given material). Equation (15) defines a range of temperatures ($T_{D1} < T < T_{D2}$) in which sensor operation should be avoided. Depending on whether T_c is smaller or larger than T_{D1} and T_{D2} , proper material use is either *grain growth-limited* or *diffusion-limited*. In the former case, models suggest choosing preparation methods yielding highly compact and coarse-grained films. In the latter, nanocrystalline films might help fast surface-bulk equilibration, preventing hysteresis.

5. Conclusions

Semiquantitative models have been suggested, describing grain growth and intragrain defect diffusion. Characteristic times have been determined, which govern the overall degradation time of the sensor. Depending on which factor actually controls the material, indications can be obtained for proper preparation procedures to obtain stable sensor materials.

References

- 1 Y. Nakamura: *Chemical Sensors Technology*, ed. T. Seiyama (Kodansha Ltd., Tokyo, 1989) Vol. 2, p. 71.
- 2 B. Gautheron, M. Labeau, G. Delabouglise and U. Schmatz: *Sensors and Actuators B* **16** (1993) 357.
- 3 I. M. Lifshitz and V. V. Slezov: *Soviet Physics JETP* **35** (1959) 331.
- 4 I. M. Lifshitz and V. V. Slezov: *J. Phys. Chem. Solids*. **19** (1961) 35.
- 5 D. Narducci, S. Pizzini and F. Morazzoni: *Proceedings of the Symposium on Chemical Sensors II, Proc. Vol. 93-7* (The Electrochemical Society, Pennington, 1993) p. 325.
- 6 D. G. Thomas: *J. Phys. Chem. Solids* **3** (1957) 229.