Modeling H_2 Adsorption Processes at SnO_2 Nanowire Surfaces:
Parameter Estimation and Simulation

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Abstract: Metal-oxide gas sensors are advantageous for various purposes due to their physical and chemical as well as electrical properties. However, a lack of selectivity remains the central issue in this field. A quantitative understanding of the processes at the semiconductor surface is crucial to overcome these difficulties. In this work, we determine numerical values for the parameters governing the interaction of H_2 with the device to obtain quantitative information regarding the influence of the atmosphere on the sensor. With the computed values, simulations regarding the surface charge can be performed to understand the sensor behavior under different ambient conditions.

1 INTRODUCTION

Metal-oxide gas sensors show high thermal stability, chemical resistivity and excellent sensitivity towards various gases. In particular, the high surface-to-volume ratio of nanowires enables detection of target gas concentrations in the low ppm range (Comini, 2006; Brunet et al., 2012). As a consequence, there are numerous potential applications, ranging from environmental monitoring to portable medical devices. However, a lack of selectivity is still the central issue in this field, which inhibits the realization of the full potential and the optimization of sensor performance.

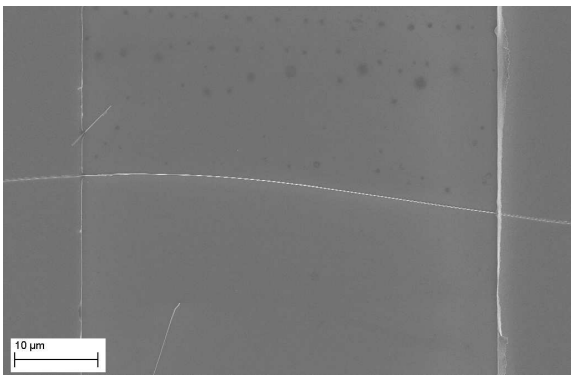

Figure 1: SEM image of an SnO_2 nanowire.

To overcome this fact, it is crucial to understand the processes taking place at the nanowire surface and their influence on the electrical properties of the semiconductor (Barsan and Weimar, 2001; Rehrl, 2011). There are several reaction path models proposed in the literature for various gases (Hahn et al., 2003; Malyshev and Pislyakov, 2008) but the determination of numerical values of the reaction parameters is still an open problem, although first steps have been made with carbon monoxide adsorption (Fort et al., 2007; Fort et al., 2010; Tulzer et al., 2012). The parameter estimation for H_2 adsorption processes in dry air will be the central part of this work.

The extracted information on the surface properties can be implemented into a self-consistent 3D-model of the carrier transport in the nanowire, as it was already done with biosensors ((Baumgartner et al., 2011; Baumgartner and Heitzinger, 2012; Baumgartner et al., 2012)).

2 MODEL EQUATIONS

Starting from the chemical reactions describing the gas-surface interactions and using a rate-equation approach (Higham, 2008), we obtain a coupled system of nonlinear ordinary differential equations, in

which the essential parameters appear as coefficients. Chemical reactions are described in terms of concentrations of the agents present at the surface and of kinetic parameters k_i. In fact, the k_i vary depending on temperature, which can be taken into account using the Arrhenius form, i.e. writing $k_i := \kappa_i e^{-E_i/k_B T}$, where κ_i is a frequency factor and E_i is an activation energy. All the charged species at the nanowire surface can be identified as occupied energy levels, the so called extrinsic surface states. Their charge may be positive or negative. The adsorption of any species at the surface also changes the electrical properties inside the nanowire, which can be described in the occupation of certain energy levels, i.e. intrinsic surface states. These states are always negatively charged. The total surface charge is given by superposition of all the intrinsic and extrinsic surface states.

2.1 Sensor in Inert Atmosphere

The occupation of the intrinsic surface states is described by the following reaction:

$$N_u + e^- \rightleftharpoons N_S, \tag{1}$$

where $N_u := N_i - N_S$ is the number of unoccupied intrinsic surface states. Applying the mass action law, the differential equation for the occupation is

$$\frac{dN_S}{dt} = k_1 n_S N_u - k_2 N_S, \tag{2}$$

where

$$n_S = N_D e^{-\frac{q^2 (N_{eff})^2}{2\varepsilon\varepsilon_0 N_D k_B T}} \tag{3}$$

is the number of free electrons in the sensor that can reach the surface. N_D is the number of ionized donors in the nanowire, which is set to be $6{\cdot}10^{23}\mathrm{m}^{-3}$ in this work. The other parameters follow the usual notation and are listed in Table 1. If the sensor is exposed to an inert (e.g. nitrogen) atmosphere, this is the only equation to investigate.

2.2 H_2 Adsorption

In the case of H_2 adsorption in an atmosphere consisting of 80% nitrogen and 20% dry air, the reaction path is (Malyshev and Pislyakov, 2008)

$$\begin{aligned} \mathrm{O_2} + S_u &\rightleftharpoons \mathrm{O_{ads}}, & (4)\\ \mathrm{O_{ads}} + e^- &\rightleftharpoons \mathrm{O^-_{ads}}, & (5)\\ \mathrm{H_2} + \mathrm{O^-_{ads}} &\rightleftharpoons \mathrm{H_2O} + e^-. & (6) \end{aligned}$$

The first and the second equation describe the adsorption and ionization of oxygen molecules from the air; the last equation describes the oxygen desorption from the surface by generation of water molecules. Note that that the gaseous hydrogen just interacts with the adsorbed oxygen and not with the nanowire lattice in this model. Using the mass action law again we obtain

$$\begin{aligned} \frac{dN_O}{dt} &= k_3 [S_u][\mathrm{O}]^{1/2} - k_4 N_{O^-} - \frac{dN_{O^-}}{dt}, & (7)\\ \frac{dN_{O^-}}{dt} &= k_5 n_S N_O - k_6 N_{O^-} - \frac{d\mathrm{H_2O}}{dt}, & (8)\\ \frac{d\mathrm{H_2O}}{dt} &= k_7 N_{O^-} [\mathrm{H_2}], & (9) \end{aligned}$$

where $[S_u] := [S] - N_O - N_{O^+}$ is the number unoccupied extrinsic surface states. The effective number of surface states is then given by $N_{eff} := N_S + N_{O^+}$. These equations together with equation (2) give the full system to investigate.

Table 1: Quantites and Symbols.

N_i	# available intrinsic surface states
N_S	# occupied intrinsic surface states
N_u	# unoccupied intrinsic surface states
S	# available extrinsic surface states
S_u	# unoccupied extrinsic surface states
N_Δ	# surface states occupied by species Δ
N_{eff}	effective # surface states
N_D	# ionized donors
k_B	Boltzmann constant
T	temperature in Kelvin
q	elementary charge
ε	relative permittivity of SnO_2
ε_0	dielectric constant
k_i	reaction constants
κ_i	frequency factors
E_i	activation energies

2.3 Parameter Estimation

The considered equations contain parameters of different orders of magnitude. To obtain accurate results, it is therefore necessary to perform a nondimensionalization and scaling step. We will here use the following scaling (similar to (Ding et al., 2001)):

$$\widetilde{N}_\Delta := \frac{N_\Delta}{N_D^{2/3}} \quad \widetilde{S}_\Delta := \frac{S_\Delta}{N_D^{2/3}} \quad \widetilde{T} := \frac{\varepsilon_0 k_B}{q^2 N_D^{1/3}} \cdot T, \tag{10}$$

where Δ stands for the symbol of any species involved in the respective framework. This procedure yields the following system

$$N_S' = k_1 e^{-\frac{(N_S+N_{O^-})^2}{2\varepsilon T}} N_u - k_2 N_S, \quad (11)$$

$$N_O' = k_3 [S_u][\mathrm{O}]^{1/2} - k_4 N_{O^-} - N_{O^-}', \quad (12)$$

$$N_{O^-}' = k_5 e^{-\frac{(N_S+N_{O^-})^2}{2\varepsilon T}} N_O - k_6 N_{O^-} - \mathrm{H_2O'}, \quad (13)$$

$$\mathrm{H_2O'} = k_7 N_{O^-} [\mathrm{H_2}], \quad (14)$$

where the k_i now may also contain further constants according to the non-scaled system.

To obtain numerical values, a simulated-annealing algorithm was used within the *Mathematica* environment. Here, the numerical solution of the system (11)-(14) is compared to the experimental data. The deviation of the model from the experimental results is then minimized with respect to the unknown parameters.

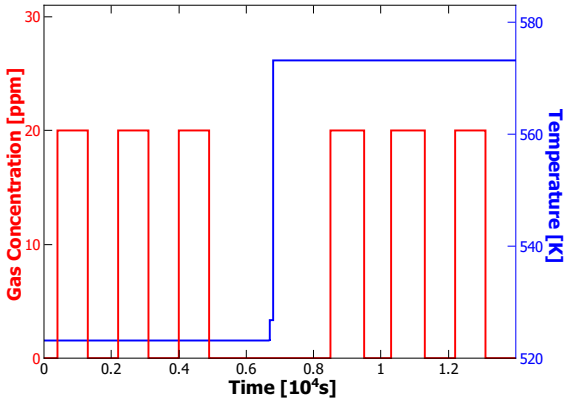

Figure 2: Experimental conditions for the investigated measurement.

3 RESULTS

The investigated experiment is described in detail in (Brunet et al., 2012), where the sensor preparation is explained as well.

In this work, we investigate the response of a single SnO_2 nanowire sensor to 20ppm hydrogen pulses in an atmosphere consisting of 80% N_2 and 20% O_2. To obtain information on the temperature dependence, the measurement is taken at 250°C and 300°C. The setup can be seen in Figure 2. The simulations show very good agreement with the experimental data and are shown in Figures 3 and 4. The deviation in the beginning of both diagrams is due to the fact that the sensor has not yet attained equilibrium regarding its resistive properties. The origin of the spikes in the 300°C degree measurement is not clear at the moment, but is under further investigation.

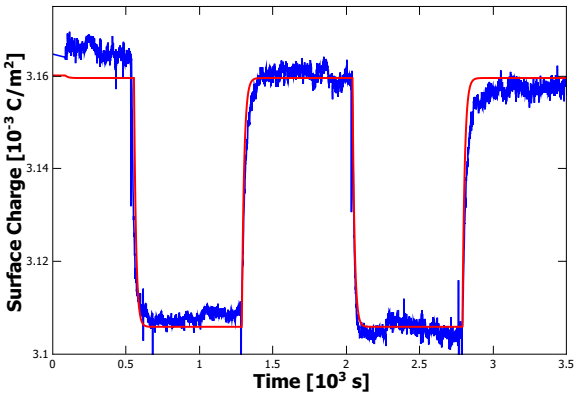

Figure 3: Comparison of experimental data (blue) to simulation results (red) at 250°C. Very good agreement is found.

4 CONCLUSIONS

Regarding the simulations at constant temperatures, the agreement of the simulation with the experimental data is very good. The qualitative as well as quantitative behavior of the sensor is covered by the investigated model. However, it turned out that the simulation of temperature changes during the measurement shows deviations from the experiment. There are many factors that may be responsible for this fact, such as response times of the sensor or non-validity of the mass action law for temperature transients. Nevertheless, the results can be used to extract characteristic features of the interaction of H_2 molecules with the SnO_2 surface.

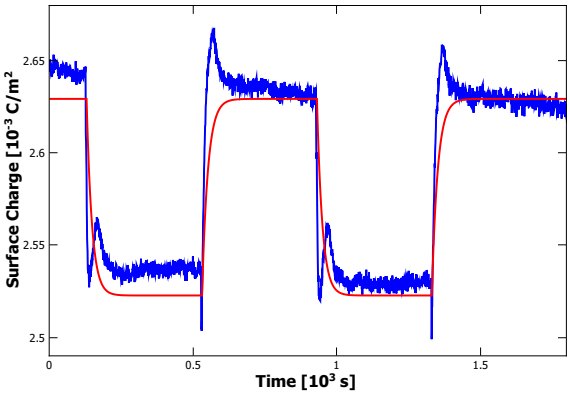

Figure 4: Comparison of experimental data (blue) to simulation results (red) at 300°C.

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REFERENCES

Barsan, N. and Weimar, U. (2001). Conduction model of metal oxide gas sensors. *Journal of Electroceramics*, 7:143–167.

Baumgartner, S. and Heitzinger, C. (2012). Existence and local uniqueness for 3d self-consistent multiscale models for field-effect sensors. *Commun. Math. Sci.*, 10(2):693–716.

Baumgartner, S., Vasicek, M., Bulyha, A., and Heitzinger, C. (2011). Optimization of nanowire DNA sensor sensitivity using self-consistent simulation. *Nanotechnology*, 22(42):425503/1–8.

Baumgartner, S., Vasicek, M., and Heitzinger, C. (2012). Modeling and simulation of nanowire based field-effect biosensors. In Korotcenkov, G., editor, *Chemical Sensors: Simulation and Modeling*, pages 447–469.

Brunet, E., Maier, T., Mutinati, G., Steinhauer, S., Köck, A., Gspan, C., and Grogger, W. (2012). Comparison of the gas sensing performance of SnO_2 thin film and SnO_2 nanowire sensors. *Sensors and Actuators B: Chemical*, 165(1):110–118.

Comini, E. (2006). Metal oxide nano-crystals for gas sensing. *Analytica Chimica Acta*, 568(12):28 – 40.

Ding, J., McAvoy, T., Cavicchi, R., and Semancik, S. (2001). Surface state trapping models forSnO2-based microhotplate sensors. *Sensors and Actuators B: Chemical*, 77(3):597–613.

Fort, A., Mugnaini, M., Rocchi, S., Serrano-Santos, M., Vignoli, V., and Spinicci, R. (2007). Simplified models for sno_2 sensors during chemical and thermal transients in mixtures of inert, oxidizing and reducing gases. *Sensors and Actuators B: Chemical*, 124(1):245–259.

Fort, A., Mugnaini, M., Rocchi, S., Vignoli, V., Comini, E., Faglia, G., and Ponzoni, A. (2010). Metal-oxide nanowire sensors for CO detection: Characterization and modeling. *Sensors and Actuators B: Chemical*, 148(1):283–291.

Hahn, S., Bârsan, N., Weimar, U., Ejakov, S., Visser, J., and Soltis, R. (2003). CO sensing with SnO_2 thick film sensors: role of oxygen and water vapour. *Thin Solid Films*, 436(1):17–24.

Higham, D. (2008). Modeling and simulating chemical reactions. *SIAM Review, Education Section*, 50(2):347–368.

Malyshev, V. and Pislyakov, A. (2008). Investigation of gas-sensitivity of sensor structures to hydrogen in a wide range of temperature, concentration and humidity of gas medium. *Sensors and Actuators B: Chemical*, 134(2):913–921.

Rehrl, M. (2011). *Differential Equation Models for Surface Reactions of SnO_2 Nanowire Gas Sensors and their Inverse Modeling.* Diploma Thesis, University of Vienna.

Tulzer, G., Baumgartner, S., Brunet, E., Mutinati, G. C., Steinhauer, S., Köck, A., and Heitzinger, C. (2012). Inverse modeling of CO reactions at SnO_2 nanowire surfaces for selective detection. *Procedia Engineering*, 47:809–812.