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Inverse modeling of CO reactions at SnO_2 nanowire surfaces for selective detection

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Abstract

Nanowire gas sensors show high sensitivity towards various gases and offer great potential to improve present gas sensing. In this work, we investigate experimental results achieved with an undoped single SnO_2 nanowire sensor device for CO pulses in N_2 atmosphere at different operating temperatures. We calculated the reaction parameters according to the mass action law including frequency factors, activation energies, and numbers of intrinsic as well as extrinsic surface sites. With the values obtained, we then calculated the surface charge of the nanowire sensor by solving the corresponding differential equations. The simulated results agree very well with the experimental values at an operating temperature of 200°C and hence provide good understanding of the chemical reaction. This can be used to simulate the current through the transducer and consequently the sensitivity of the device, and the parameters provided here are useful for computational procedures to provide selectivity.

Keywords: nanowire; gas sensors; selectivity; inverse modeling; surface reactions; SnO_2.

1. Introduction

Metal-oxide gas sensors are widely used due to their high chemical resistance and thermal stability. In particular, nanowire sensors are preferable because of their large surface-to-volume ratio leading to high sensitivity enabling the detection of various toxic gases with concentrations in the low ppm range [1]. However, a lack of selectivity, which also leads to the problem of cross sensitivity, remains the central

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issue of gas sensors. In order to achieve selectivity, a quantitative understanding of the underlying chemical reactions at the sensor surface and their influence on its electric conductivity is crucial [2].

In this work, we present an approach to determine the essential parameters of the gas interactions with the nanowire surface, which are described in terms of electron transfer. Finding numerical values of these parameters is essential to optimize sensor performance regarding selectivity.

Nomenclature

k_i	frequency factors (i=1,...,6)	N_i	number of available intrinsic surface sites
E_i	activation energies (i=1,...,6)	$[S]$	number of available extrinsic surface sites
q	elementary charge	n_S	number of free electrons at the surface
N_D	number of ionized donors	N_S	number of occupied intrinsic surface states
T	temperature in Kelvin	N_C	number of charged occupied extrinsic surface states
k	Boltzmann constant	N_{CO}	number of uncharged occupied extrinsic surface states
ε	permittivity of SnO_2		

2. Methods

2.1. Underlying Reactions

The sensor conductivity is influenced, following the potential barrier theory [3], by its surface charge due to the occupation of electronic states slightly below the conduction band level, the so called *surface states*. These consist of states stemming from the gas adsorption (namely *extrinsic* states) and states stemming from free electrons in the nanowire (*intrinsic* states) [4]. Proposed reaction paths describing the occupation of the surface states are [5]

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

$$\mathrm{CO} + S \rightleftharpoons [\mathrm{CO} - S], \tag{1b}$$

$$[\mathrm{CO} - S] \rightleftharpoons [\mathrm{CO}^+ - S] + e^-. \tag{1c}$$

The first equation describes the occupation of intrinsic surface states, while the last two equations describe the occupation of extrinsic uncharged and charged ones, which is a two-step mechanism. In the following, we will denote them by N_S, N_{CO} and N_C, respectively. Since the extrinsic surface states are positively charged while the intrinsic ones are negatively charged, the effective charge of the surface is given by $q(N_S - N_C)$.

Using the mass action law and the Arrhenius form for the reaction constants to take the influence of temperature into account, we have a system of nonlinear ordinary differential equations modeling the quantitative behavior of the state occupation. The system is

$$\frac{dN_S}{dt} = k_1 e^{-\frac{E_1}{kT}} n_S (N_i - N_S) - k_2 e^{-\frac{E_2}{kT}} N_S, \tag{2a}$$

$$\frac{dN_{CO}}{dt} = k_3 e^{-\frac{E_3}{kT}} ([S] - N_{CO} - N_C)[\mathrm{CO}] - k_4 e^{-\frac{E_4}{kT}} N_C - \frac{dN_C}{dt}, \tag{2b}$$

$$\frac{dN_C}{dt} = k_5 e^{-\frac{E_5}{kT}} N_{CO} - k_6 e^{-\frac{E_6}{kT}} n_S N_C, \tag{2c}$$

where the number of electrons at the surface is given by $n_S=N_D \exp[-q(N_S - N_C)^2/(2N_D\varepsilon kT)]$, which makes the system nonlinear and coupled.

The parameters to be determined are the frequency factors k_i (i=1,…,6), the activation energies E_i (i=1,…,6) and the available intrinsic and extrinsic surface sites N_i and [S].

To find the correct parameters, we first note that $(N_S - N_C)$ is the effective number of occupied surface states, which can be computed from the experimental data. Using this in the equations above, the ODE system becomes linear. The parameters are now found using a simulated annealing algorithm.

2.2. Measurements

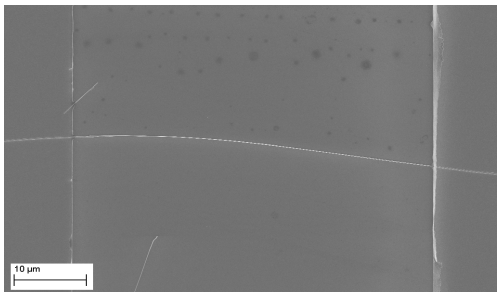

Figure 1: SEM image of the SnO_2 nanowire.

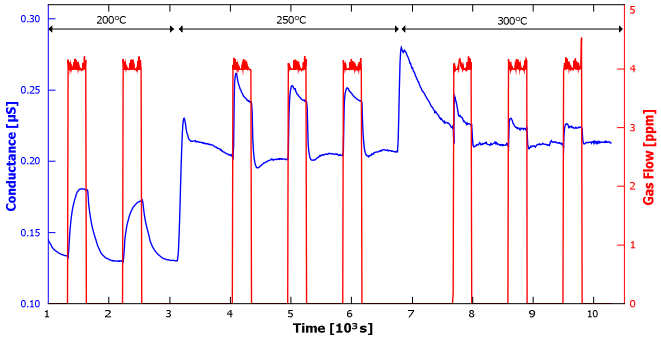

Figure 2: Measured conductance and gas flow. At t=3000s and t=7000s, the temperature was increased. The sensitivity is in the low ppm range.

In this work, we investigate a measurement of 4 ppm CO pulses in an inert atmosphere of N_2 at a temperature of 200°C, 250°C and 300°C carried out with a single undoped SnO_2 nanowire gas sensor. Every pulse lasts 300s, where at least 600s lie between two pulses (see Figure 2). In this case, we can estimate the parameters in two steps, i.e. finding parameters for equation (2a) when no CO is present and then using these values for the determination of the remaining parameters in equations (2b) and (2c) when CO is present.

3. Results and Discussion

The estimated parameters are given in Table 1. These values seem to be physically reasonable and, moreover, the subsequent simulation of the sensor behavior using these parameters shows very good agreement to the experimental data at 200°C, as can be seen in Figure 3. We will use these results to simulate the current through the transducer as in [6-9] to gain more quantitative insight into sensitivity. However, it is important to note that the sensor behavior at higher temperatures is different and cannot be described with the reaction path proposed in this work despite extensive inverse-modeling efforts.

Table 1. Estimated values for the parameters

Parameter	Value	Parameter	Value	Parameter	Value
k_1 [m^3/s]	8.87×10^{-6}	k_2 [1/s]	5.62	k_3 [1/s]	1.25
k_4 [1/s]	1.76	k_5 [1/s]	1.36	k_6 [m^3/s]	2.45
E_1 [meV]	0.25	E_2 [meV]	0.182	E_3 [meV]	0.057
E_4 [meV]	0.131	E_5 [meV]	0.152	E_6 [meV]	0.051
N_i [1/m^2]	2.34×10^{15}	[S] [1/m^2]	7.8×10^{14}		

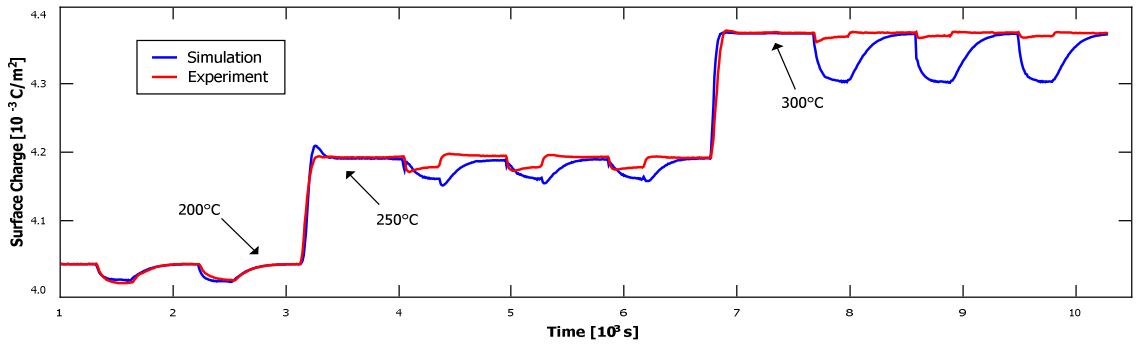

Figure 3: Comparison of the simulated surface charge and the surface charge computed from the experiment at 200°C, 250°C and 300°C. For 250°C and 300°C, extensive inverse-modeling computations indicate that the reactions paths are different than at 200°C.

4. Conclusions

In this work we presented an approach to determine numerical values for the parameters governing the chemical reactions at the surface of SnO_2 nanowire gas sensors.

Since the proposed estimate procedure is complex and involves many parameters, the authors are convinced that further improvements of the computations are possible. This, as well as a quantitative description of the surface reaction at higher temperatures will be the subject of future investigations. Moreover, the validity of reaction paths for other gases will be studied in order to extract significant sensor responses establishing selectivity.

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