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Response modeling of temperature modulated array of chromium doped nanostructured TiO₂ gas sensors

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Abstract

The aim of this work is to demonstrate that thermal modulation improves the selectivity of TiO₂-based resistive-type gas sensors. Sensor array, operating upon sinusoidal temperature profile over a temperature range of 240 – 300°C, is comprised of nanocrystalline TiO₂:Cr (0.1 – 10 at.% Cr) semiconductors switching from n-type to p-type at about 1 at.% Cr. Electrical resistance responses to reducing and oxidizing gases such as NO, NO₂, H₂, CH₄, C₃H₆ (0 – 3000 ppm) are dynamically recorded and compared in order to assess cross-sensitivity as well as humidity interference. Theoretical model developed for simple gas-solid interactions is extended to hydrogen.

1. Introduction

The main advantage of nanocrystalline gas sensors is their improved sensitivity due to the reduced grain size. However, the most important issue related to cross-sensitivity to humidity or interfering gases remains unresolved. Techniques like temperature modulation and dynamic response analysis have been investigated to enhance the measuring capabilities of arrays based on metal oxide gas sensors [2]. Gas sensing properties of TiO₂ doped with Cr for detection of hydrogen at a constant operating temperature (static mode) have been studied in [1]. Based on these results an array of nanocrystalline sensors operating upon temperature modulation was designed and tested [2]. The current work explores sensing behavior to other target gases and focuses on modeling of the dynamic sensor response. Substantial effort has been recently spent on modeling of the temperature modulated metal oxide sensor response to

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reducing and oxidizing gases [3-6]. However, the models discussed in the literature deal with simple gas-solid interactions, typical for CO or/and NO₂ with SnO₂. In this study, the model proposed in [4] is extended to simulate the TiO₂-based sensor response to hydrogen.

2. Experimental details

Nanocrystalline powders of TiO₂:Cr (0.1 - 10 at.% Cr) were used as a base material for preparation of gas sensors. The detailed study of physical and sensing properties at a constant temperature can be found in [1]. An array consisting of eight different nanostructured metal oxide gas sensors has been constructed and tested. The sensing properties have been measured in a self-assembled experimental setup presented in [2]. The sensor responses upon sinusoidal temperature modulation (240-300°C, frequency 2.1·10⁻³ Hz) have been recorded for H₂, NO, NO₂, CH₄, C₃H₈ (0 – 3000 ppm).

3. Results

The resistance changes of the n and p-type TiO₂:Cr nanomaterials over one sinusoidal temperature modulation period to various concentrations of hydrogen are presented in Fig. 1. TiO₂:Cr (0.1 at.% Cr) behaves like an n-type semiconductor sensor, i.e., its resistance decreases upon exposure to hydrogen (Fig. 1 a). On the other hand, reversed behavior of the TiO₂:Cr (1 at.% Cr) upon interaction with the same reducing gas (H₂) indicates a p-type conductivity. Moreover, as one can see in Fig. 1, the changes in the sensor resistance follow the sinusoidal profile of the operating temperature.

![Fig. 1. Dynamical changes in the electrical resistance of TiO₂:Cr (0.1 at.% Cr) (a) and TiO₂:Cr (1 at.% Cr) (b) upon one temperature modulation cycle (240 - 300°C) for different concentrations of H₂ at 0%RH.](image)

The responses of all the sensors in the array are presented in Fig. 2. In order to compare the numerical values of responses of n-type and p-type sensors, the following definitions have been adopted: R₀/R for n-type and R/R₀ for p-type, where R₀ is the electrical resistance in the reference atmosphere (air) while R corresponds to that upon exposure to target gas.
As one can observe in Fig. 2a, the p-type nanosensors have better response to hydrogen compared to other studied sensors. However, it can be seen that humidity affects the response to hydrogen of p-type sensors to a bigger extent than that of the n-type. At temperatures above 200ºC the interaction with water vapor creates chemisorbed hydroxyl groups OH⁻. The following equation has been proposed [3]

\[ H_2O_{(g)} + 2Ti_{Ti}^+ + O_{\alpha} \leftrightarrow 2(Ti_{Ti}^+ - OH^-) + V_{\alpha}^{**} + 2e^- \]  

As it is seen in Eq. (1) hydrogen molecules form the defect complexes with the lattice Ti ions. The resulting oxygen vacancies are a source of additional electrons. As shown in Fig. 2a, the best response to H₂ at 0% RH is obtained for the TiO₂:Cr (10 at.% Cr) nanosensor. Therefore, its response to all studied gases is presented in Fig. 2b. One can conclude that this sensor has a high selectivity to hydrogen compared to other studied gases. Similar results indicating high response to hydrogen are obtained for other studied sensors.

In order to simulate the dynamic responses, the surface state model of a metal oxide gas sensor described in [4, 5] was applied. The model includes parameters related to the gas adsorption, reaction processes, sensing material and the gas type. Assuming small contact between grains, the free conduction electrons have to overcome the surface potential barrier \( V_s \) when hopping from one grain to another. Under this hypothesis, the electrical conductance \( G \) can be expressed as [4]

\[ G(T) = G_0 \exp(-\frac{V_s}{kT}) + G_c = G_0 \exp\left(-\frac{q^2N_s^2(T)}{2\varepsilon_r\varepsilon_0N_dkT}\right) + G_c \]  

where \( G_0 \) is the pre-exponential factor, \( G_c \) corresponds the baseline level, \( q \) denotes the electron charge, \( k \) represents the Boltzmann’s constant, \( T \) stands for the absolute temperature, \( N_d \) is the total density of surface states, \( \varepsilon_r\varepsilon_0 \) is the electrical permittivity of the semiconductor and \( N_s \) is the density of the occupied states.

At temperatures higher than 240ºC, the chemisorption of oxygen may be described as:

\[ nS + \frac{1}{2}O_2 + e^- \rightarrow S - O^- + (n-1)S \]  

where \( S \) is a surface adsorption site, \( e^- \) is a free electron and \( S - O^- \) an ionosorbed oxygen. Hydrogen is considered to react at the oxide surface with the preadsorbed oxygen species \( S - O^- \).

Compared to a single step reaction to CO presented in [6] in this paper a three step response to H₂ is taken into account. Therefore, the following reactions are proposed:

\[ H_2 \rightarrow 2H \]
where \( k_i \) (\( i = -1, 1, ..., 4 \)) are the rate constants. The rate constants depend on the temperature according to the Arrhenius equation:

\[
k_i = k_{10} \exp \left( \frac{-E_i}{RT} \right)
\]

Thermally modulated responses of TiO\(_2\)-based sensors have been simulated assuming that the slowest, rate determining reaction is that given by (5). The results of conductivity simulation for n-type semiconductor upon interaction with hydrogen are given in Fig. 3.

As indicated in Fig. 3, the simulated responses reproduce the character of the experimental responses included in Fig. 1.

4. Conclusions

Nanocrystalline materials based on TiO\(_2\) doped with chromium have been successfully used in construction of thermally modulated sensor array to monitor selectively hydrogen at the presence of other reducing and oxidizing gases under influence of humidity. Dynamic resistance changes follow the profile of the operating temperature and are sensitive to target gas concentration. Switching from n-type to p-type conductivity is observed at 1 at.% Cr similarly to the result obtained under static mode of operation. P-type gas sensors exhibit higher response to H\(_2\) than those of n-type although their behavior is affected by the humidity to a greater extent. Theoretical simulation reproduces properly experimental sensor responses.

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References