

# INFLUENCE OF CATALYTIC METALS ON THE SURFACE REACTION RATES AND RESPONSE KINETICS IN SnO<sub>2</sub> THIN FILM GAS SENSORS

A. Šetkus<sup>a</sup>, C. Baratto<sup>b</sup>, E. Comini<sup>b</sup>, G. Faglia<sup>b</sup>, A. Galdikas<sup>a</sup>, Ž. Kancleris<sup>a</sup>,  
G. Sberveglieri<sup>b</sup>, D. Senulienė<sup>a</sup>, and M. Senulis<sup>a</sup>

<sup>a</sup> *Semiconductor Physics Institute, A. Goštauto 11, LT-01108 Vilnius, Lithuania*

E-mail: setkus@pfi.lt

<sup>b</sup> *University of Brescia, 9 Via D. Valotti, 25133 Brescia, Italy*

Received 14 January 2004

The resistance response to a steep change in gas composition is experimentally investigated in SnO<sub>2</sub>-based thin film sensors doped with catalytic metals Pt, Ag, W, and Mo. The influence of the catalyst on kinetics of response is analysed. The dependence of the signal on time is measured for a thin film exposed to the steep change in gas composition. Based on an approximation by multiexponential decays, the response time is evaluated from the experimental transients. The dependence of the response time on the metallic catalyst is explained in terms of dependence of the surface reaction rates on the impurity.

**Keywords:** metal oxide, thin films, metallic impurities, clusters, gas sensors, kinetics

**PACS:** 73.25.+i, 81.05.Rm, 81.70.Jm, 85.80.Dg

## 1. Introduction

The response and recovery times are commonly used to describe the rise and fall of the signal of metal oxide gas sensors. In general, these parameters are assumed equal to the time interval during which a major portion of the response signal is measured [1]. In most applications it is preferable that the advanced gas sensors were of fast response and recovery.

Diffusion of gas particles through the thickness of the sensitive material was proposed as a limiting process for the kinetics of the response of metal oxides to gas [2]. Effect of diffusion was experimentally verified in pressed pellets and thick films. In contrast to this, thin and ultrathin films were characterised by much slower response than it might be expected from the diffusion-based model.

Usually, surface chemical reactions are the target of modifications performed by the technological methods. Some of the methods are based on chemical catalysts that modify the surfaces in metal oxide sensors [3,4]. Present study deals with the influence of metallic impurities on kinetic characteristics of metal oxide sensors. Experimental tests are performed for tin-oxide-based thin film sensors. A phenomenological model

was employed for the interpretation of experimentally measured response to a steep change in gas composition of the atmosphere. We suppose that the dynamics of surface chemical reactions is the most important limitation for the kinetics of response in thin film metal-oxide-based gas sensors.

## 2. Model considerations

It is commonly accepted [1–4] that the surface oxygen controls the electron transport in polycrystalline metal oxide sensors. In oxygen-rich atmosphere, the surfaces of metal oxide are covered with oxygen species. The density of surface species is determined by equilibrium between chemisorption and desorption of gas. A small amount of target gas changes the density of the surface oxygen mainly because of chemical interaction between the gas and the oxygen. Since the surface oxygen is related to the electronic localisation states on the surfaces, a change of the oxygen density modifies the surface electrical charge and the surface potential barrier. As a result, the electron transport in the film depends on chemical composition of the atmosphere and, consequently, the response to gas is generated.

The unique aspect of our theoretical approach is the joint dynamic picture that includes all such processes as adsorption, desorption, bimolecular interaction, change of the surface electrical charge, and electron transport over the barrier. In contrast to other studies, we do not simplify analysis by separating the process flow into individual stationary steps, but aim at building a dynamic picture of the response [5].

Three interrelated stages are included in our analysis of the sensitive system. First we describe the surface coverage by oxygen after injection of the target gas into the air. The description is based on coupled rate equations for the coverage with oxygen  $\Theta_A$  and target gas  $\Theta_B$ :

$$\frac{d\Theta_A(t)}{dt} = F_A \sigma_A S_{0A} (1 - \Theta_A(t)) - \beta_A \Theta_A(t) - \nu_{AB} \Theta_A(t) \Theta_B(t), \quad (1)$$

$$\frac{d\Theta_B(t)}{dt} = F_B \sigma_B S_{0B} (1 - \Theta_B(t)) - \beta_B \Theta_B(t) - \nu_{AB} \Theta_A(t) \Theta_B(t), \quad (2)$$

where  $F$  is the flux of the particles hitting the unit area of the surface from the gas phase at pressure  $P$ ,  $\sigma$  is the area of one adsorption site,  $S$  is the sticking coefficient,  $\beta$  is the probability to desorb from a site per time unit, and  $\nu_{AB}$  is the rate of bimolecular interaction between the chemisorbed target gas and the oxygen species. The index  $A$  is for surface oxygen, while  $B$  is for target gas. The first term in the right-hand sides of both equations describes the adsorption rate. The second term is the desorption rate, while the third term is the rate of the Langmuir–Hinshelwood bimolecular step in which the adsorbed species are involved.

Second, the dependence of the surface potential barrier on the surface electronic states is described by the Poisson equation

$$\frac{d^2}{dx^2} \Phi(x) = \frac{\rho(x)}{\varepsilon \varepsilon_0}, \quad (3)$$

where  $\Phi(x)$  is potential energy of electrons,  $\rho(x)$  is electrical charge density.

Third, the resistance in a surface-controlled polycrystalline structure is typically determined by thermally activated electron transport:

$$R_{\text{film}} = R_0 \exp\left(\frac{\Delta E_a}{k_B T}\right). \quad (4)$$

Here  $R_0$  is the resistance of a homogeneous film,  $\Delta E_a$  is an activation energy for the electron transport,  $k_B$  is the Boltzmann constant.

In accordance with the present analysis the relationship between the kinetics of resistance response and the rate parameters of the surface chemical reaction is defined by

$$\frac{R(t)}{R(0)} = \exp\left\{Z \Theta_{A0}^2 \left[ \left(1 - \frac{q\eta}{\Theta_{A0}} \times \frac{1 - \exp(-t/\tau)}{1 - q/p \cdot \exp(-t/\tau)}\right)^2 - 1 \right]\right\}. \quad (5)$$

Here  $\Theta_{A0}$  is the initial coverage of the surfaces by oxygen and  $\tau$  is the time constant of the response. The parameters  $Z$ ,  $\eta$ ,  $q$ , and  $p$  are certain defined functions of the gas and reaction characteristics. Their explicit description can be derived in our model (see [5]).

As follows from Eq. (5), the kinetics of the resistance response is related to the surface reaction rates, namely, gas adsorption rate, desorption rate, and rate of bimolecular interaction. The time constants  $\tau$  can also be defined [5] by the reaction rate parameters. Assuming that the surface charge depends on the reaction between gas and one type of the chemisorbed oxygen species, the following expression is derived for the time constant:

$$\frac{1}{\tau} = [(\alpha_B S_{0B} + \beta_B + \nu_{AB} \Theta_{A0})^2 - 4\nu_{AB} \alpha_B S_{0B}]^{1/2}, \quad (6)$$

where parameter  $\alpha_B$  is the rate of the incident flux and  $S_{0B}$  is the sticking probability for the target gas molecules,  $\beta_B$  is the desorption rate. The time constant  $\tau$  in Eq. (6) defines the rise time of the response signal after the injection of target gas into the test chamber. The time constant is a useful characteristic of kinetics of the sensor response because it can be evaluated from the experimental transients by analysis of the signal rise. In the present study the response signal was expanded into multiexponential decays. Within the framework of the phenomenological model [5] in the limit of weak response signals (the resistance change is  $R_{\text{gas}}/R_0 \ll 1$  in the layers), a sophisticated description of the resistance response to gas can be replaced by a simple series like

$$R(t) = a_0 + \sum_{i=1}^{\infty} a_i \exp\left(-\frac{t}{\tau_i}\right). \quad (7)$$

Weighting coefficients  $a_0$  and  $a_i$  are related to the rate parameters of the surface chemical reaction. This relationship is not the subject of present study and will

be reported elsewhere. It is important to note that the time constants  $\tau_i$  in Eq. (7) are proportional to the time constants determined by Eq. (6). Equation (7) describes the approximation of multiexponential decays used for evaluation of time constants  $\tau$  (see [6]).

### 3. Experimental

Gas sensors were produced by sputtering of metallic Sn films on the insulating substrates. Thin Sn films were oxidised by subsequent heat treatment in humid synthetic air. Four types of the sensors (initially analogous) were obtained using the initial films by post-growth sputtering of metallic impurities Pt (SR22Pt), Mo (SR22Mo), W (SR22W), Ag (SR22Ag). The fifth type (SnMo) was manufactured of the oxidised films initially grown by a sequential deposition of pure Sn and Mo.

The sensors were exposed to a steep change in the atmosphere composition that was produced by switching the chamber inlet from the clean air channel to the channel in which the contaminated air was flowing. Time dependence of dc-electrical resistance was measured in the sensors. For this, the signal was sampled with the rate of about 10 Hz. The dependences were measured at temperatures from 450 to 800 K in air with relative humidity (RH) from 0% to about 70%. Based on analysis of the experimental transients, time constants were evaluated by approximation of these transients by multiexponential decays. The fitting of the theory to the experiment was accomplished by an original program utilising the algorithm developed by Tittelbach-Helmrich [6].

### 4. Results

The transients were measured at various concentrations from about 10 to 80 ppm of  $H_2$  gas and from about 50 to 1200 ppm of CO gas. The steep change in gas composition was produced in the test chamber during these measurements: the switching time from  $H_2 = 0$  ppm to  $H_2 = P_{\text{fixed}}$  ppm was about 2 ms. The transients were approximated by multiexponential decays. Three exponential components were typically obtained from the analysis of experimental transients in the present study, but this is not a general rule. Weighting coefficients  $a_i$  and time constants  $\tau_i$  were evaluated for each component.

Influence of the metallic impurities on the saturated resistance response to  $H_2$  gas is illustrated in Fig. 1 by

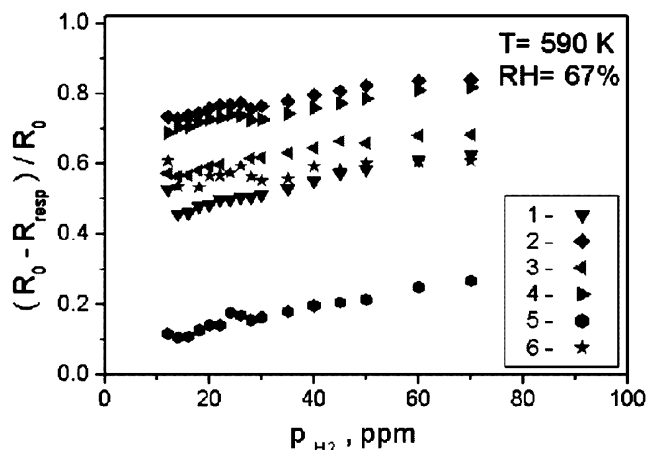


Fig. 1. Saturated response to  $H_2$  gas versus the gas concentration in air for the sensors (1) SR22Pt, (2) SR22Mo, (3) SR22W, (4) SR22Ag, (5) SnMo, and (6)  $SnO_2$  pure.

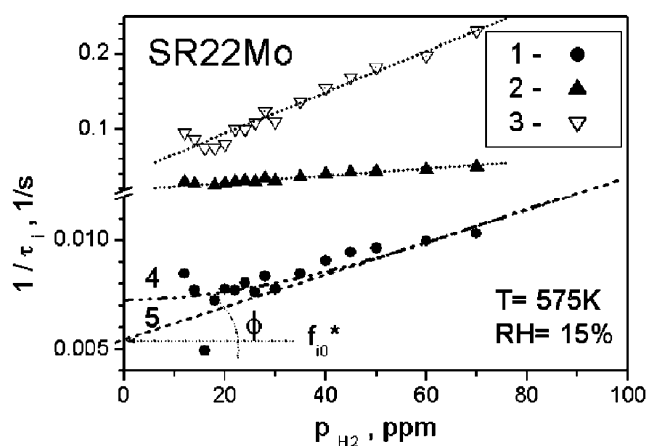


Fig. 2. Dependences of reciprocal time constants on  $H_2$  concentration for sensor SR22Mo. Labels 1, 2, and 3 are the indices of individual time components in the set. Labels 4 and 5 are for theoretical approximations.

typical dependences of the resistance change on gas concentration. The saturated response was strongest for the sensors modified with Ag and Mo, while the response of the sensor with Pt was weakest within the entire interval of concentrations. The dependences of saturated response of all the sensors to  $H_2$  gas on concentration are sublinear.

According to the phenomenological model, the largest time constant evaluated from the transient describes the limiting process of the response mechanism. This time constant (curve 1 in Fig. 2) was calculated according to Eq. (6) which defines the dependence of the constant on gas concentration ( $F_B \sim P_{\text{gas}}$ ). The fitting of the calculated and experimental curves is illustrated by curve 4 in Fig. 2. These basic (the largest) time constants were evaluated and analysed for all tran-

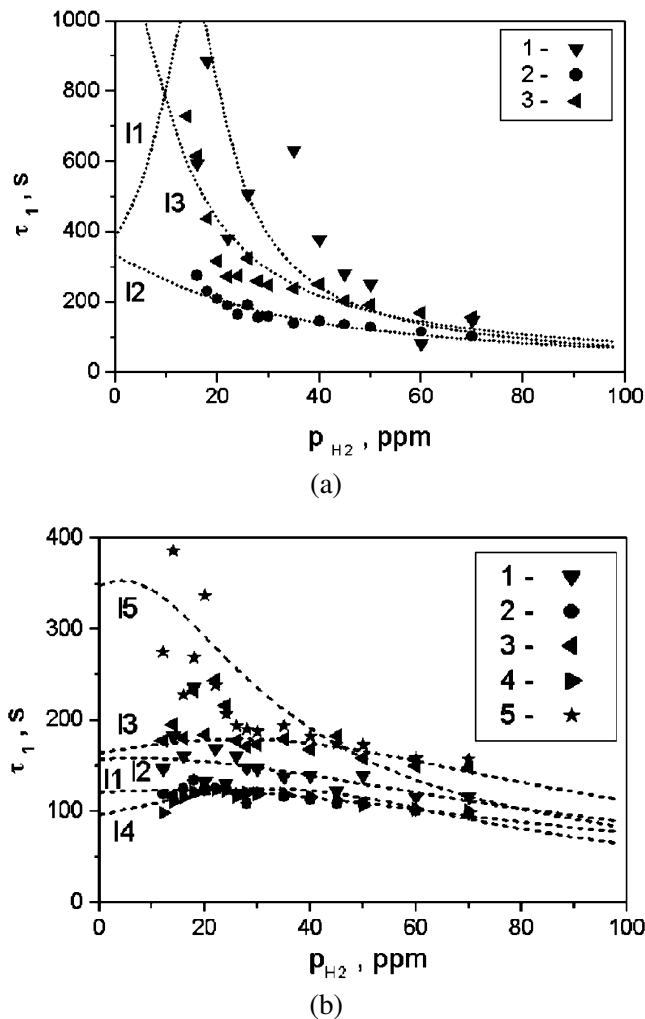


Fig. 3. Influence of the impurity catalyst on the basic time constant evaluated from the experimental transients on  $H_2$  concentration for the sensors (1) SR22Pt, (2) SR22Mo, (3) SR22W, (4) SR22Ag, and (5) SnO<sub>2</sub>-pure at  $T = 590$  K in air of (a) RH = 0% and (b) 35%. Curves labelled by 11, 12, ..., 15 are for theoretical dependences fitted to experiment.

sensors measured in our experiments. Theoretical dependences were fitted to the experimental data by variation of the surface rate parameters  $\alpha_B$ ,  $S_{0B}$ ,  $\beta_B$ , and  $\nu_{AB}$  in Eq. (6) assuming that the coverage of the surface with oxygen is constant,  $\Theta_{A0} = 0.98$ .

Typical sets of the time constants are demonstrated for SR22Mo in Fig. 3. The sensor was exposed to various  $H_2$  concentrations in individual experiments, and dependences of the constants on concentration were obtained.

The effect of catalytic metals used for the modification of the sensors is illustrated in Fig. 3. The influence of the surface modification by metallic impurities on the dependence of the time constant on  $H_2$  concentration is compared in air with different relative humidity.

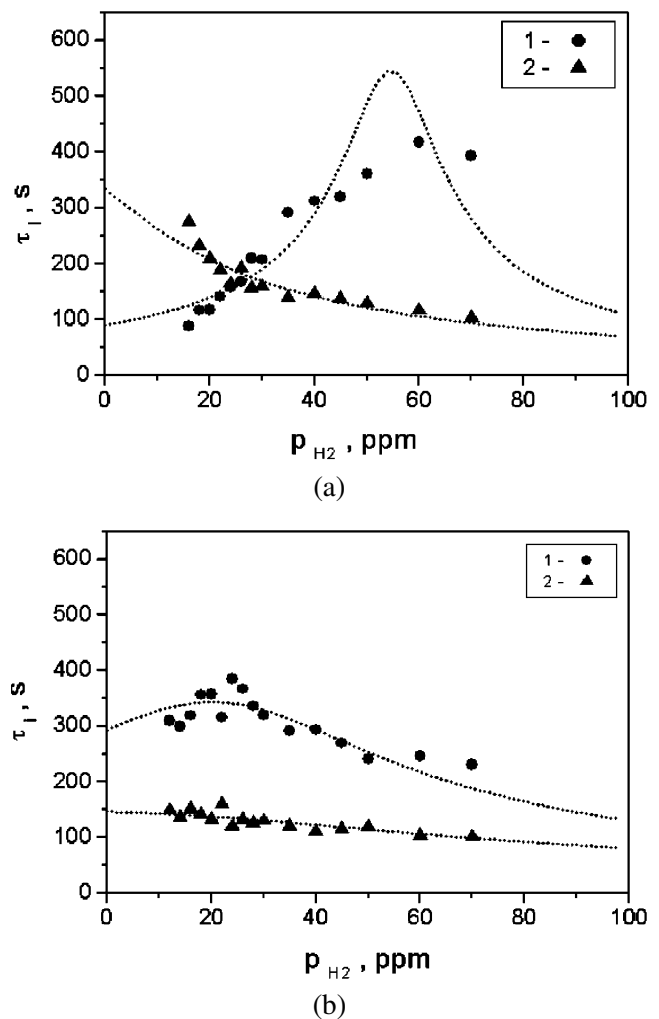


Fig. 4. Influence of the method used for the modification with impurity on the dependences of the basic time constant on  $H_2$  concentration for (1) SnMo and (2) SR22Mo at  $T = 590$  K in air of (a) RH = 0% and (b) 67%.

The kinetics was analysed at several magnitudes of relative humidity RH from 0% to about 70%. In Fig. 3 the relative humidity is (a) 0% and (b) 35%.

In Fig. 4 the influence of the technology of the modification by metallic impurity is illustrated. The influence is compared for two types of technologies: (1) the multilayer structure produced by sequential deposition of Sn and Mo, and (2) the surface doping by a Mo overlayer deposited on SnO<sub>2</sub> film. In Fig. 4 the relative humidity is (a) 0% and (b) 67%.

The transients were measured at various concentrations of  $H_2$  gas from about 10 to 100 ppm and CO gas from about 50 to 1200 ppm. Monotonous resistance decrease was typically observed for the sensor response to these gases within the interval of their concentrations.

The phenomenological time constants  $\tau_i$  and the weighting coefficients  $a_i$  were evaluated by fitting the

calculated transient (Eq. (7)) to experimental response. The method proposed in [5] was used for evaluation of the time constants. Responses to various concentrations of gases were analysed and the dependences of the time constants  $\tau$  on the gas concentration  $P_{\text{gas}}$  were obtained.

## 5. Discussion

The rate parameters obtained by fitting the phenomenological theory to the experimental data for the sensors with various metallic impurities are summarised in Table 1 and Fig. 5. These parameters were similarly evaluated from the responses to  $\text{H}_2$  and  $\text{CO}$  gases measured at various temperatures of the sensors in the air of different relative humidity.

The results in Table 1 and Fig. 5 might be summarised as follows:

- *The response to  $\text{H}_2$  gas.* The additive catalyst modifies the chemisorption rate of  $\text{H}_2$ . Desorption and bimolecular interaction on the surfaces modified with the metals is higher than on the pure  $\text{SnO}_2$ . The differences between magnitudes of these parameters are not significant for the modified sensors except for the rate of the bimolecular interaction on sensors with Mo and Ag.
- *The response to  $\text{CO}$  gas.* First, the  $\text{CO}$  chemisorption rate is lower and the  $\text{CO}$  desorption rate is higher than other rate parameters for the surfaces with Mo. Second, the presence of catalysts Pt and W is associated with a significant increase in the rate of the bimolecular reaction between  $\text{CO}$  and oxygen on the surfaces of the sensors.

Typical dependences of the reciprocal time constant ( $1/\tau_{i0}^* = \beta + \nu(\Theta - 2)$ ) on reciprocal temperature are illustrated in Fig. 6. The time constant was evaluated by extrapolation of the dependence in Fig. 2 ( $f_{i0}^* = 1/\tau_{i0}^*$ ). In general, the activation energy evaluated from the Arrhenius plot seems independent of the metallic catalysts (labels 1, 2, and 4 in Fig. 6) except for W. The use of special technology for modification of the  $\text{SnMo}$  sensor (labels 3 and 5) is also related to a change in the activation energy.

## 6. Conclusions

Using the phenomenological model, the experimental results can be related to additional chemisorption

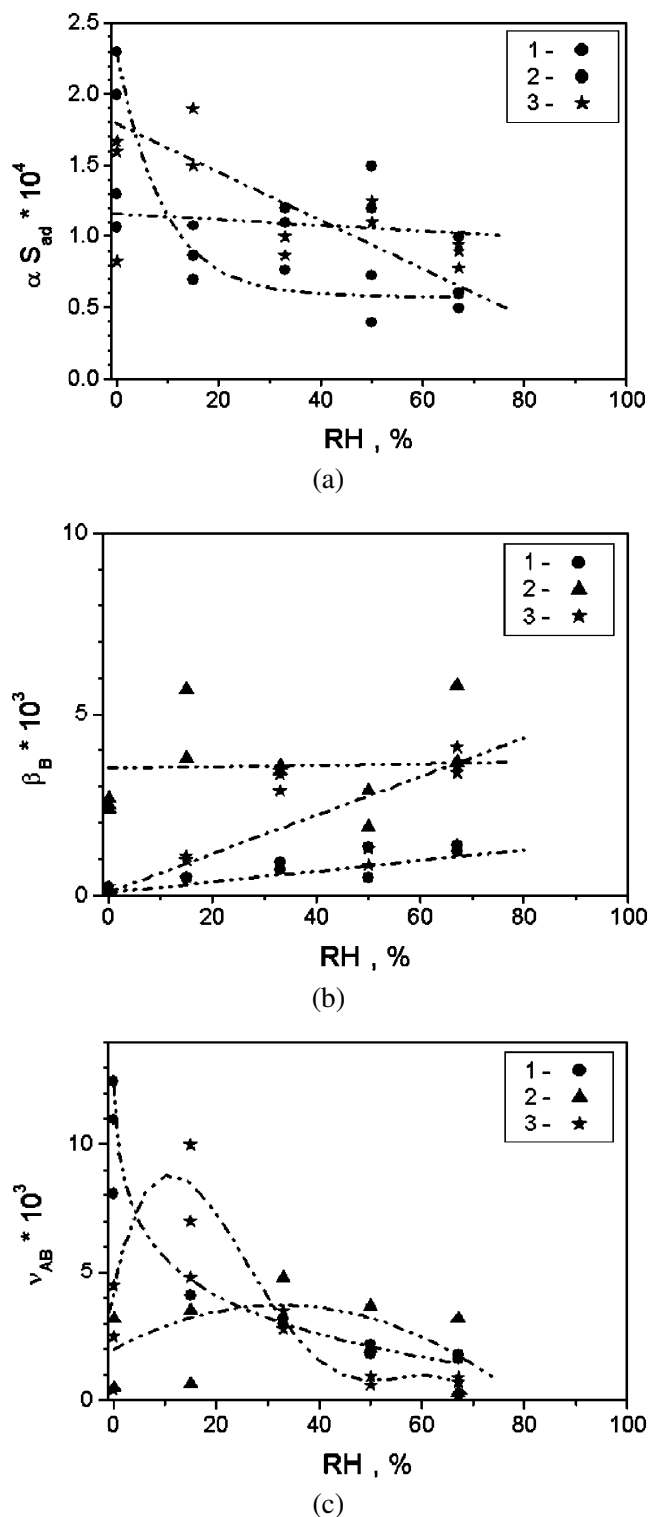


Fig. 5. Parameters versus relative humidity of air with  $\text{H}_2$  gas for sensors (1)  $\text{SnMo}$ , (2)  $\text{SR22Mo}$ , and (3)  $\text{SR22Pt}$ :  $\alpha$  is gas flux and  $S_{\text{ad}}$  is sticking coefficient;  $\beta_B$  is desorption rate;  $\nu_{AB}$  is the rate of bimolecular interaction between the gas and the surface oxygen.

centres for the target gas. These centres might be associated with the clusters of the catalytic metals. Assuming that the centres are located at the edges of the

Table 1. The rate parameters of the surface chemical reaction ( $\alpha_B S_{0B}$  is the chemisorption rate,  $\beta_B$  is the desorption rate, and  $\nu_{AB}$  is the rate of bimolecular interaction) evaluated by fitting the phenomenological expression Eq. (1) to the experimental dependence of  $\tau$  on  $P_{\text{gas}}$  for the sensors exposed to  $\text{H}_2$  and CO gases at temperature  $T = 575$  K in the air of relative humidity  $\text{RH} = 33\%$ . The surface oxygen occupation  $\Theta_{\text{O}_2}$  was assumed equal to 0.986.

Impurity	$\text{H}_2$			CO		
	$\alpha_B S_{0B} \cdot 10^4$	$\beta_B \cdot 10^3$	$\nu_{AB} \cdot 10^3$	$\alpha_B S_{0B} \cdot 10^4$	$\beta_B \cdot 10^3$	$\nu_{AB} \cdot 10^3$
SnO <sub>2</sub> (pure)	1.23	1.2	1.7	–	–	–
Ag	1.4	2.9	6.7	0.58	0.7	8
Mo	1.2	3.5	4.8	0.2	2.6	3
Pt	0.94	3.1	3.3	0.65	0.55	28
W	0.8	2.3	3.4	0.97	0.9	18

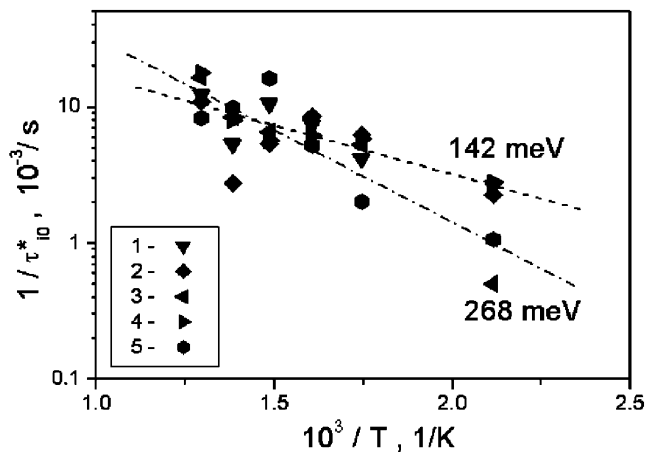


Fig. 6. Dependences of extrapolated to  $P_{\text{H}_2} = 0$  ppm basic time constants on reciprocal temperature (Arrhenius plot) for sensors (1) SR22Pt, (2) SR22Mo, (3) SR22W, (4) SR22Ag, and (5) SnMo.

clusters and in the vicinity of the reaction sites, an increase in the density of the centres will increase the response. In contrast to this, the rate parameters of the bimolecular interaction will be constant. This mechanism suggests the criteria for choosing a catalyst increasing the response: it should be an impurity metal, characterised by higher gas binding energy and, consequently, by lower desorption rate.

It follows from the accepted model that doping should modify the kinetics of the response if most of the oxygen chemisorption centres are created by the catalyst point defects near the reaction centres of the basic metal oxide. It seems reasonable to expect that the rate parameters of the reaction in these combined centres will differ as compared to the centres on the pure metal oxide surfaces.

Considering the role of metallic catalysts, the changes of the parameters related to the response kinetics of metal-oxide-based sensors exposed to certain light reducing gases (e. g.,  $\text{H}_2$  and CO) can be summarised as follows:

1. The response time (rate of response) slightly depends on surface metals, but the shape of the transient of the response (the set of exponential decay components) is effectively modified by the additive metal.
2. The rate of bimolecular interaction  $\nu_{AB}$  is independent of the surface impurity metals in the oxide sensors. The chemical reaction, determining the surface electrical charge, occurs on the clean surfaces of the basic oxide. Mixture of metal oxides (e. g., in the SnMo sensor) introduces new centres for the chemical reaction which changes the electrical charge on the surface of sensor.
3. The chemisorption rate  $\alpha_B S_{0B}$  (or the flux of chemisorbed particles) depends on the surface modification with metals. This can be explained assuming the increase of the sticking coefficient  $S_{0B}$  on the modified surfaces of the oxides.
4. The desorption rate  $\beta_B$  is a surface reaction rate parameter most sensitive to the surface modification with impurity metal.
5. The co-adsorption of water molecules significantly suppresses the influence of the surface metals on the chemical reaction rate parameters.

### Acknowledgements

The joint project was supported by Network of Excellence “NOSE II.” The research at Semiconductor Physics Institute in Vilnius was supported by Lithuanian State Science and Education Foundation.

### References

- [1] N. Butta, M. Melli, and S. Pizzini, Influence of surface parameters and doping on the sensitivity and on the re-

- sponse times of tin oxide resistive sensors, *Sensors Actuators B* **2**, 151 (1990).
- [2] J.W. Gardner, A non-linear diffusion–reaction model of electrical conduction in semiconductor gas sensors, *Sensors Actuators B* **1**, 166–170 (1990).
- [3] M. Morimitsu, Y. Ozaki, S. Suzuki, and M. Matsunaga, Effects of surface modification with platinum and ruthenium on temperature and humidity dependence of SnO<sub>2</sub>-based CO gas sensors, *Sensors Actuators B* **67**, 184–188 (2000).
- [4] S. Matsushima, Y. Teraoka, N. Miura, and N. Yamazoe, Electronic interaction between metal additives and tin dioxide in tin dioxide-based gas sensors, *Jpn. J. Appl. Phys.* **27**, 1798–1802 (1988).
- [5] A. Šetkus, Heterogeneous reaction rate based description of the response kinetics in metal oxide gas sensors, *Sensors Actuators B* **87**, 346–357 (2002).
- [6] K. Tittelbach-Helmrich, An integration method for the analysis of multiexponential transient signals, *Meas. Sci. Technol.* **4**, 1323–1329 (1993).

## KATALITINIŲ METALŲ ĮTAKA PAVIRŠINIŲ CHEMINIŲ REAKCIJŲ SPARAI IR VARŽOS ATSAKO Į DUJAS KINETIKAI PLONASLUOKSNIUOSE SnO<sub>2</sub> DUJŲ JUTIKLIUOSE

A. Šetkus<sup>a</sup>, C. Baratto<sup>b</sup>, E. Comini<sup>b</sup>, G. Faglia<sup>b</sup>, A. Galdikas<sup>a</sup>, Ž. Kancleris<sup>a</sup>,  
G. Sberveglieri<sup>b</sup>, D. Senulienė<sup>a</sup>, M. Senulis<sup>a</sup>

<sup>a</sup> Puslaidininkų fizikos institutas, Vilnius, Lietuva

<sup>b</sup> Brescia universitetas, Brescia, Italija

### Santrauka

Eksperimentiškai ir teoriškai ištirtos iš plonųjų SnO<sub>2</sub> sluoksnių pagamintų ir įvairiais katalitiniais metalais – Pt, Ag, W ir Mo – primaišytų dujų jutiklių varžos atsako į šuolinį aplinkos dujų sudėties pokytį laikinės priklausomybės. Varžinių SnO<sub>2</sub> dujų jutiklių signalų kitimas dėl šuolinio H<sub>2</sub> ir CO dujų sudėties pokyčio aprašytas, naudojant daugiaekspontentės relaksacijos metodiką. Pagal fenomenologinį modelį varžos atsako į šuolinį aplinkos dujų sudėties pokytį kinetiką nulemia tiek paties sluoks-

nio savybės, tiek cheminių reakcijų sparta ant paviršiaus. Atsako nusistovėjimo trukmę tiesiogiai nulemia tikrai paviršinės reakcijos sparta. Įrodyta, kad SnO<sub>2</sub> dujų jutiklių atsako į redukuojančias dujas (H<sub>2</sub>, CO) kinetika apibūdinama savitu parametru rinkiniu, priklausančiu nuo primaišytojo katalitinio metalo. Eksperimentiniai rezultatai aiškinami papildomais deguonies chemisorbcijos centrais, kuriuos sukuria primaišyto katalitinio metalo taškiniai defektai pagrindinio metalo oksido (SnO<sub>2</sub>) reakcijos centrų aplinkoje.