

CHEMISORPTIONAL APPROACH TO KINETIC ANALYSIS OF SnO₂:Pd-BASED THIN FILM GAS SENSORS

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The chemisorptional approach to conductivity kinetics of thin film SnO₂:Pd gas sensors is presented. The base of this model is the experimental study and theoretical simulation of gas sensitive characteristics. The main idea of the proposed approach is the existence of neutral atomic form of chemisorbed oxygen on the SnO₂ surface due to oxygen spillover from Pd metal particles. This form competes with molecular oxygen for absorption sites. Finally, the kinetic process is determined by the rate of absorption/desorption reactions of molecular oxygen.

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In our previous work [1] we have developed a chemisorption model of TFGS without surface metal catalysts. A good agreement with experiment in steady-state and transient cases has been demonstrated. The main idea of our approach was the existence of neutral form of chemisorbed particles. This gave the possibility to overcome the so-called Weisz limitation in the amount of surface coverage. The further development of this model on the basis of experimental study of transient characteristics of conductivity for SnO₂:Pd films is presented.

SnO₂ thin films on alumina substrate with thickness 30-50 nm were deposited by spray pyrolysis method using SnCl₄ water solution [2]. For Pd surface doping the same method was used. The transient characteristics of gas sensitivity have been measured by monitoring the conductivity using the measurement cycles: air ⇒ (0.07-1.7 % CO + air) ⇒ air; air ⇒ (1 % H₂ + air) ⇒ air, or air ⇒ (0.5 % O₂ + air) ⇒ air.

The most important results of our experimental study are the following:

- Transient curves in the shape ($\Delta G(t)/\Delta G$) are close to exponential for response mode. The recovery curves consists of two parts – linear and exponential;
- The response times do not depend on the type of reducing gas (H₂, CO) (Fig. 1) and its concentration;
- At low temperatures (T = 50-150 °C), the transient time constants (τ) for surface doped SnO₂:Pd films are more than 10³ times less than for undoped films;
- The slope of Arrhenius dependencies $\tau(1/T)$ is ~ 0.6 eV for response and ~ 0.3 eV for recovery modes. These values don't depend on the atmosphere used in experiments (H₂, CO, O₂) (Fig. 2);
- The activation energy got from conductance G(1/T) dependencies for SnO₂:Pd films is 0.5-0.55 eV. The same value is observed for undoped films (Fig. 3).

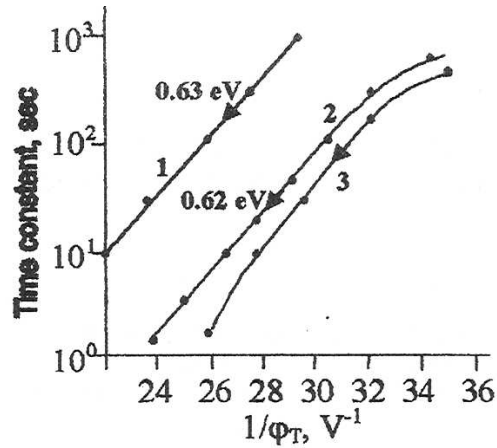


Fig. 1. Temperature dependencies of response time constants of gas sensitivity for various gas measurement cycles (experiment).

The experimental facts show that for surface doped SnO_2 , both kinetic law of gas sensitivity and the main features of this process remain the same as for undoped films [1]. This situation indicates that for SnO_2 :Pd films, as well as for undoped films, the chemisorbed oxygen determines the transient process of gas sensitivity. There are only considerable decreasing of τ and corresponding activation energy, E_{act} , of $\tau(1/T)$ dependencies. Earlier we have shown [3], the impossibility to describe GS behaviour in the frame of the existence of just ionosorption form of oxygen (O_5^-). In that case the energetic position of chemisorbed level in SnO_2 band gap should determine simultaneously such physical parameters as surface potential (U_s), energy of desorption, E_{act} got from $\tau(1/T)$ and $G(1/T)$ dependencies. Actually, one can see that these parameters are rather different in their values. Besides that, TPD experiments [4] gives the amount of desorbed oxygen (0.1-0.2 monolayer) in the temperature range 200-500 °C. That is considerably higher than for ionosorption form. Often given interpretation of this oxygen as a "bringing" oxygen is in contradictin with its amount, which is far from one monolayer. Its kinetic law could be determined by charged form thus τ should depend on U_s and finally, the transient curves would be more complicated than simple exponential would.

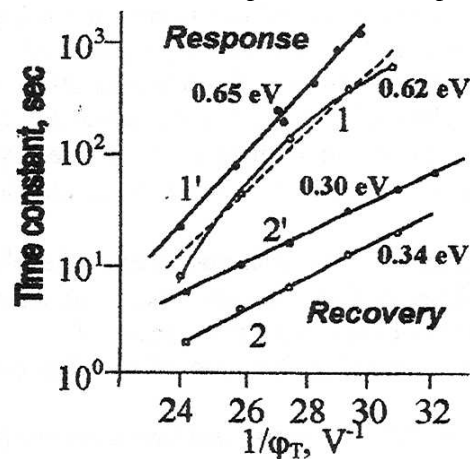


Fig. 2. Results of experiment and simulation for response and recovery times for air \Rightarrow (0.5 % O_2 + N_2) \Rightarrow air cycle.

It seems that the surface doping by noble metal catalysts isn't electrically active [5]. Film conductivity and its activation energy practically are the same for undoped films. Some spectroscopy measurements confirm the constancy of U_s during surface doping by noble metal catalysts. One believes that contact potential at the Pd- SnO_2 interface is low due to close work function values of Pd

and SnO₂. So, we consider that at first approximation the Pd-SnO₂ interface, as Schottky barrier contact, doesn't influence the sheet conductivity. Another point of view on the role of metal catalyst is connected with so-called effect of oxygen spillover. This phenomenon can be defined as the migration of chemical species from the catalyst onto inert support. Now, there are not direct measurements, which confirm such effect for oxygen on SnO₂ surface. On more like systems such as Pt/SnO₂ such behavior have been demonstrated [6]. However, there are many reasons and indirect results to link the spillover with enhanced catalytic activity and sensor sensitivity. Display of spillover effect will be determined by ratio between affinities of metal oxide and metal cluster surfaces as well as the activation energy of surface diffusion of oxygen on metal oxide. Last one can be estimated from general expression [7] as $E_{act} < 1.0$ eV. Thus the sensor operation temperatures are sufficiently for activation of this process. We believe that surface oxygen diffusion from Pd is the main cause of observed temperature transformations of GS characteristics. An important component of chemisorbed flow is oxygen in neutral atomic form (O^0). This very process leads to noticeable competition between atomic and molecular oxygen for adsorption sites (N^*) on the SnO₂ surface, and modulates film conductivity through the charged atomic form. The neutral form is not uptaken in direct sense. The complex of negatively charged chemisorbed oxygen and positively charged lattice oxygen vacancy can be one of these possible forms. Therefore, a neutral form means only an absence of surface charging with changing of U_S and G .

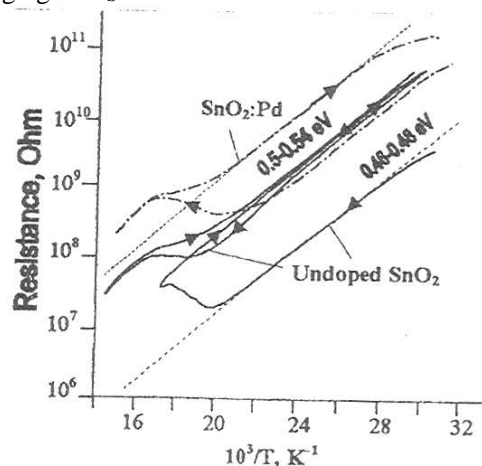


Fig. 3. Temperature dependencies of conductivity in air for undoped and Pd-doped SnO₂ films.

As we assumed before, oxygen adsorption/desorption (A/D) processes determine the kinetics. Numerical simulation in the frame of second order A/D reactions on Pd surface gives E_{act} of $\tau(1/T)$ larger than 1.0 eV, which contradicts our experiment (Fig. 1). Experimental results are rather in agreement with the results of simulation of time constants of A/D reactions for molecular oxygen on SnO₂ surface (first order reaction). Therefore, we have supposed that one must take into account two forms of oxygen on SnO₂ surface while considering the kinetics in the temperature range 50-150 °C.

We have proposed the following mechanism of kinetics for SnO₂:Pd film (see Fig. 4a).

1. At low temperatures the dissociative adsorption occurs only on metal catalyst surface;
2. There is a spillover effect of oxygen from Pd to SnO₂ surface;
3. The rate of 2-nd order A/D reactions on Pd surface with following spillover of atomic oxygen from Pd to SnO₂ exceeds the rate 1-st order A/D reactions of molecular oxygen on the SnO₂ surface, therefore, kinetics of both surface refilling by oxygen and gas sensitivity is determined by the last process;
4. Surface coverage of SnO₂ by oxygen is determined by competition of two neutral forms of oxygen: molecular and atomic;
5. The charged form of atomic oxygen determines the film conductivity, because $O^- \gg O_2^-$. We got the expression for G through surface concentration of neutral form of molecular oxygen $G(t) \sim [N^* - N_{O_2}^0(t)]^{-m}$, where N^* is surface concentration of adsorption sites and m is some

parameter, described in [1]. From our model for Pd doped SnO_2 films follows that dependence of $N_{\text{O}}^0/N_{\text{O}_2}^0$ ratio on oxygen pressure is proportional $\sqrt{P_{\text{O}_2}}$. It is important to note that this dependence is opposite to $N_{\text{O}}^0/N_{\text{O}_2}^0 = f(P_{\text{O}_2})$ dependence determined for undoped SnO_2 films. For undoped SnO_2 films $N_{\text{O}}^0/N_{\text{O}_2}^0 \sim 1/\sqrt{P_{\text{O}_2}}$. This means we are dealing with different mechanism of surface covering by oxygen for doped SnO_2 films. Above we mentioned that for doped films kinetic law order of surface adsorption/desorption processes changes from second order to the first one.

Our estimations show that substantial increasing of sensitivity is reached when oxygen diffusion length equals the average distance between metal particles.

The schematic illustration of such a case is shown in Fig. 4(b). Effective size of metal clusters will be determined by the reactivity of metal surface and its area as a source of dissociative oxygen, needed for covering the spillover zone near the cluster.

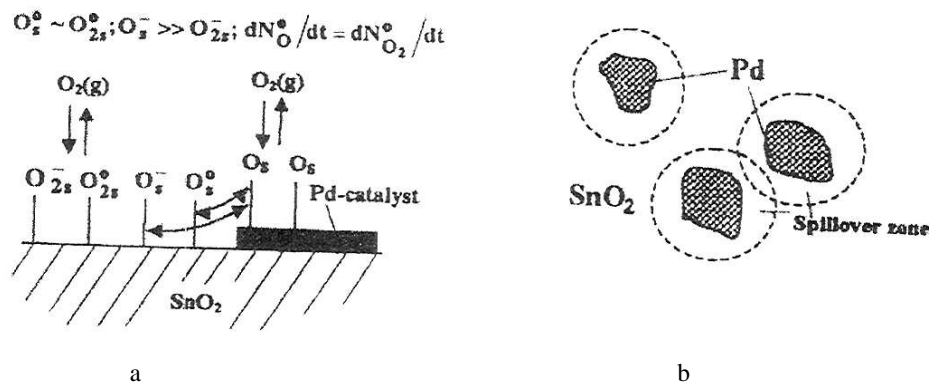


Fig. 4. Schematic illustration of oxygen interaction with SnO_2 :Pd surface (a) and spillover zone overlapping on metallized surface (b).

The experimental results [8] show a considerable increase of sensitivity for metal particles of size smaller than 5 nm. As a rule, the preparation methods of metallized surfaces make the average distances between clusters comparable to their size. Thus, in the first approximation, the spillover zone has the same dimensions. It is interesting to note that in the frame of other mechanism the gas sensitivity increase with metal catalyst doping is explained by the Pd/ SnO_2 Schottky barrier contacts. Thus, dispersion of metal particles is not obligatory. This needs only thin enough, discontinuous, metal layers.

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