

ФІЗИЧНІ, ХІМІЧНІ ТА ІНШІ ЯВИЩА,  
НА ОСНОВІ ЯКИХ МОЖУТЬ БУТИ СТВОРЕНІ СЕНСОРИ

PHYSICAL, CHEMICAL AND OTHER PHENOMENA,  
AS THE BASES OF SENSORS

UDC 681.586.772

ANALYSIS OF AGEING MECHANISMS OF GAS MIS SENSORS  
WITH Pd (Cu<sub>x</sub>Pd) GATE

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**Аннотація**

АНАЛІЗ МЕХАНІЗМІВ СТАРІННЯ МІН СЕНСОРІВ  
З Pd (Cu<sub>x</sub>Pd) ЗАТВОРОМ

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В загальному виді викладена макроскопічна теорія газового сенсора з каталітичним затвором, яка застосована для пояснення процесів старіння та механізмів стабілізації параметрів сенсора. Дана класифікація мікро механізмів домінуючих процесів старіння. Результати розрахунків та комп'ютерного моделювання співставлені з експериментальними даними, що дозволяє ідентифікувати природу старіння в конкретних випадках і дозволяє рекомендувати методи стримування чи гальмування процесів старіння МДН газових датчиків. Одним з найбільш ефективних методів є легування поверхні Pd електроду атомами міді Cu, що супроводжується створенням певних структурних конфігурацій Cu-Pd. Зокрема, найбільш ефективною виявилась конфігурація з роздільним фрагментарним “острівцевим” легуванням (на противагу рівномірно-стохастичного розподілу атомів Cu по поверхні каталітичного електроду).

**Introduction**

The ageing of MIS gas sensors (being a result of a long time interaction of the sensitive electrode layer with the environment) is manifested itself in partial or total loss of the sensitivity, selectivity, increase of the response time, and in deterioration of other parameters of the devices. Because of both functioning and storage of sensors occur under real atmospheric conditions the surface of a sensitive Pd (Pt) layer is transformed due to ageing and became “ill-defined” from physical and chemical points of view. Therefore, in spite of the practical importance, the study of the physical mechanisms of ageing and the processes on the aged surface encounters with a lot of difficulties.

From a practical point of view it would be nice to develop the methods of the preventing or/and

slowing down of the ageing, by means of the *stabilizing of the initial state* of a sensitive layer. So, the theoretical understanding of the detail mechanisms of ageing itself from both chemical and structural points of view is necessary. On the other hand; the problem of good long time sensor operation may be solved by the method of quick “*promoted initial ageing*”, which results in the subsequent stabilization of sensor’s characteristics at the acceptable level. For this reason it is desirable to create the physical model of operating of the “aged” sensors. In particular, one should describe the chemical reactions between molecules on the “real” aged surface in multicomponent ambient. As a rule, the problems mentioned may be treated only qualitatively, or in the framework of some phenomenological approach.

We used here the approach based on a computer simulation of chemical interactions between multicomponent gas ambient and metal electrode in MIS structure. As a result we have calculated the output response of the sensor on the gas pulse input and other related properties of the device depending on different types of physical and chemical transformations of the layer. The comparison with the experiment allows us to select the respective **macroscopic** processes, which take place in real structures.

After this we considered and discussed some possible **microscopic** mechanisms of these degradation processes of sensitive layers namely (i) the reorientation or reattachment of surface chemical bonds, (ii) electronic transfer between the substrate atom and the impurity one, (iii) dissolution of the surface by the foreign atoms (decrease of number of active centres), (iv) modification of transport properties of the layer and some others. The last allowed us to propose both micro- and macroscopic physical models of operating of the “aged” sensors, describe the surface chemical reactions under multi component gas mixture action, propose the qualitative model of the aging and consider some approaches for ageing preventing.

In the present paper we consider one of such approaches, namely alloying the *surface of Pd layer* with copper.

Therefore the theoretical study of main difference between MIS structure with Pd/Cu electrode and MIS sensors only with Pd one was also carried out.

## 1. General macroscopic theory of MIS gas sensor operation

In order to describe the processes in the aged MIS gas sensors let us describe in brief the principles of their operation. As a starting point we shall consider an extended variant of the classical model, proposed by Lundström [1-4].

Let the multi component gas mixture in the ambient interacts with a sensitive metal layer of a MIS structure and the gas ambient contains  $N_m$  types of molecules with partial pressures  $P_m(t)$  ( $m=1, 2, \dots, N_m$ ) as a functions of time. The time dependences correspond to shape of gas pulses supplying into the working chamber. The primary process that determines the gas sensitivity is the catalytic dissociation of the *detected* molecules (e.g.  $H_2$ ) at the *active adsorption centers* on the *external* surface. According to Lundström we shall denote the surface concentrations of adsorption centers at the *external* surface and at the MI *interface* as  $N_e$  and  $N_i$  correspondingly (Fig.1, a).

Other background molecules (e.g.  $H_2O$ ,  $O_2$ ) can be also adsorbed on the external surface with or without dissociation. As a result the external surface will be covered both with molecules and with various products of their dissociation ( $H$ ,  $OH$ ,  $H_2O$ ,  $O$  etc.) as shown in Fig.1. We shall number all this particles with the index  $k$ . Some of these particles can *move through the active layer* and recaptured at the MI interface (Fig. 1, a,b). Therefore the non-zero forward and the reverse transport coefficients  $K_k$  and  $S_k$  for each such component are introduced. For MIS sensors with a “dense” gate film only atomic hydrogen  $H_a$  is assumed to be able for such movement (Fig.1, a). It should be noted, however, that for

other types of the sensitive film more “large” atoms or molecules can also participate in a transport processes (Fig. 1, i,j). In some cases the capture of atoms in the bulk of a film are also to be considered in the model (Fig. 1, b,c). Therefore, the effective surface concentration  $N_b$  of these bulk centers should be taken into account.

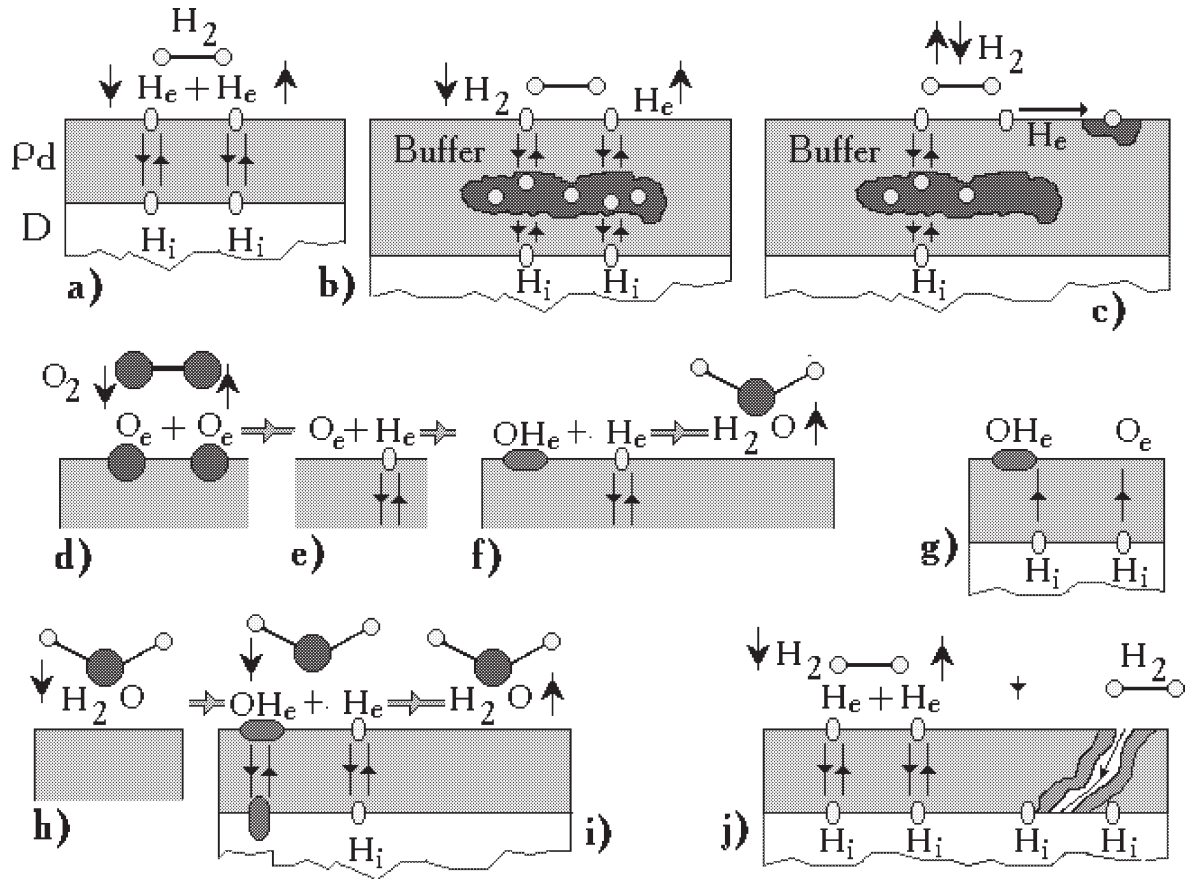


Fig. 1. Different scenarios for  $H_2$ ,  $O_2$  and  $H_2O$  behavior in the Pd/Dielectric layered system.

- (a) Classical Lundstrom's model for dense Pd films  
 (b) The same model with atomic hydrogen capture in the bulk of the film  
 (c) The model with additional  $H_e$  trapping at the external surface and slowing down atomic transport through the film  
 (d)-(f) The scheme of the air induced reset of the sensor due to quick remove of  $H_e$  via *pure surface reactions* with  $O_e$  and  $OH_e$   
 (g) Direct recombination of  $H_i$  with  $O_e$  and  $OH_e$  captured on the center  
 (h)-(i)  $H_2O$  interaction with the aged Pd surface: (h)-(i) Two-step adsorption / dissociation of water (i) direct dissociative adsorption of  $H_2O$ . Due to a sponge like substructure of the film (Fig 2, c) here the transport of both  $H_e$  and  $OH_e$  is possible.  
 (j) Middle temperature scenario for hydrogen in sponge-like film.

It is suitable to consider separately the *direct* and *indirect* interactions between the ambient and the layer. The direct one consists in adsorption and desorption and is determined by a set of adsorption/desorption coefficients  $c_{km}$  and  $d_{km}$  for *molecules* and by the order of adsorption reaction  $\mu$  (multi centered dissociative, or mono-centered). These parameters are functions of the temperature of a substrate. The indirect interaction takes place at the external surface between the products of dissociation of the molecules. The rates of these surface reactions are described by non linear functions  $R_k(n_{1e}, n_{2e}, \dots, n_{ke}, \dots)$  according to the theory of absolute chemical reaction rates. The right view of these functions for each type of particle is the key for understanding of MIS gas sensor operation in multi component ambient. It should be noted also that we neglect here all possible chemical reactions between atomic particles at the *MI interface*.

Taking into account all mentioned above the general view of a system of equations for surface ( $n_{ke}$ ) and interface ( $n_{ki}$ ) concentrations for  $N_p$  particles in the model is follows ( $k = 1, 2, \dots, N_p$ ):

$$\begin{aligned} \frac{dn_{ke}}{dt} &= R_k(n_{1e}, n_{2e}, \dots, n_{ke}, \dots) + c_k P_m N_{ef}^\mu - d_k n_{ke}^\mu - \frac{dn_{ki}}{dt} \\ \frac{dn_{ki}}{dt} &= K_k n_{ke} N_{if} - S_k n_{ki} N_{ef} \end{aligned} \quad (1)$$

Here power  $\mu$  is equal to 2 for dissociative (two-center) adsorption (associative desorption) of a molecule containing the atom of  $k$ -th type.  $N_{if}$  and  $N_{ef}$  are the numbers of centers available for adsorption, i.e. free from adsorbed particles:

$$N_{ef} = N_e - \sum_k v_k n_{ke}; \quad N_{if} = N_i - \sum_k v_k n_{ki}; \quad (2)$$

Additional parameter  $v_k$  is a number of centers occupied (or blocked) by one captured particle.

The relation (2) means there is only one sort of centers of adsorption exists on the surface and it is the same for all molecules and particles. This is one of the most important simplifying assumption in the Lumström's model. On the other hand for aged layers quite another situation may be realized, when different types of particles adsorbs preferentially on its own type of active centers.

The initial condition for the system (1) is usually zero value for all concentrations of the components at  $t = 0$ . The solution of the system at appropriate time dependences for  $P_m(t)$  gives us, in particular, respective time dependences for surface concentrations at the MI interface:  $n_{ki} = n_{ki}(t)$ . Different components captured by the centers at the MI interface will give, generally speaking, different shares into interface polarization and the shift of flat band voltage. The main hypothesis about the MIS sensor operation is the assumption about the proportionality between interface concentration(s) and measured signal  $V(t)$ :

$$V(t) = \sum_k v_k n_{ki}(t) \quad (3)$$

where  $v_k = \mathbf{p}_k / \epsilon_0$  (voltage $\times$ cm<sup>2</sup>) is a constant share (positive or negative) of the  $k$ -th particle captured at the MI interface into the total measured signal;  $\mathbf{p}_k$  is a permanent or induced dipole moment of  $k$ -th particle captured at the interface. The maximum (or steady state) value of response of the sensor under action of only one type of gas at fixed temperature may be presented as:

$$V_1^{(0)} = v_1 N_i \theta_i(P_1) |_{T, t \rightarrow \infty} \quad (3')$$

$$\theta_i(P_1) = a_p P_1^{1/2} / (1 + a_p P_1^{1/2}) \quad (3'')$$

Here  $\theta_i(P_1) |_{T, t \rightarrow \infty}$  is the coverage for the interface at the given temperature and partial pressure (isotherm).  $a_p = (K_1/S_1)(c_1/d_1)^{1/2}$  is a characteristic constant related to heat of adsorption (see below);  $(c_1/d_1)^{1/2} = 1/P_1^*$ , where  $P_1^*$  is a characteristic pressure for *external surface*:  $\theta_e(P_1^*) = 1/2$ .

So, an experimental transient response of the sensor measured under pulse-like gas inlet and isotherms may be compared with the theory using (3), (3') and (3'').

For the case of hydrogen pulse supplying upon Pd-gate MIS sensor followed by oxygen pulse we have the theoretically calculated response kinetics based on model Fig.1 (d, e, f, g) shown in Fig.2. We calculated numerically also the dependences of main macroscopic parameters of the sensors on rate constants  $c_1$ ,  $d_1$ , etc. of respective chemical reactions and then on microscopic parameters of elementary processes such as energy barrier heights and potential well depth.

These calculations show (Fig. 3) that the maximum response at the given partial pressure  $P_1$  depends on

(i)  $N_i$ ; (ii)  $(c_1/d_1)$  (Fig. 3, d) and  $(K_1/S_1)$  ratios and on (iii) partial pressures of other active components in the gas mixture.

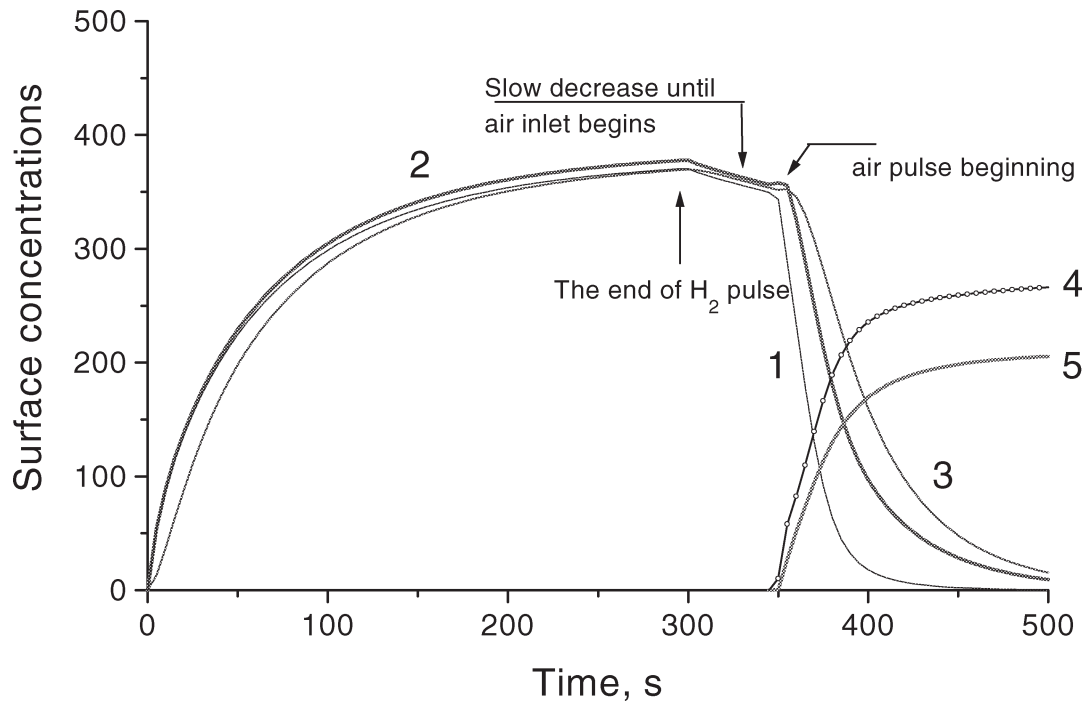


Fig. 2 Theoretical calculation of concentrations at the external metal surface ( $H_e$ ,  $O_e$ ,  $OH_e$ ) and at the metal-insulator interface ( $H_i$ ) of the MIS gas sensors under the action of the consequence of  $H_2$  and air pulses: 1  $H_e$ ; 3  $H_i$ ; 4  $O_e$ ; 5  $OH_e$ ; 3 is a concentration of hydrogen dissolved in the bulk of the layer.

For  $c_i/d_i$  ratio such estimation is possible [5,6]:

$$c_i/d_i = [L_w s_o / (\pi Q_a kT)]^{1/2} \exp(Q_a/kT) = 1/P^{*2} \quad (4)$$

where  $L_w$  is a width of a potential well for adsorbed particle,  $s_o$  is a cross-section for adsorption and  $Q_a$  is the heat of adsorption for given molecule. According to [1,2]  $\beta = (K_i/S_i)$  ratio differs from unit only when the centers at the interface have another value of heat of adsorption. According to Lundström:

$$(c_i/d_i) \beta^2 = (c_{i_i}/d_{i_i}) \sim A_{oi} \exp(Q_{ai}/kT) \quad (5)$$

where  $c_{i_i}$ ,  $d_{i_i}$ , and  $Q_{ai}$  are the respective parameters for the interface centers. Here, however, we could not estimate the absolute values of coefficients  $K_i$  and  $S_i$  separately. They are important for transient responses of a sensor.

The *time of the response* (Fig. 3, a, b, c) of the sensor is determined by (i) the adsorption coefficient  $c_i \sim \exp(-E_a/kT)$ , where  $E_a$  is the barrier for adsorption; (ii) concentration of centers  $N_c$ ; (iii) transport coefficients  $K_i$  and  $S_i$ .

The *time of the recovery* of the sensor depends on both transport coefficient  $S_i$  and (in pure hydrogen) on desorption coefficient  $d_i \sim \exp(-E_d/kT)$ . Here  $E_d = E_a + Q_a$  is an energy of desorption. When hydrogen pulse is followed by oxygen pulse the recovery is accelerated significantly as one can see from Fig. 2, and 4 because of oxygen related reactions with hydrogen and water molecule desorption proceed much faster than associative hydrogen desorption.

The next most important factor, which influences on parameters of a sensor (shape of response signal and view of isotherm), is the so-called *surface reaction scenario*. (Fig.1) It depends both on the function  $R$  and on the coefficient  $\mu$ , which determines the number of centers, which are necessary for adsorption.

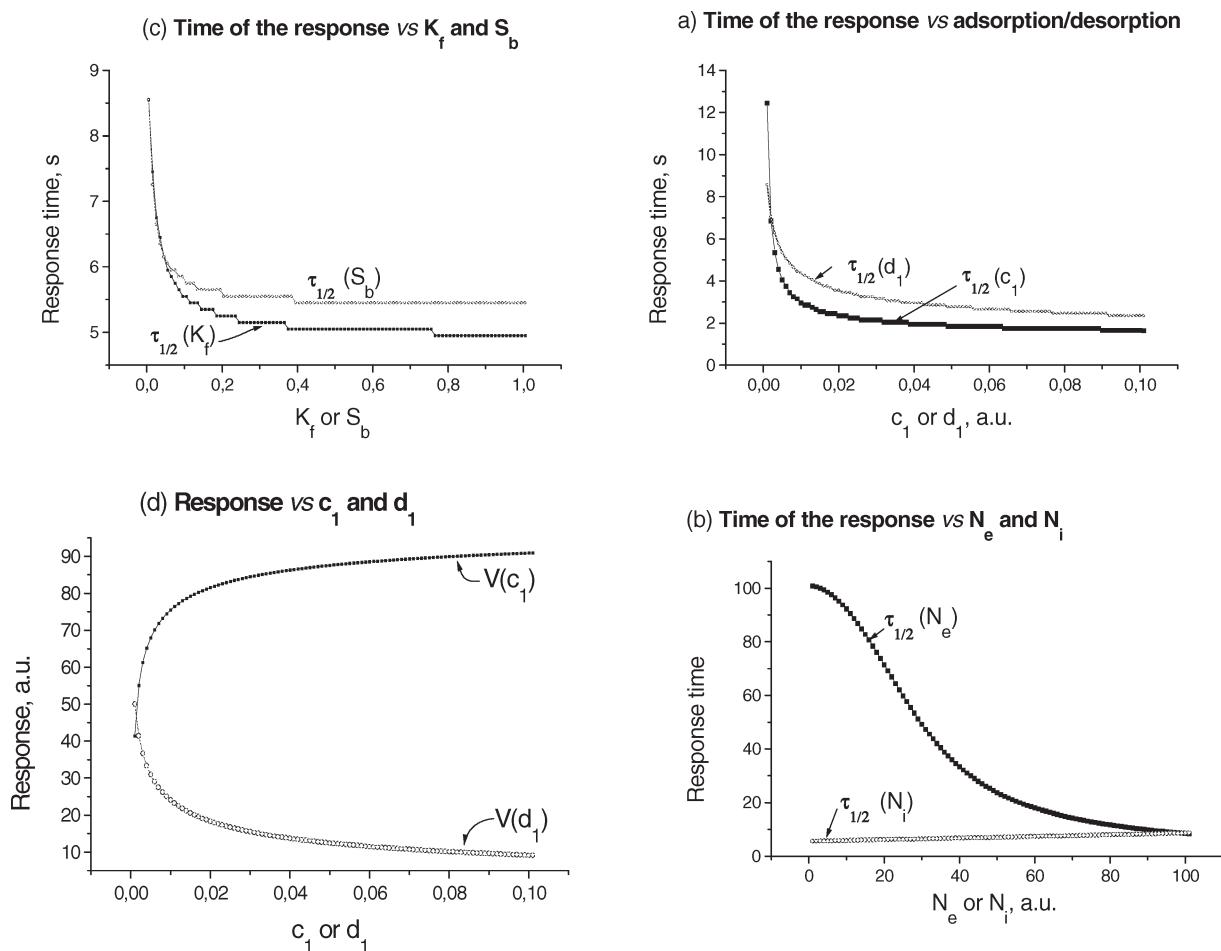


Fig. 3 Calculated dependences of response time and the maximum response of a MIS sensor on macroscopic parameters of the model (3): a)  $t_{1/2} = f(c_1)$ ,  $t_{1/2} = f(d_1)$ ; b)  $t_{1/2} = f(N_e)$ ,  $t_{1/2} = f(N_i)$ ; c)  $t_{1/2} = f(K_f)$ ,  $t_{1/2} = f(S_b)$ ; d)  $V_{max} = f(c_1)$ ,  $V_{max} = f(d_1)$ ;

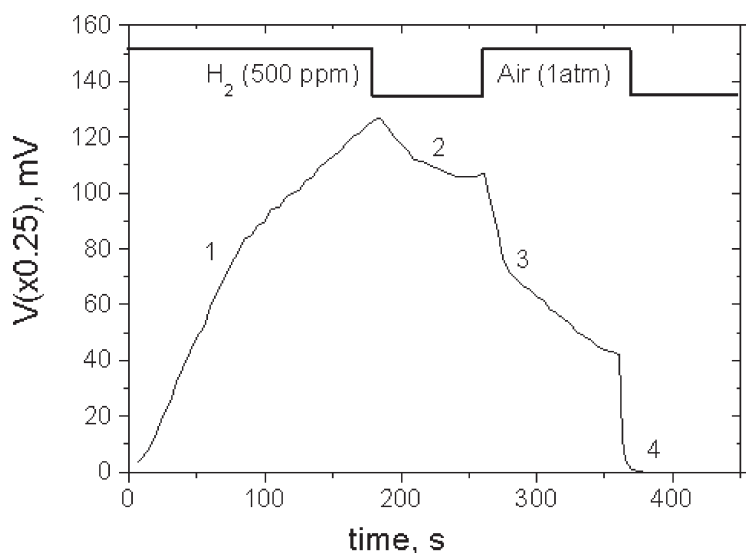


Fig. 4. Transient response of the sensor under combined influence of hydrogen and water molecules. 1 is experiment, 2 is the calculation according to (1)-(3) in the model Fig. 1, a, h, i. Two consequent pulses of hydrogen are superposed onto one long pulse of moisture. The first quick positive pulse corresponds to hydrogen released during water molecules dissociation. Slow negative component of signal is (ascribed according to simulations) to hydroxyls transport through nano-channels formed in aged active layer.

## 2. Explanation of experimentally observed peculiarities of aged MIS gas sensors in the framework of the macromodel [5,6,11].

We briefly present below some experimental data concerning the behavior of sensors naturally aged during about of two years.

(i) The maximum response to hydrogen proved to be about 10 times smaller (50 mV) in comparison with initial values. According to (3) -(3'') it may be caused both by decrease of  $N_i$  and  $v_1$  and  $a_p$ .

(ii) Time of response increases up to one order of magnitude. There are three reasons for this: increase of barrier for adsorption, decrease of  $N_e$  and decrease both of  $S_1$  and  $K_1$ .

(iii) At  $T=150^\circ\text{C}$  the shape of isotherm changed: instead of (3'') was described by a quasi-linear relation

$$\theta_i(P_1) = a_p^2 P_1 / (1 + a_p P_1^{1/2} + a_p^2 P_1) \quad (3''')$$

Such isotherm describes a situation when *in average* only one  $H_a$  atom from each adsorbing  $H_2$  molecule can reach the interface.

(iv) The heat of adsorption  $Q_a$  decrease from 1.1 eV to 0.64 eV per molecule.

(v) The sensitivity to humidity was observed. It manifested itself in the appearance of the negative (slowly-developed) response caused by transport of hydroxyls (Fig.5) through the metal layer.

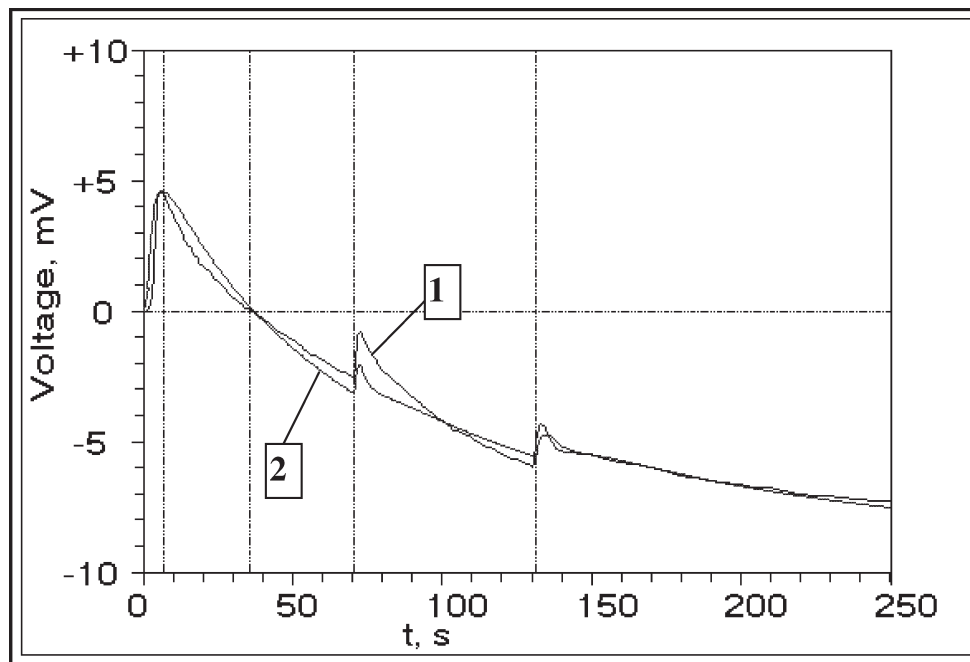


Fig. 5. Transient response of the sensor under combined influence of hydrogen and water molecules. 1 is experiment, 2 is the calculation according to (1)-(3).

(vi) The top part of Pd layer proved to be oxidized according to AES data. The composition of this subsurface layer corresponds to  $\text{Pd}_{50}\text{O}_{50}$ .

## 3. Comparison with the microscopic theory

Hence one can derive such possible macroscopic mechanisms of sensors degradations due to ageing: (i) decrease of number of active centers both on external surface and at the interface; (ii) Change of dipole moment  $p_k$  in the dipole layer leading to decrease of  $v_k$  in (3); (iii) the change of the param-

eters of adsorption centers ( $E_a$  and  $Q_a$ ); (iv) decrease of the value of transport coefficients within the active layer; (v) change of the scenario of the surface reaction of the detected molecule, when one of hydrogen atoms per molecule is captured by some trap immediately at the surface; (vi) such change of the properties of the layer, when not only atomic particles but also some molecules ( $H_2$ , OH) can penetrate to the interface. Let us consider each of points separately and discuss their microscopic reasons.

### 3.1. *Decrease of a number of active centers.*

The active centers at the interface are vanished mainly due to penetration of foreign atoms. It was shown by Lundström that introduction of conductive non-catalytic layer (Au) at the interface results in the total deactivation of a sensor. The oxidation of the interface should also be important in aging. However, it does not act directly on  $N_i$  but changes other parameters. The role of oxide phase formed the external surface is more obvious. The atoms adsorbed on the surface of the oxide spots proved to be captured and could not participate in transport through the film. This factor acts mainly on response time of a sensor.

### 3.2. *Change of the effective dipole moment in the dipole layer*

Possible influence of oxide phase formation at the interface on the sensitivity is not quite clear up to now. Apparently, detected atoms captured within this oxide or hydroxide phase could not form a dipole layer with the same orientation of dipoles. For this reason such important parameter as  $v_k$  in (3) decreases.

### 3.3 *Change of the parameters adsorption center.*

The reconstruction of the layer at the surface and near the interface, which accompanied by a rotation of small crystallites and, as a result, a roughness is generated. Microcrystallites with planes (111) and (100) are formed. On these planes d-orbitals are pulled to the surface (the angle between the orbital and the surface is varied from  $30^\circ$  to  $45^\circ$  instead of the normal orientation) and barrier for adsorption increases. The presence of isolated electronegative impurities (such as oxygen) on the surface on the metal suppresses the molecular dissociative adsorption increasing the potential barrier  $E_a$  due to partial re-attachment of d-orbitals of the metal to the surface and hampered transfer of d-electrons to an anti-bonding orbital of a molecule.

### 3.4. *Co-existence of atomic and molecular transport through metal film.*

If we summarize the results of AES, SEM, transient responses and isotherms measurements, we can deduce some peculiarities of the Pd layers macrostructure. Freshly prepared films are practically pure, uniform, and "dense" (in Lundström's sense) but contain some quantity of holes (about 20% of surface area). These holes are permeable for  $H_2O$  molecules and they demonstrate rather high mobility in such channels. The intensive trapping/detrapping of  $H_a$  may be caused by a small microcrystalline substructure of the films. So only  $H_a$  is able to move through the bulk of the film. In the naturally aged films the holes are vanished. But instead of them atomic size channels, permeable for hydroxyls and  $H_2$  molecules, appear due to some aggregation of small crystallites. The results observed here are similar to those for polycrystalline NiO ( $d=200$  nm) where the transport of  $H_2$  molecules (without dissociation, trapping and detrapping) through micropores between NiO grains has been revealed [12]. Just such behavior is determined not only by the geometry and configuration of micropores but also by electronic structure of the inner surface of grains. In our case those part of hydrogen which is transferred through *the bulk of Pd grains* should be moved in atomic form. Another dominating group of molecules moves along the surface of channels similar to those in NiO or graphite films in [12] with sufficiently less velocities.



### 3.5. Decrease of the value of transport coefficients.

Sufficient increase of response times is caused by decrease of transport coefficient (both  $K$  and  $S$ ). Therefore, some additional traps for atomic hydrogen appear in the bulk of the film. These traps could not be caused by oxide phase because according to AES the main part of the layer is not oxidized. The most probable reason is structural changes of the film.

### 3.6. Change of the scenario.

Retrapping of atomic hydrogen at the aged external surface takes place due to some inactive pure surface centers. These centers are situated not in local atomic vicinity of the catalytic active centers. Indeed the microscopic parameters of the active centers ( $E_a$  and  $Q_a$ ) are not influenced by the presence of the traps.

## 4. Application of $\text{Cu}_{(1-x)}\text{Pd}_x$ surface alloy as a protective and sensitivity enhancing remedy for Pd gate

Introducing of some foreign atoms at the surface is a classical way to change the surface scenario and obtain the response with quite unusual kinetics, enhanced stability against aging, and higher sensitivity.

The doping with copper is widely used in catalysis [7-9]. It was established also that dissociative adsorption of hydrogen on Pt atoms takes place at the surface of  $\text{Cu}_3\text{Pt}$  alloy [10]. It is possible to expect the similar behavior of hydrogen for Cu-Pd alloys, too. On the other hand we expected that Cu being more active in regard to oxygen than Pd will protect active centers against aging. These considerations were the arguments for the Pd/Cu composite layer choose as a sensitive element in MIS sensors. There are two additional reasons, supporting the use of PdCu surface alloy. (i) Copper being slightly more electropositive than palladium proves to be a promoter of catalysis (according to well-known empirical rule [7, 8]). (ii) Some additional electron density from Cu-neighbors is transferred to d-states of Pd. This results in an additional compensation of nuclear charge and increase of the depth of potential well at Pd atom [13].

In Fig.6 the typical experimental kinetic dependences of responses (on  $\text{H}_2$  pulse, followed by air pulse) for MIS gas sensor with CuPd/Pd gate electrode (500 Å, room temperature) are shown in comparison with similar Pd-gate structures. Depth distribution of components, along the structure obtained by AES is shown in Fig. 7. It indicates, in particular, that copper dominates over palladium at the surface.

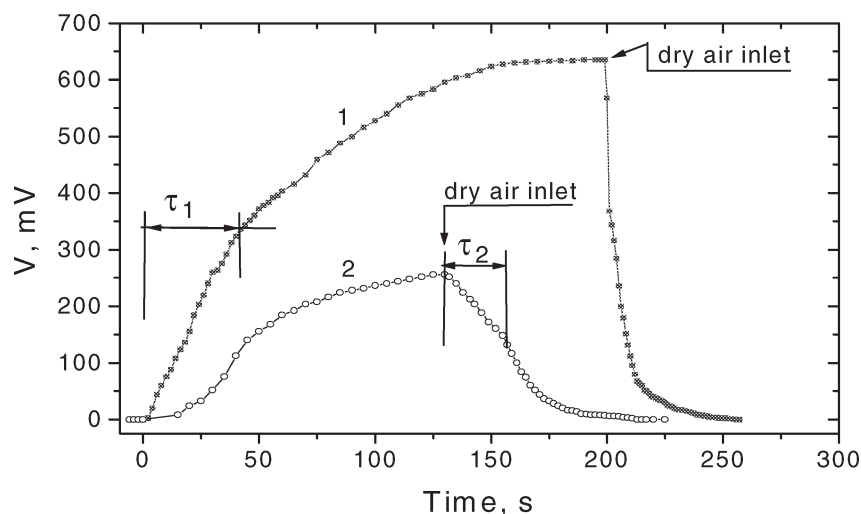


Fig. 6. Transient responses (room temperatures) of Pd-Si<sub>3</sub>N<sub>4</sub>-SiO<sub>2</sub>-Si sensor with freshly prepared Pd layer.

1 is the response on the  $\text{H}_2$  pulse supplying. 2 is a slow recover or reset of the sensor under pumping out. 3 more rapid reset due to air inlet; 4 quick reset under subsequent pumping out.

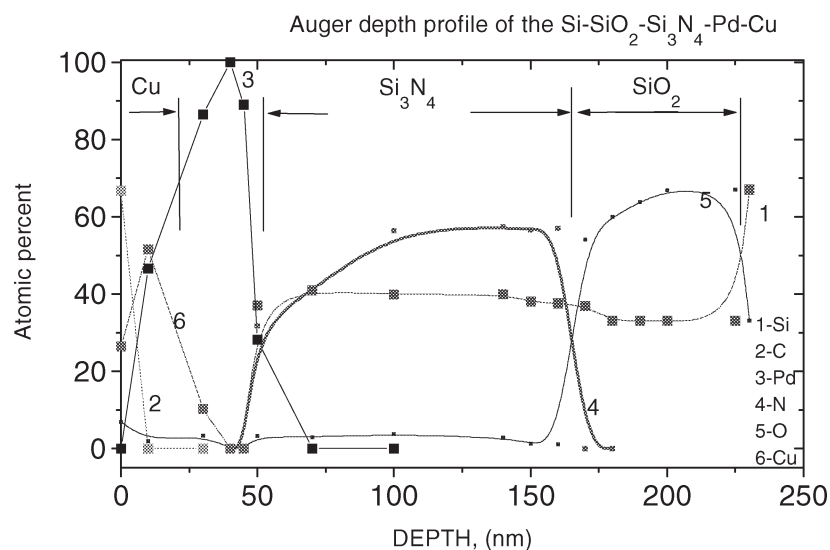


Fig.7. AES depth profiles for freshly prepared  $\text{Cu}_x\text{Pd}/\text{Pd}/\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Si}$  MIS structures: 1 Si, 2 C, 3 Pd, 4 N, 5 O, 6-Cu

The main features of the response of the structures with copper-doped active layer are (i) noticeably higher absolute value of response; (ii) specific quasi-linear initial part of the response with a pronounced flat forepart; (iii) quicker reset of sensor with subsequent air pulse. To understand the nature of these peculiarities the following simulations was done.

#### 4.1. Surface atomic arrangement

As it was shown in [14]  $\text{Cu}_x\text{Pd}$  surface alloys, adsorbed Cu/Pd and Pd/Cu monolayers have some specific features namely:

- Even if Pd atoms are deposited onto Cu substrate there is a strong tendency for copper atoms to go over to overlayer;
- If copper atoms are deposited onto Pd substrate they prefer to form 2D islands attached to palladium surface steps
- When copper is presented in a noticeable excess (which corresponds to the method magnetron sputtering of copper onto Pd gate) more or less large pure copper parts of the surface (or an atomic plane in the bulk) are formed. They alternate by the similar parts of the surface with  $\text{Cu}_{50}\text{Pd}_{50}$  composition (Fig. 8 a, b).
- Atoms, which formed an alloy, are disposed in the form of parallel Cu and Pd alternating rows or chains as is shown in Fig. 8.
- The average composition depends on relation between Cu and Pd parts areas.

Starting from the results of Bazzolo et al [14] let us assume the model for atomic arrangement on the surface of CuPd surface alloy as shown in Fig. 8

In the model the following processes are important.

- Adsorption/desorption on palladium chains (Pd-Pd pairs consisting of neighbor atoms)
- Quick exchange of hydrogen adatoms between Cu- и Pd-chains.
- Quasi one-dimensional hydrogen diffusion along Cu- и Pd-rows toward the large copper parts (islands).
- Spreading and accumulation of hydrogen on copper parts.
- Transfer of H from external surface to the bulk of the Pd layer and backward.
- Transfer of H from the bulk to the internal surface of the Pd layer and backward.

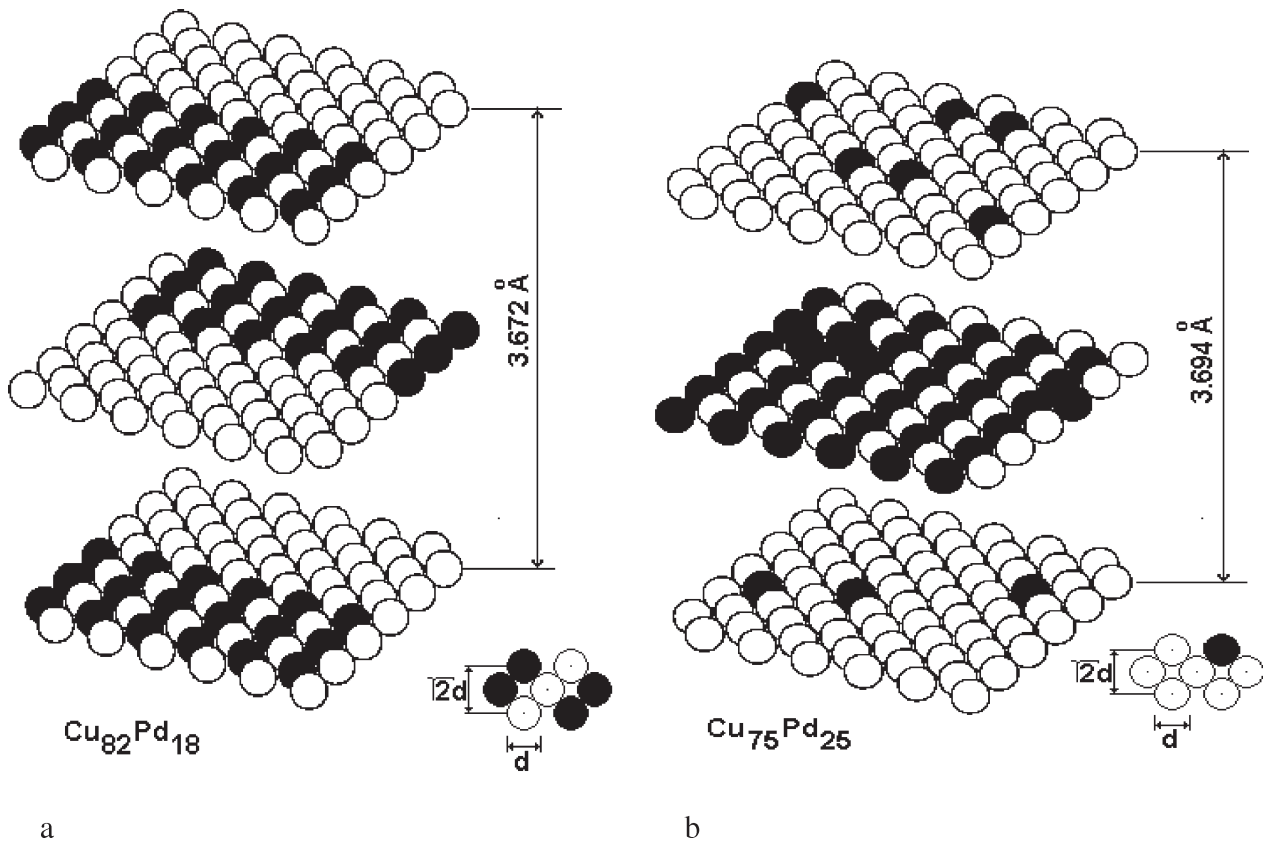


Fig. 8. Atomic configuration of 3 neighbor atomic planes in  $\text{Cu}_{82}\text{Pd}_{18}$  (a) and in  $\text{Cu}_{75}\text{Pd}_{25}$  (b) alloy cluster (BFS calculations [14]). Insertions: both side cross-section of 3 atomic layers and plan-view of individual atomic plane;  $d$  is the compositionally dependent lattice spacing. Black circles are Pd and white are copper.

### The main parameters of the process

$c_1$	coefficient of dissociative $\text{H}_2$ –adsorption on Pd-Pd pair
$d_1$	coefficient of associative desorption from occupied Pd-Pd pair
$k_{cp}, k_{pc}$	rate constants for hydrogen exchange between Cu and Pd chains
$P$	hydrogen partial pressure
$K_{eb}$	rate constant for hydrogen forward transfer from external surface to bulk
$K_{be}$	rate constant for hydrogen backward transfer from bulk to external surface
$K_{bi}$	rate constants for hydrogen forward transfer from bulk to internal surface of the layer.
$K_{ib}$	rate constants for hydrogen backward transfer from internal surface of the layer to bulk
$\tau_D = \pi L^2 / D_{ch}$	an effective diffusion time for atom migration along chains, $L$ is a length of a chain and $D_{ch}$ is a respective diffusivity.

### The main parameters of the active layer

$\theta$	a coverage of palladium chains with hydrogen;
$\theta_i$	a coverage of internal surface of the layer with hydrogen;
$\theta_b$	an occupation degree of bulk centers with hydrogen;
$\Xi$	a coverage of copper chains with hydrogen;
$\Phi$	a coverage of copper areas with hydrogen;

$N_i$  a surface concentration of adsorption centers at the internal surface of the layer;  
 $N_b$  a number of bulk absorption centers recalculated per unit area of the surface;  
 $N_e$  a number of Pd (Cu) atoms belonging to Pd (Cu) chains per unit area of the external surface;  
 $N_c$  a number of Cu atoms located at copper islands per unit area of the layer.

### Kinetic equations for hydrogen coverage

(i) Hydrogen at Pd atoms

$$\begin{aligned}
 d\theta/dt &= c_1 P N_e (1-\theta)^2 - d_1 N_e \theta^2 - && //\text{adsorption-desorption} \\
 k_{PC} N_e \theta(1-\Xi) + k_{CP} N_e \Xi(1-\theta) &&& //\text{exchange between Pd and Cu chains} \\
 - \theta N_e (1-\Phi)/\tau_D &&& // \text{diffusion along Pd chains} \\
 - k_{eb} \theta N_b (1-\theta_b) + k_{be} \theta_b (1-\theta) N_b &&& //\text{exchange between external and bulk}
 \end{aligned}$$

(i) Hydrogen at Cu atoms in CuPd subsystem

$$\begin{aligned}
 d\Xi/dt &= +k_{PC} \theta N_e (1-\Xi) - k_{CP} \Xi(1-\theta) N_e && //\text{exchange between Cu and Pd chains} \\
 - N_e \Xi(1-\Phi)/\tau_D &&& // \text{diffusion along Cu-chains} \\
 - k_{eb} N_b \Xi(1-\theta_b) + k_{be} N_b \Xi(1-\theta_i) &&& //\text{exchange between external and bulk}
 \end{aligned}$$

(iii) Hydrogen trapped by copper atoms at Cu areas

$$\begin{aligned}
 d\Phi/dt &= N_e \theta(1-\Phi)/\tau_D + && // \text{diffusion along Pd chains} \\
 N_e \Xi(1-\Phi)/\tau_D &&& // \text{diffusion along Cu chains} \\
 - k_{eb} N_b \Phi(1-\theta_b) + k_{be} N_b \theta_b (1-\Phi) &&& //\text{exchange between external and bulk}
 \end{aligned}$$

(iv) Hydrogen trapped in the bulk of active layer

$$\begin{aligned}
 d\theta_b/dt &= \\
 - k_{bi} \theta_b (1-\theta_i) N_i + k_{ib} \theta_i (1-\theta_b) N_i &&& //\text{exchange between bulk and internal //centers}
 \end{aligned}$$

(v) Hydrogen trapped at internal surface of the active layer

$$\begin{aligned}
 d\theta_i/dt &= \\
 +k_{bi} \theta_b (1-\theta_i) N_b - k_{ib} \theta_i (1-\theta_b) N_b &&& //\text{exchange between bulk and internal}
 \end{aligned}$$

In Fig. 9 the results of simulations of sensor response at different average copper content according to equation above are presented. One can see that the presence of copper suppresses sufficiently hydrogen associative desorption backward to gas ambient, results in strong accumulation of atomic hydrogen in the layer and in particularly at the internal surface, increasing the useful signal. However, the times of response and especially of reset increase and the forced reset by air inlet is quite necessary. It is interesting that the value of response increases practically linearly with average copper content at the external surface, however, the time of the response increase respectively and some optimum may be chosen. These results are in a good accordance with the recent experimental study of thermo-desorption of hydrogen from ultra-thin Pd layers covered by mono- (submono-) layer of copper [15]. The presence of copper results in intensive transfer of atomic hydrogen from external surface of the considered system  $Cu_m/Pd_n/W$  ( $n=1\dots4$ ,  $m = 0.5\dots1.5$ ) to the bulk as well as to the Pd/W interface. Besides intensive reaction between atomic hydrogen and oxygen in the presence of copper overlayer was confirmed by in situ AES data.

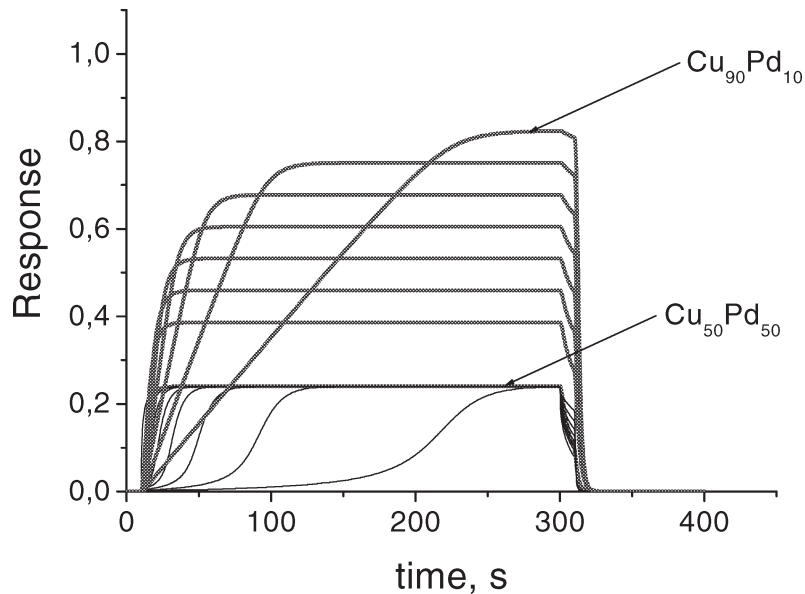


Fig. 9. Results of theoretical simulations of  $\text{Cu}_x\text{Pd}/\text{Pd}$  –MIS sensor response for different average compositions at the surface for the surface atomic arrangement given in [14]. Hydrogen pulse is applied and then, after short delay, the oxygen pulse come. Thick lines correspond to atomic hydrogen accumulated at the internal surface of the layer (useful signal) and thin lines are atomic hydrogen trapped by Pd chains at the external surface.

## Conclusion

The simulation shows that the aged MIS sensors have (i) another energetic parameters of adsorption centers; (ii) something another scenario of adsorption and surface reactions on the external surface of the layer; (iii) additionally the atomic transport through the sensitive layer becomes much slower. (iv) For some types of films and under special conditions molecular transport together with atomic one may be realized (v) The main processes responsible for aging are, probably, the interaction of the surface and interface with oxygen and water and the recrystallization of the bulk of the metal layer.

From the considerations above four ways for preventing of aging of MIS sensors may be proposed:

Chemical modification of the external surface via surface alloy formation such as PdCu or PdCu<sub>3</sub>. (Fig. 8). It was shown that Cu do not hamper of dissociative adsorption of hydrogen on. On the other hand Cu atoms will stabilize the local atomic environment of each Pd atom fixing Pd- bonds orientation. Also they may serve as interceptors of oxygen.

The periodical short-time hydrogen treatments should be used for reduction of the surface from oxide phase.

Initial artificial aging of metal film by means of heat treatments in neutral ambient should be used to accelerate the structure relaxation in the bulk of the layer.

For the same aim it is perspective to replace the pure Pd layer on  $\text{Cu}_x\text{Pd}$  one, where the content of copper  $x$  is varied over the depth of the electrode layer.

On the other hand aged structures have some interesting features, which allow using them in special applications.

## Acknowledgments

This work was performed in the framework of INTAS project **2001-0009**

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