

Adsorption-Catalytic Properties of Thin Pd and PdCu_x Films

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Interaction of H₂ with thin (30–50 nm) and ultra-thin (1–4 monolayers) pure Pd films and Pd films with copper-doped surface, as well as H₂+O₂ co-adsorption, were studied by Auger electron spectroscopy, low energy electron diffraction, thermal desorption spectroscopy and response measurements of metal-insulator-semiconductor (MIS) gas sensors. Pd films were deposited onto layered insulator-semiconductor structure and single crystalline tungsten substrates. The measurements were carried out in Ar+H₂ (500 ppm) mixtures in the case of MIS-structures. For Pd/W(110), Cu/Pd/W(110) and O₂/Cu/Pd/W(110), the measurements under ultra-high vacuum conditions (1×10^{-9} Torr) were performed. It was shown that ultra-thin copper layers deposited onto Pd surface promote the dissociative adsorption, suppress the hydrogen desorption, and contribute to the transfer of atomic hydrogen into the film bulk. As a result, the sensitivity of MIS structures with copper-doped surface Pd gate increases with respect to hydrogen. The mechanisms of enhanced hydrogen dissociation on the Cu_xPd surface are discussed and validated by computer simulation of MIS sensor response, MD simulation of adsorption/desorption processes, and *ab initio* calculations of Cu_xPd cluster properties.

1. Introduction

Catalytic properties of surfaces of transition metal thin films were studied in many works [1–7]. In particular, dissociation of hydrogen and other hydrogen-containing molecules on palladium and platinum surfaces was investigated in detail [5–9]. It was established that this process is rather sensitive to the structure and composition of the metal surface. In particular, the catalytic activity appreciably increases for surfaces covered with isolated transition metal clusters, or with surface alloys (e.g., PdCu₃). These peculiarities may be explained in the framework of stereo- and topo-chemical considerations. The following key factors should be considered for dissociative adsorption: (i) orientation (relative to the surface) of d-orbitals of the atom which is the adsorption center, (ii) conformity between the point symmetry of adsorption center and the symmetry of adsorbed molecule [7–9]. Thus, different kinds of surface reorganization such as reconstruction, formation of micro- and nano-crystals with low-index planes, formation of surface alloys etc., may be applied to enhance the surface catalytic activity to certain types of chemical reactions [12–14]. Simultaneously, a modified surface should meet additional requirements dictated by real conditions of adsorption and catalytic reactions. The most important of these requirements is the inertness of local adsorption centers to the action of oxygen and others chemically active compounds of atmospheric environment.

To reveal the detailed mechanisms of phenomena outlined above, the study of adsorption on single layered films under ultrahigh vacuum (UHV) conditions would be interesting when the surface structure and composition can be changed controllably. Such structures are good model systems [15, 16] for the analysis of behavior of thin near-surface layers of the real films of catalysts, or gas-sensitive layers in gas chemical sensors [1, 2, 12–14]. In this case modeling of environmental influence on adsorption of studied gases is also possible by means of molecular beam induced pre-adsorption of molecules of oxygen on the surface. Despite the processes on the surface of the gas sensitive layer of a sensor and in the ultra-thin films under UHV are not completely identical it is possible to reveal certain common features between the model and real experiments. Besides, model experiments allow to reveal the physical mechanisms of the complex phenomena on the surface of a catalyst layer under real conditions. Indeed, the processes taking place either on the surface or in a thin subsurface layer, are the most important ones in catalysis. For example, a typical sequence of the processes is as follows: (i) adsorption – (ii) chemical reaction(s) – (iii) by-product desorption, (iv) dissolution of a part of adsorbed molecules or atoms in the bulk of the catalyst film or in the non-catalytic substrate.

For the investigation of four processes mentioned above under real environ-

mental conditions, MIS structures with the field electrodes of catalytically active metals (Pt, Pd, Ni, etc.) are very suitable [1, 2]. The response of such structures to hydrogen or other gases is formed primarily by the dissociative adsorption of molecules on the external surface of metal films. It is possible to enhance this stage by special modification of the metal surface, e.g., by doping the surface and thin subsurface region with foreign atoms.

In the present work, the role of Pd surface doping with copper, and related mechanisms of adsorption, desorption and bulk dissolution of hydrogen were considered both under UHV and in the real atmosphere. Two types of catalytic layers, namely (1) ultra-thin (one to four monolayers thick) palladium films on W(110), and (2) thin (30–50 nm) palladium films in MIS chemical gas sensor, were studied. In both cases, the parameters of adsorption centers were determined.

Besides, UHV experiments on co-adsorption of H_2 , O_2 and Cu on Pd/W(110) surface were carried out. The obtained results allow to explain observed copper-induced decelerated aging of Pd surface and degradation of MIS structures. We also developed mathematical models to describe those four processes mentioned in relation with the MIS structure on a copper-doped palladium surface.

2. Experimental technique

We studied the adsorption/desorption processes on Metal/Insulator/Semiconductor (MIS) capacitors and transistors with catalytically active Pd and composite Cu-Pd films as gate electrodes. MIS structures were created on p-type Si(100) substrates with the resistivity $\rho = 7.5 \Omega \cdot \text{cm}$ by conventional silicon technology. The insulator consisted of thermal SiO_2 and Si_3N_4 layers. These layer thicknesses were 800 and 600 Å, respectively. Palladium and copper films were prepared by the magnetron deposition technique at the deposition rate of $\sim 1 \text{ Å/s}$. During the film deposition, the substrate was not heated deliberately, but its temperature was about 50–60°C due to the action of argon plasma during palladium and copper target sputtering. The substrate temperature was monitored by a chromel-alumel thermocouple. The thickness of palladium layers was about 1000 Å in transistor structures, and about 500 Å in MIS capacitors. The copper layer thickness was about 300 Å.

The kinetic dependences of a MIS structure response to the action of rectangular gas (H_2 , H_2 +air) pulses were measured in a steel chamber which was attached by an electrical valve to the volume with specially prepared hydrogen-helium or hydrogen-argon gas mixture. The concentrations of hydrogen in helium were 200 ppm, 500 ppm, 800 ppm and 1000 ppm, and in argon this con-

centration was 500 ppm. Prior to measurements, the chamber was pumped out down to 2×10^{-3} Torr. The gas mixture was then injected into the chamber. A standard high-frequency (1 MHz) C-V method was used to measure the kinetic characteristics of response and restoration of Pd- and Cu/Pd-MIS structures. The structure capacity at the flat band voltage was measured at room temperature.

Measurements on Pd-MIS transistors were carried out at a temperature $T = 150^\circ\text{C}$ at a fixed current of $100 \mu\text{A}$ in the channel of a field transistor. Chemical composition along the depth of Pd and Cu-Pd layers in MIS structures was determined by Auger electronic spectroscopy (AES) with depth profiling.

Simultaneously, model experiments on hydrogen and oxygen adsorption on ultra-thin Pd and Cu/Pd layers deposited on W(110) were carried out under ultrahigh vacuum conditions (residual gas pressure $\sim 1 \times 10^{-9}$ Torr).

The experimental setup combining low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and thermal desorption (TD) techniques were used. Pd layers were deposited on the front faces of W(110). All Pd structures are related to fcc Pd(111) with $\theta = 1$ corresponding to a Pd coverage of the Pd(111) surface atom density, as described in previous paper [10]. AES was used to determine the surface purity, relative Pd/Cu coverage, growth model, and the homogeneity of deposition. All Auger intensities were measured by comparison with the line of a pure W surface (169 eV). Thermodesorption spectra (TDS) were measured by the flash method. The thicknesses of palladium films were 1, 2 and 4 monolayers. We denote these structures as Pd₁/W, Pd₂/W, and Pd₄/W, respectively. A part of samples with palladium layers were annealed for 1–2 minutes at $T = 840\text{--}920^\circ\text{C}$. Ultra-thin Cu/Pd composites were formed by deposition of $m = 0.5\text{--}1.5$ monolayers of copper on the surface of Pd_{*n*}/W structures. These Cu_{*m*}Pd_{*n*}/W composites were also subjected to anneals at $T = 500\text{--}600^\circ\text{C}$ for 1–2 minutes. Influence of oxygen adsorption on adsorption of hydrogen on the surfaces of annealed and non-annealed composite Cu/Pd films was investigated.

3. Results

3.1. AES analysis of Pd and Cu/Pd electrodes in MIS-structures.

MIS structures with Pd electrodes partly lose their sensitivity to hydrogen after a natural storage in air during some time, as well as after measurements in air containing ambient at increased temperature. Pd MIS transistors with freshly prepared Pd layers demonstrate maximum response of 500 mV at hydrogen concentration of 500 ppm. This response signal to hydrogen fell down to

approximately 250 mV after carrying out measurements during one month. According to theoretical considerations described below, the reason for this effect is a decrease of the concentration of active adsorption centers on both surfaces of Pd electrode.

AES depth profiling with layer-by-layer sputtering has shown that a palladium oxide layer on the surface of aged Pd films is formed [14]. The thickness of this oxide layer is about one third (~ 300 Å) of the thickness of initial Pd film. In the case of Pd electrodes with copper-covered surface, no oxygen was found in the entire metal layer after storage under the same conditions. Instead, a thin (10 nm) subsurface layer with Cu_xPd ($x \approx 1$) composition was formed.

3.2. Kinetic response of Pd and Cu/Pd MIS structures

The presence of oxide phase on Pd surfaces will surely influence the character of kinetic response of the structure. The typical kinetic dependences of response of MIS transistors with (i) freshly prepared and (ii) aged 1000 Å thick Pd electrodes measured at 150°C and hydrogen concentration in argon equal to 500 ppm, are shown in Fig. 1. Since the hydrogen diffusivity in Pd is high, a balance between the hydrogen adsorbed on the external surface, in the bulk, and that captured at the metal-dielectric interface should be established very quickly. According to Ref. [12], for 1000 Å thick Pd films the diffusion time at $T = 423$ K is $\sim 10^{-5}$ s. It is commonly accepted that for the freshly prepared films there is no barrier between the surface (or interface) centers of adsorption and the centers of absorption in the film bulk. Therefore, for the freshly prepared Pd electrodes, the absorption or transport through the film would not be a limiting stage for MIS sensor response formation. The characteristic response time t_{resp} (at 150°C) is small (~ 5 s). The appearance of more or less thick (sub)oxidized layer on the surface of an electrode results in an increase of t_{resp} and reduces of the response amplitude (~ 90 % and ~ 50 %, respectively).

Kinetic characteristics of MIS transistors and capacitors with thin (500 Å) Pd and Cu/Pd electrodes are shown in Fig. 2. The measurements were carried out at room temperature at hydrogen concentration in the gas mixture equal to 500 ppm. The response time amounts to ~ 20 s and ~ 35 s for MIS structures with Cu/Pd and Pd-electrodes, respectively. The kinetic curves for annealed structures were also measured at $T = 473$ K during 1 hour. The response time for such systems was ~ 35 s and ~ 50 s, respectively.

Thus, MIS-structures with thin Pd and Cu/Pd electrodes operate efficiently even at room temperature. According to electron microscopy data, the structure of such films changes from island-like [3] to porous [14] with the growth of thickness. This allows atomic hydrogen to reach easily the metal-dielectric interface by migration along the grain surface.

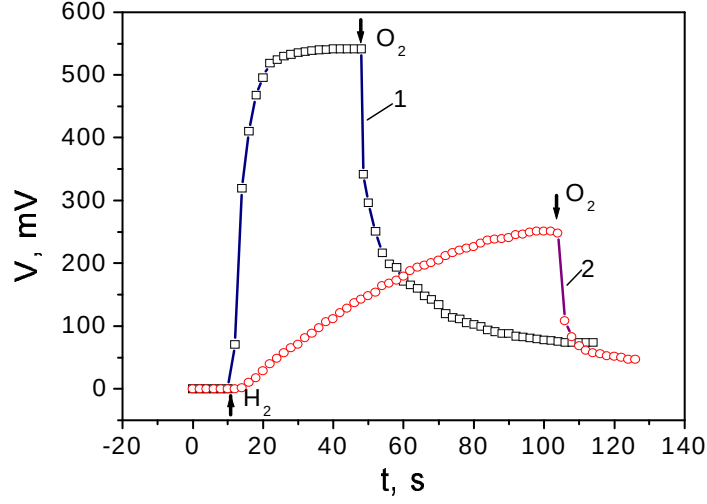


Figure 1. Kinetic response for MIS-FET structures with thick (~ 1000 Å) Pd freshly prepared (1) and aged (2) gate electrodes. Measurements were carried out at 423 K. Arrows indicate the beginning of the inlet of respective gas.

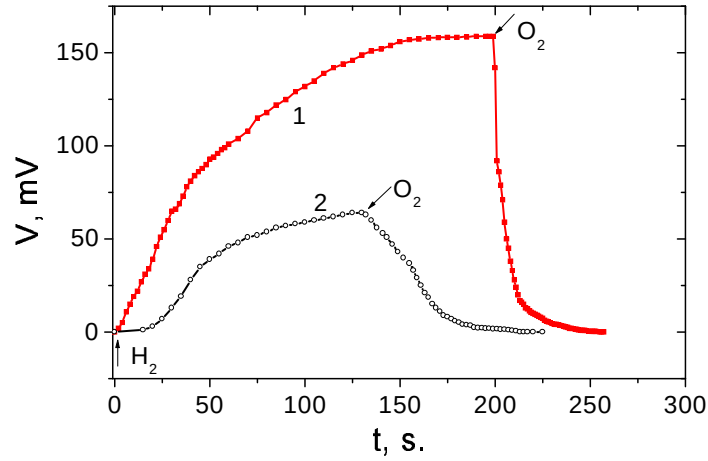


Figure 2. Kinetic dependences of MIS capacitors with thin (~ 500 Å) Cu/Pd (1) and Pd (2) electrode layers. Measurements were carried out at room temperature just after fabrication. Arrows indicate the beginning of the inlet of respective gas.

3.3. Ultra-thin film Pd and Cu/Pd on a W (110) surface

Another type of the structures being investigated is the ultra-thin (one to four monolayers) Pd and Cu/Pd films on the surface of single crystalline tungsten.

Low Energy Electron Diffraction and AES-spectra

According to LEED data, the structure of Pd_n layer depends both on the number of monolayers n and the temperature of substrate [10]. Only the first Pd monolayer deposited on W(110) strongly demonstrates one- or two-dimensional pseudomorphism. In the case of room temperature deposits, the second and further layers gradually come to a normal Pd(111) structure. In the case of annealed deposits, the (1×1) diffraction pattern is observed.

Deposition of 0.5–1.5 monolayers thick copper films on the non-annealed Pd/W(110)

substrate does not result in the appearance of additional structure. However, the additional structure arose from copper deposition on annealed Pd/W(110) sample. It can be considered as a combination of Pd (111)/W (110) structures and structures similar to Cu(111), and may be treated as a Cu_xPd alloy. Additional reflexes at room temperature are to some extent diffused, but after annealing at 500–600 K the picture becomes clear.

AES peak amplitudes were measured *in situ* during the formation of multilayered Cu/Pd composite films on W(110) substrate, and after the adsorption of oxygen and hydrogen on annealed and non-annealed composite copper-palladium film. In this case, the adsorption dose of oxygen amounts to $(1-3) \times 10^{-7}$ Torr during 30 minutes (~ 180 L), and the adsorption dose of hydrogen is equal to $(1-3) \times 10^{-8}$ Torr·s during 30 minutes (~ 18 L). Oxygen adsorption on non-annealed composite film results in a reduction of amplitudes of AES peaks of copper and palladium. Subsequent hydrogen adsorption results in the restoration of AES peak amplitude. Under oxygen and hydrogen adsorption on annealed Cu/Pd composite films, the amplitude of these peaks practically does not change.

TDS of hydrogen for Pd_n/W(110) films

In Fig. 3 (a, b, c), hydrogen TD-spectra for non-annealed Pd_n/W(110) system are shown at the dose of H₂ inlet corresponding to 18 L; $n = 1 \dots 4$ is the number of monolayers. H₂ TD-spectra from Pd₁/W(110) demonstrate the presence of *chemisorbed* hydrogen state, which results in the desorption at higher temperature (~ 450 K) than the temperature of chemisorbed state for H₂ adsorbed on Pd(111) [11]. The second TD peak at $T \sim 510$ K is also observed. This rather intensive peak is unlikely to be formed from bulk-like hydride state in Pd monolayer, and should be ascribed to H₂ desorption from Pd/W(110)

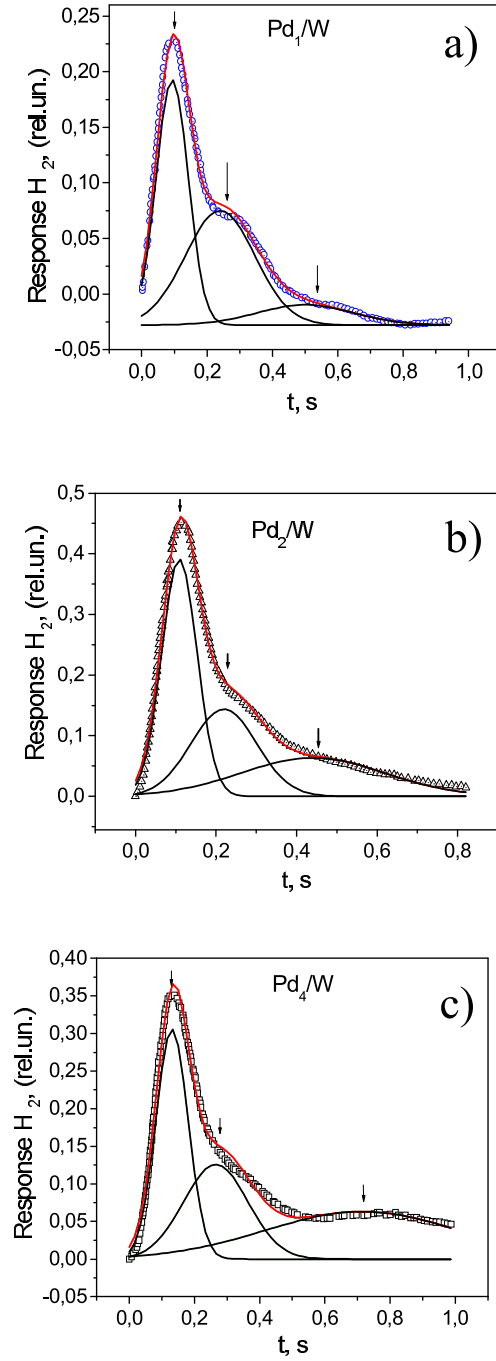


Figure 3. Hydrogen thermodesorption spectra for $\text{Pd}_n/\text{W}(110)$ system. (a) $n = 1$; (b) $n = 2$; (c) $n = 4$.

Averaged Parameters	Pd electrode (freshly prepared)	Pd electrode (annealed)	Cu/Pd electrode (freshly prepared)	Cu/Pd electrode (annealed)
ΔV_{FB} , mV	500	400	550	570
Time of response, s	5-35	20	25	15
Time of reset, s	45	10	5	2

Table 1. Electro-physical parameters of MIS structures.

Pd		Cu/Pd		
Pd-MIS Maximum response (mV)	Pd ₄ /W, Relative area of TD-peak (%)	Cu/Pd – MIS Maximum response (mV)	Cu/Pd ₂ /W Relative area of TD-peak (%)	O ₂ /Cu/Pd ₂ /W Relative area of TD-peak (%)
	(%)		(%)	(%)
400	(β_1 peak) 33.29	600	(β_1 peak) 15.67	9.50
	(β_2 peak) 28.24		(β_2 peak) 63.00	21.22
	(β_3 peak) 38.47		(β_3 peak) 21.33	69.28
	(β_2 peak + β_3 peak) 66.71		(β_2 peak + β_3 peak) 84.33	90.50

Table 2. Comparison of adsorption parameters obtained in TD-experiments, with sensitivity of MIS structures (β_1 pike + β_3 pike) vs MIS maximum response.

interface. If our assumption is valid the intensity of the second peak should not significantly change with the increase of the number of Pd monolayers, and this is really observed. For 2...4 monolayers thick palladium films (Fig. 3 b, c), the third broadest peak appears and significantly increases. This peak is located at higher temperatures (≥ 640 K) and could be related to the component dissolved in the bulk, as observed for single-crystalline palladium. Indeed, the area of this peak increases with the increase of the number of Pd monolayers. Moreover, further detailed analysis shows that the small amount of bulk-dissolved hydrogen may be revealed from TDS even for the Pd₁/W(110) system. Below we shall denote these three states and corresponding peaks in TDS as β_1 , β_2 , and β_3 , respectively. The increase in hydrogen inlet dose does not result in the essential changes of peak positions. Only their amplitudes somewhat increase.

TDS of hydrogen for Cu/Pd/W (110) films

In Fig. 4, TD-spectra for the Cu₁Pd₂/W(110) composite system are presented. The subscripts denote respective numbers of monolayers. In this system, the same three peaks as before are observed. However, the estimation of amount of desorbed hydrogen from the area of peaks suggests the redistribution

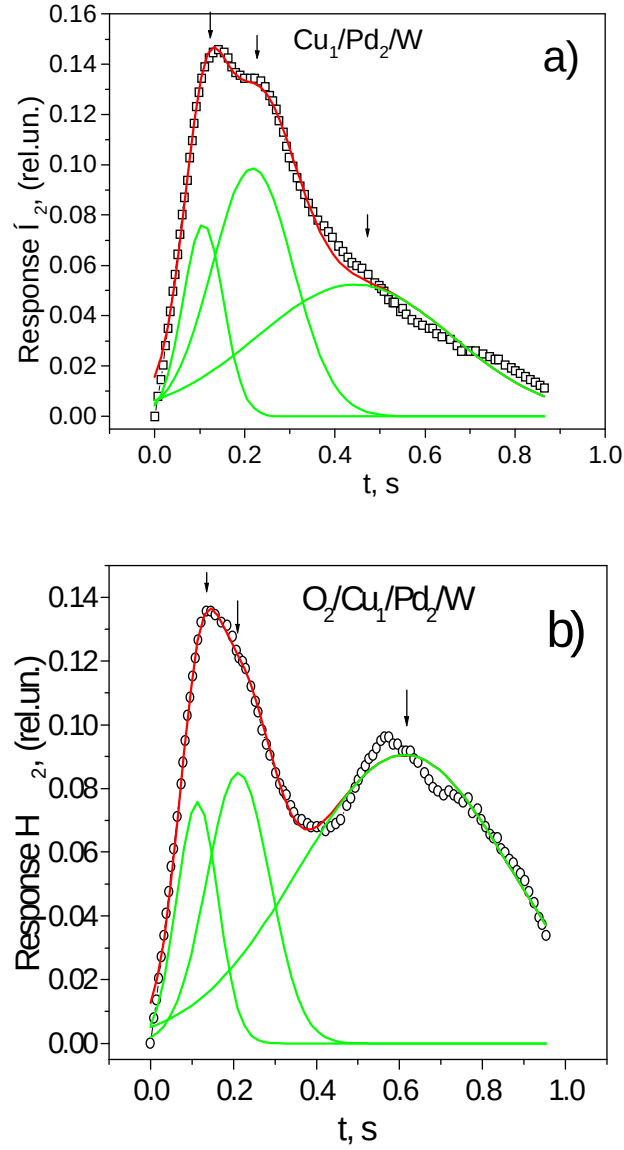


Figure 4. Thermodesorption spectra for $\text{Cu}_1\text{Pd}_2/\text{W}(110)$ (a) and $\text{O}_2\text{Cu}_1\text{Pd}_2/\text{W}(110)$ (b) systems.

between different components with the essential reduction of contribution of a surface-related component β_1 and the increase of β_3 (see Table 2). On the other hand, β_2 remains practically the same as for previous case. The $\beta_1 \rightarrow \beta_3$ redistribution becomes even more pronounced in the case of H_2 and O_2 co-adsorption on $\text{Cu}_1\text{Pd}_2/\text{W}(110)$ surface (Fig. 4, b).

4. Discussion of results. A model

4.1. Computer deconvolution of TD spectra

As was already mentioned, computer deconvolution of TD spectra into Gauss components (MICROCAL ORIGIN 4 software) has generally revealed three constituent peaks (β_1 , β_2 , β_3) (see Figs. 3, 4, and Table 2). The peak maxima correspond to ~ 450 K, ~ 510 K and ~ 640 K. The values of desorption energy of hydrogen from these states are $E_d = 1.18$, 1.33 and 1.66 eV, respectively [18]. When the thickness of palladium layer increases up to four monolayers, the maximum located in the TD spectrum at $T \sim 640$ K gradually raises, but the peak β_2 remains practically unchanged. This peak behavior allows us to ascribe the third, wider peak β_3 , to bulk absorption of hydrogen, and the second one to Pd/W interface adsorption. For Cu/Pd/W systems these three peaks are also revealed in TD spectra.

The deposition of additional monolayer of Cu (Fig. 4) results in an increase of amount of hydrogen dissolved in the bulk of Pd film. This can be inferred from the growth of the β_3 peak. Preliminary oxygen adsorption on the surface of Cu/Pd composite results in the reduction of β_1 peak and a small decrease of the interface peak β_2 accompanied by at least two-fold enhancement of the “bulk-related” peak. Thus copper, as well as adsorbed oxygen in the presence of copper, assist more efficient penetration of hydrogen into film bulk creating a sort of “atomic pump”. Calculated values of desorption heat for peaks β_1 , β_2 , and β_3 remain almost unchanged for different adsorption systems studied in the present work. This supports the location of the centers of hydrogen adsorption on palladium atoms, despite the changes in their local atomic environment. According to Ref. [20], adsorption centers on the surface of Cu_xPd -like alloy may even consist of isolated Pd atoms surrounded by copper atoms. The centers of adsorption/desorption may also be located on the surface of nano-scaled Pd particles [21] or two-dimensional isles surrounded by other atoms (e.g., Cu), which are inactive to molecular dissociative adsorption. In the case of Cu_xPd alloy, the following four items become very important:

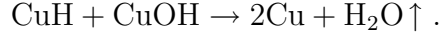
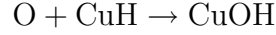
(i) The so-called spillover effect of both hydrogen and oxygen [21]. In this case O_2 and H_2 dissociatively adsorb on the surface of Pd isles only, but can spillover in atomic state onto surrounding parts of the substrate.

(ii) Generated in this way *atomic* hydrogen may be actively trapped by copper atoms [23], while copper itself is inactive to dissociative H_2 adsorption.

(iii) It is known that for $\text{H}_2 + \text{O}_2$ reaction on Pd surface, H_2O production occurs via Langmuir-Hinshelwood (L-H) mechanism [21]. Therefore, spilled over

atomic H and O may interact each with other outside Pd isles too. Such interaction can occur e.g., on copper parts of the film.

(iv) Atomic hydrogen trapped by copper seems to be a good sink for atomic oxygen with subsequent formation and removal of water molecules, for example by means of the following reactions:



This process seems to be responsible for the higher protecting ability of Cu-doped Pd gate electrode surface against environmental action, comparing to pure Pd gate, in MIS gas sensors.

It should be noted that the energy of hydrogen desorption E_d calculated from TD experiments (1.18 eV) almost coincides with the heat of adsorption (1.16–1.17 eV) determined earlier from adsorption isotherms of response of MIS sensor with Pd gas sensitive electrode suggesting the similarity of initial mechanisms of interaction of H_2 molecule with both real and atomically clean film surface formed *in situ* under UHV conditions [22]. This is an additional argument for comparison of results obtained in the present work in both series of experiments.

4.2. Computer modeling of response of MIS structures

To model the response of MIS structures under investigation, consider the interaction of the molecules of gas environment with a film of catalytically active metal, in the framework of kinetic chemical approach. A set of kinetic equations which describe the dissociative adsorption of molecules, chemical surface reactions between products of dissociation, diffusion of some types of atomic particles through the film, and their trapping/de-trapping at the metal-dielectric interface, have been solved numerically [12, 13, 19, 22]:

$$\begin{aligned} \frac{dn_e^{(m)}}{dt} &= c_m P_\mu(t) (N_e - \sum_m n_e \nu_m)^\nu - d_m n_e^2 - R(n_e^{(1)}, n_e^{(2)}, n_e^{(3)}, \dots) - \frac{dn_i^{(m)}}{dt} \\ \frac{dn_b^{(m)}}{dt} &= K_{mf} n_e^{(m)} (N_b - n_b) + K_{mb} n_b^{(m)} (N_e - \sum_m n_e \nu_m) \quad (1) \\ \frac{dn_i^{(m)}}{dt} &= K_{mf} n_b^{(m)} (N_i - \sum_m n_i \nu_m) + K_{mb} n_i^{(m)} (N_e - \sum_m n_e \nu_m) \end{aligned}$$

These equations describe the change of the surface concentration of atoms of m -th sort ($n^{(m)}$) adsorbed on external (subscript “e”) and internal (subscript

“i”) surfaces of the active layer and in its bulk (subscript “b”), respectively. Here, $P_\mu(t)$ is the partial pressure of μ -th gas (e.g., H_2 , O_2) which is analyzed. It is assumed that it consists of molecules of ν atoms. During dissociation the molecule detaches from the m -th atom ($m = H, O$). N_e and N_i are the numbers of available centers of adsorption per unit area on both surfaces; ν_m is the number of adsorption centers blocked by one adsorbed atom of given type. N_b and $n_b^{(m)}$ are the surface concentrations of the bulk centers of absorption and the atoms trapped by them, recalculated per unit area, respectively. The factors K_{mf} and K_{mb} describe the forward and backward transfer of atoms through the film.

For the gas mixture (H_2+O_2) only hydrogen atoms have an opportunity to reach the metal-dielectric interface, and just they are responsible for the signal registered by MIS structure. In the absence of oxygen, the following chemical reactions take place here [1, 2, 13, 14, 19, 21, 22]: (i) adsorption (determined by the rate constant c_1), (ii) desorption (rate coefficient d_1) and migration in the film bulk to the interface between metal layer and dielectric substrate and in the opposite direction:



The function $R(n_e^{(1)}, n_e^{(2)}, n_e^{(3)}, \dots)$ describes chemical reactions (for example $H + O \rightarrow OH$, $OH + H \rightarrow H_2O$) between the products of dissociation of different molecules on the external surface. Theoretically calculated response of MIS structure to a rectangular pulse of hydrogen with pressure $P_{H_2}(t)$ followed by a pulse of oxygen $P_{O_2}(t)$ is presented in Fig. 5.

One can see that in the case when the following oxygen pulse was not supplied, the termination of H_2 pulse results in very slow sensor recovery to the initial state (“reset”). This process is limited by the $(H+H)$ associative desorption. On the contrary, the time of reset (t_{Reset}) significantly decreases due to the chemical reactions between H , OH , and O which results in formation of quickly desorbing compounds. Numerical analysis of the shape of response pulse allows us to obtain the value of coefficients c_1 and d_1 for hydrogen, which are related to microscopic parameters of the adsorption centers [12,19]:

$$c_1 = A \exp(-E_a/k_B T), \quad A = (2\pi m k_B T)^{-1/2}, \quad (3a)$$

where E_a is the activation barrier for dissociative adsorption, $d_1 = B \exp(-(E_a + Q_a)/k_B T)$, Q_a being the adsorption heat of appropriate molecule.

The important parameter of this process is the characteristic pressure $P_{H_2}^*$ [12,19] that determines the maximum sensor sensitivity to hydrogen. It is expressed through the adsorption heat Q_a as follows:

$$P_{H_2}^* = (c_1/d_1)^{-1} = C \exp(-Q_a/k_B T), \quad C = (\pi Q_a k_B T)^{1/2} / L_w s_0. \quad (3b)$$

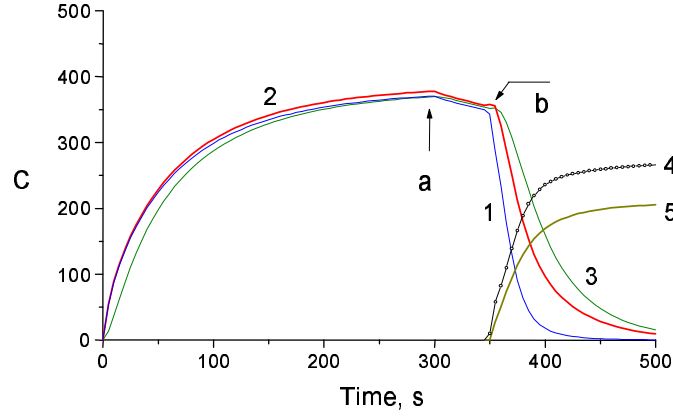


Figure 5. Theoretical dependence for the surface concentrations C (arb. units) of atoms or molecules adsorbed on the external (H_e , O_e , OH_e) and internal (H_i) surface of sensitive layer, respectively under consecutive action of rectangular pulses of hydrogen and oxygen. 1 — H_e ; 3 — H_i ; 4 — O_e ; 5 — OH_e ; 2 — Hydrogen dissolved in the bulk of the layer; a) the end of the hydrogen pulse b) the beginning of the oxygen pulse.

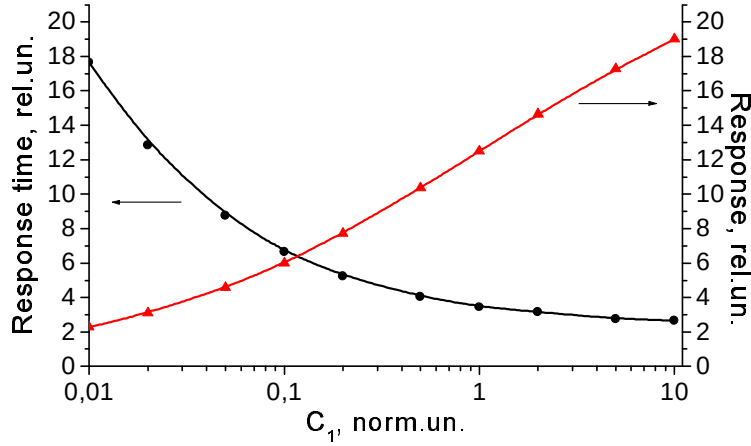


Figure 6. Calculated response time and maximum response value against the dissociation rate constant c_1 .

Here L_w and s_0 are the geometrical width of the potential well and the dissociation cross-section, respectively. The relation of these factors to macroscopic parameters of response (characteristic times of response and reset and response amplitude) is shown in Fig. 6.

Performed calculations allowed us to describe the kinetics of MIS response

and to find out some dependences of the macroscopic pulse parameters (t_{Reset} , V_{max} , t_{Resp}) upon microscopic parameters of the adsorption centers. Comparison of experimental results (Tables 1 and 2) shows that the presence of copper

(i) does not prevent H adsorption on Pd atoms and even stimulates it (increase of c_1);

(ii) reduces the probability of associative desorption of atomic hydrogen. As was mentioned above, this process seems to be effective only via Pd...Pd pairs of neighboring surface Pd atoms. This process is forbidden by Cu...Cu pairs formation, and the information about desorption via Cu...Pd pairs located on the surface is missing. Besides, sufficient part of atomic hydrogen is trapped on Cu and cannot migrate to the centers of desorption. Due to the delay in desorption, prevailing transfer of atomic hydrogen into the bulk of the film occurs, and the balance in Eq. (2) is shifted to the right. Therefore, an increase in the MIS sensor signal is observed.

This point is in a good agreement with TD data (Table 2). It is also interesting that the time of reset after oxygen supply becomes very small for freshly prepared Cu/Pd layers (Fig. 2, curve 1). It should be reminded in the case of Cu_mPd_n/W system that AES data indicate intensive mutual reactions between oxygen and hydrogen. Hence, one can suppose more intensive reactions between hydrogen and oxygen (or OH-groups) on copper-doped surface in real environment also (Fig. 5). The latter is possible, for example, due to spillover of both hydrogen and oxygen toward Cu parts of the surface with subsequent reaction and H_2O production as was mentioned above.

4.3. Molecular dynamics (MD) analysis of dissociative adsorption on Cu_xPd surface

To reveal the differences in the mechanisms of adsorption on Pd and PdCu surface, computer modelling of the considered processes was undertaken by molecular mechanics approach (simplified variant) [9].

In this case the adsorption centers were treated as atomic force centers acting on the atoms belonging to the approaching molecule. All interactions were described within the framework of classical mechanics. The general outline of the process is presented in Fig. 7.

For a two-nuclear hydrogen molecule which is adsorbed on some part of the surface with N force centers of several kinds, the Hamiltonian can be written as follows:

$$H(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_1, \mathbf{r}_2) = \sum_i p_i^2/2m + \sum_i \sum_k U_{ik}(\mathbf{r}_i, \mathbf{R}_k, \Theta_k) + V_m(|\mathbf{r}_1, \mathbf{r}_2|), \quad (4)$$

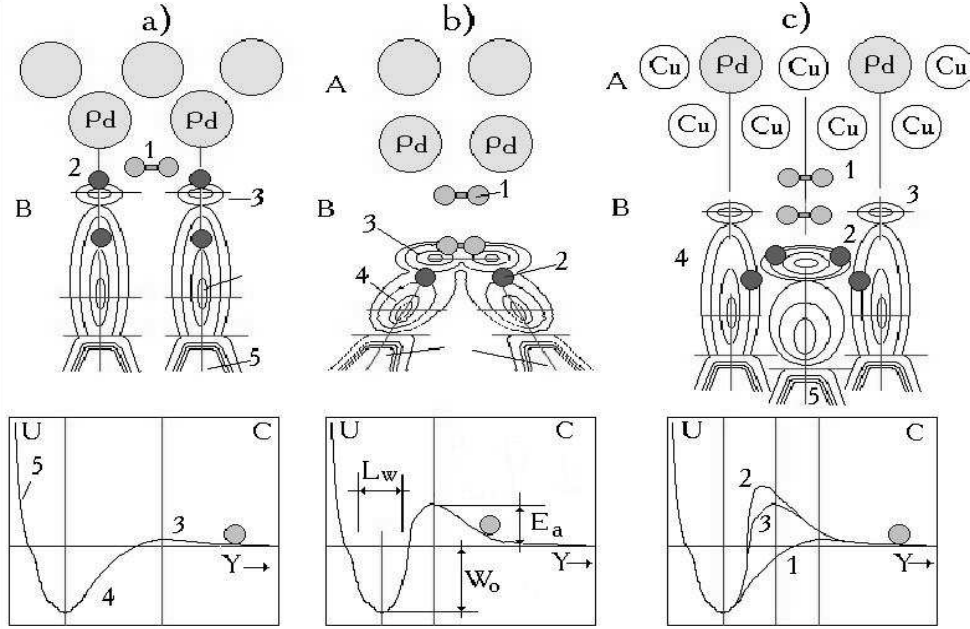


Figure 7. Interaction of hydrogen molecules with different types of surface, according to MD simulations. Upper part of the sketch: different types of Pd and Cu₃Pd surface. Middle part of the sketch: respective two-dimensional potential energy map for each type of atomic-force center and positions of moving atoms in consecutive moments of time according to simulations. Lower part of the sketch: one-dimensional potential energy curve for each type of atomic-force center along the normal to the surface. Left – pure Pd with normal orientation of d-orbitals. Middle – Pd with tilted orientation of d-orbitals. Right — PdCu₃ alloy with normal orientations of d-orbitals.

where $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{r}_1$, $\mathbf{r}_2$ are the momenta and radius-vectors of atoms in the molecule, and $V_m(|\mathbf{r}_1, \mathbf{r}_2|)$ is the potential energy of the interatomic interaction in the molecule.

To describe this potential energy we have applied the known expression for the two-particle Morse potential (more general Rappe's approximations are under consideration):

$$V_m(r) = D_0 \exp(-(r - r_0)/L_D) [\exp(-(r - r_0)/L_D) - 2] \quad (5)$$

where D_0 is the molecule dissociation energy, r_0 is the equilibrium interatomic distance, L_D is the effective width of appropriate potential well which is defined by the oscillation frequency $\omega_m = (1/L_D)(2D_0/m)^{1/2}$ and determines the maximum amplitude (without dissociation) of oscillations. $U_{ik}(\mathbf{r}_i, \mathbf{R}_k, \Theta_k)$ describes

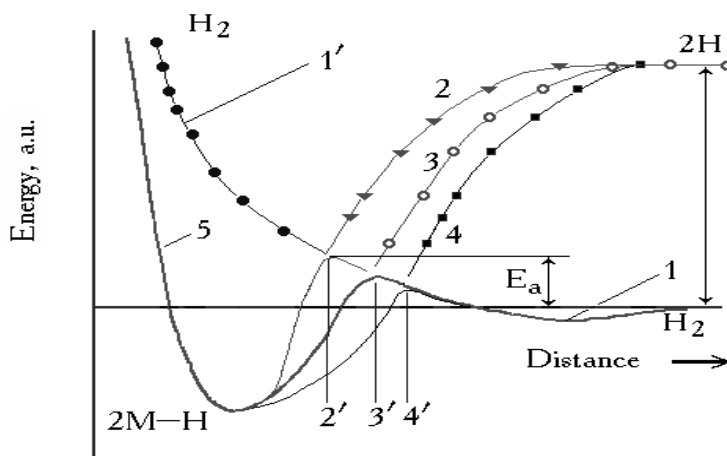


Figure 8. One-dimensional diagram for the interaction potential energy between H_2 molecule and a pair of adsorption centers on the surface. 1–1' is the repulsive potential curve for H_2 molecule; 1 is the pre-chemisorption state; 2, 3, 4 are different potential curves corresponding to attracting forces between atomic H and different types of adsorption centers. The cross-over between 1–1' and 2, 3, and 4 gives the position and the height of potential barriers denoted as 2', 3', and 4', respectively. 5 is the repulsive part of the potential curve for atomic hydrogen.

the interaction between i -th atom ($i = 1, 2$) in the molecule and k -th surface force center ($k = 1 \dots, N$), located at point $\mathbf{R}_k$.

According to the one-dimensional potential diagram (Fig. 8), this function describes the presence of a potential well with the depth corresponding to the adsorption heat. It also depends on the orientation of d -orbitals of surface atoms (for transition elements) belonging to the center (Θ_k is the respective angle relative to the normal).

For the function $U_{ik}(\mathbf{r}_i, \mathbf{R}_k, \Theta_k)$ we used an analytical approximation in the case of dissociative adsorption which gives the anisotropic potential well with the depth W_0 and the barrier A_0 shown in Fig. 9. The cross-section of this potential surface along the bond direction corresponds to the curve 1 in Fig. 10 [7]. The appropriate equations of motion were solved by a modified Verlet method [24,25].

This approach provided the energy conservation to within $\sim 1\%$. The initial code was written in the Visual C++ programming language and realized on the personal computer running under Windows operation system. During simulations, Pd atoms were modelled by anisotropic, elongated and oriented potential

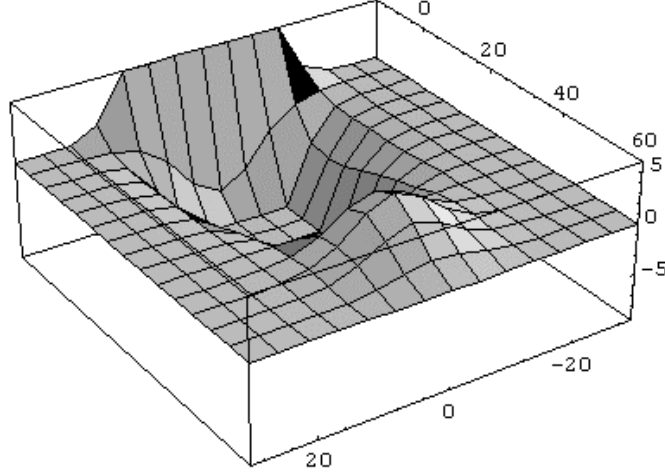


Figure 9. Three-dimensional view of the potential energy surface for the interaction between H (in a molecule) and Pd (in an adsorption center) used in the MD simulations.

wells with the barrier height depending on the orientation angle. Copper atoms were modelled by isotropic potential wells with higher barriers for adsorption of fixed value.

Calculations of the atomic trajectories in the molecule approaching a group of force centers showed that when Cu atoms are located between Pd atoms, the potential field configuration created by the Cu atom barrier favors the stretching of H_2 molecule and facilitates its dissociation [9] (Fig. 6). Desorption of a molecule is therefore blocked due to the specific surface potential relief. As a result, the residence time of atomic hydrogen on the surface increases. Thus, the balance in the surface reactions is shifted towards H transfer to the bulk of the film. This mechanism allows to explain the effects observed in the present work.

4.4. *Ab initio* calculation of the $Cu_{1-x}Pd_x$ state density

To clarify the mutual influence of electronic subsystems of Pd and Cu which determines the catalytic properties of surface coatings based on these alloys, the Pd-Cu system was studied.

Ab-initio calculations were carried out using the linear muffin-tin orbital (LMTO) method in the framework of coherent potential approximation (CPA). The program BGFM was used. This code was chosen as a fast scheme for direct calculation of the electronic structure of atomic system. With self-consistently

obtained bands, the program calculates the total energies and the density of states (DOS) of the system. The uncertainty in the absolute values of energy gaps was reduced by the use of a special extended k -point basis. For the total energy calculations, the convergence criterion was chosen at 0.001 mRy.

The following results were obtained.

A considerable influence of Pd component on Cu component is observed in Pd-Cu solid solution. Transformations of electronic states significantly depend on the component percentage in the system. The Cu content of 50% and Pd 50% determine the boundary for transformation of the electronic states in this system. For Cu content less than 50%, the total DOS (DOS_{tot}) are close to DOS_{tot} of pure Pd. At larger Cu content the DOS_{tot} are almost the same as DOS_{tot} for pure Cu.

For the Cu content in the range of 0–50%, the partial DOS (DOS_{part}) for s -states of Cu decreases (comparing to corresponding DOS_{part} of pure Cu) with the increase of Cu content. DOS_{part} for Pd do not changed. We observed only a small decrease of DOS_{part} for d -states of Pd. At the same time, DOS_{part} for p -states of Cu significantly increase, comparing to corresponding states of pure Cu. A small increase of the density of promoted f -states for Cu is also observed.

For Cu contents more than 50%, DOS_{part} of Cu return to their values inherent to pure Cu. We observed the changes in the DOS_{part} structure for p -states of Pd in spite of the unchanged number of these states for all relations between the components in this region.

The results lead to a conclusion that for $x > 0.5$ a reconstruction of electronic states of Cu leads to formation of new intermetallic bonds in Pd_xCu_{1-x} systems. Analysis of the DOS_{part} shows that p -electrons of Cu are responsible mainly for chemical binding in new phases. For $x < 0.5$ the role of Pd in formation of new phases increases in spite of its decreasing content.

Our results enable to predict the participation of different electronic states of Pd and Cu in the formation of catalytic and sensor centers in the Pd_xCu_{1-x} system in a wide range of x . The substitution of one transition metal by another strongly influences the crystal lattice structural stability. Therefore, by changing x we change not only the electronic structure of the system but simultaneously create new atomic configurations in surface layers, which also influence the efficiency of surface reactions.

Some predictions about catalytic activity may be also deduced. Indeed, the results of DOS calculations have shown that the total DOS spectrum of pure palladium contains four well-resolved peaks located at $E = -0.362, -0.203, -0.116$ and -0.014 Ry, respectively (Fig. 1 a). Further step-by-step copper introduction into palladium up to 50% results only in the broadening of the peaks and

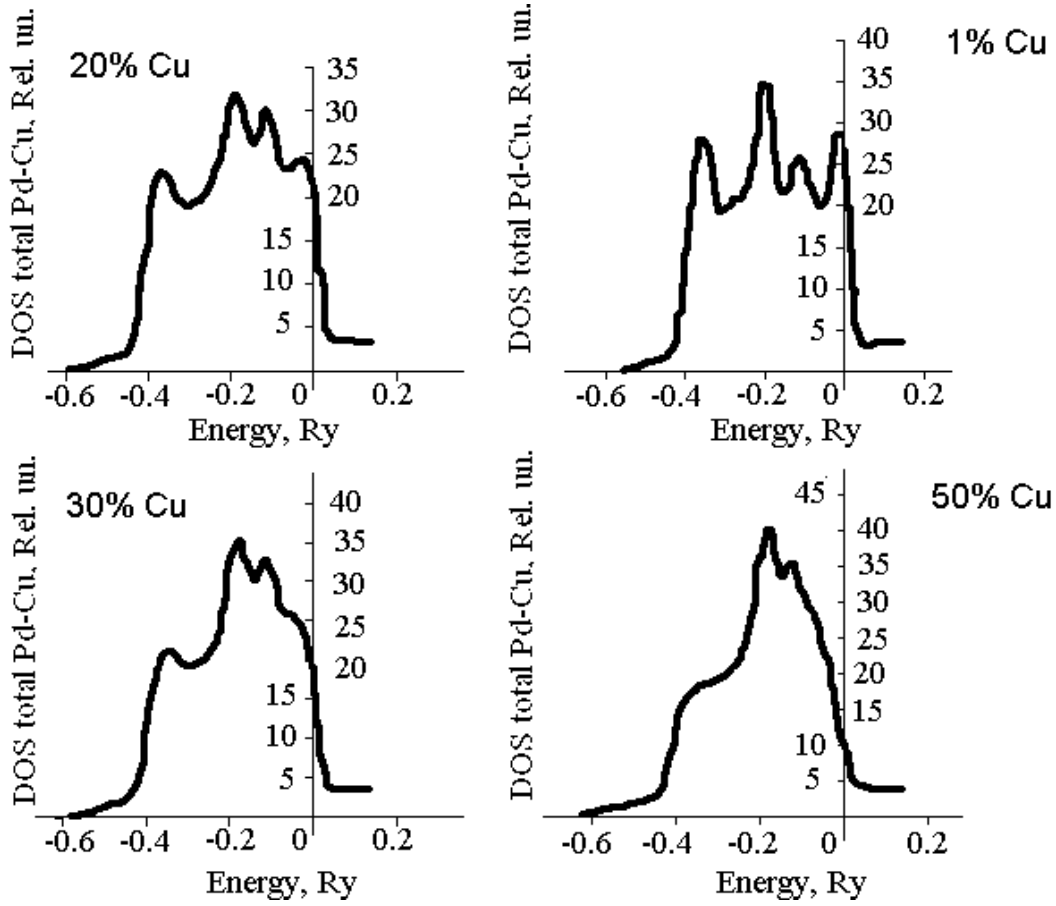


Figure 10. Calculated total density of states for $\text{Cu}_x\text{Pd}_{1-x}$: (a) 1% Cu, (b) 20% Cu, (c) 30% Cu, (d) 50% Cu.

on the whole in smoothing of the spectrum which remains qualitatively similar to the initial one (Fig. 10 b–d). On the other hand, partial DOS for d -orbitals of Pd, which are the most important orbitals in adsorption and catalytic processes, proved to be weakly disturbed (Fig. 11 a–d). It should be noted that addition of copper increases the DOS in the energy range near -0.2 Ry which may be important for the interaction between the electronic subsystems of adsorbing molecule and the substrate, as well as for more intensive dissociation. According to this calculation, copper addition to Pd does not suppress the catalytic activity of the alloy.

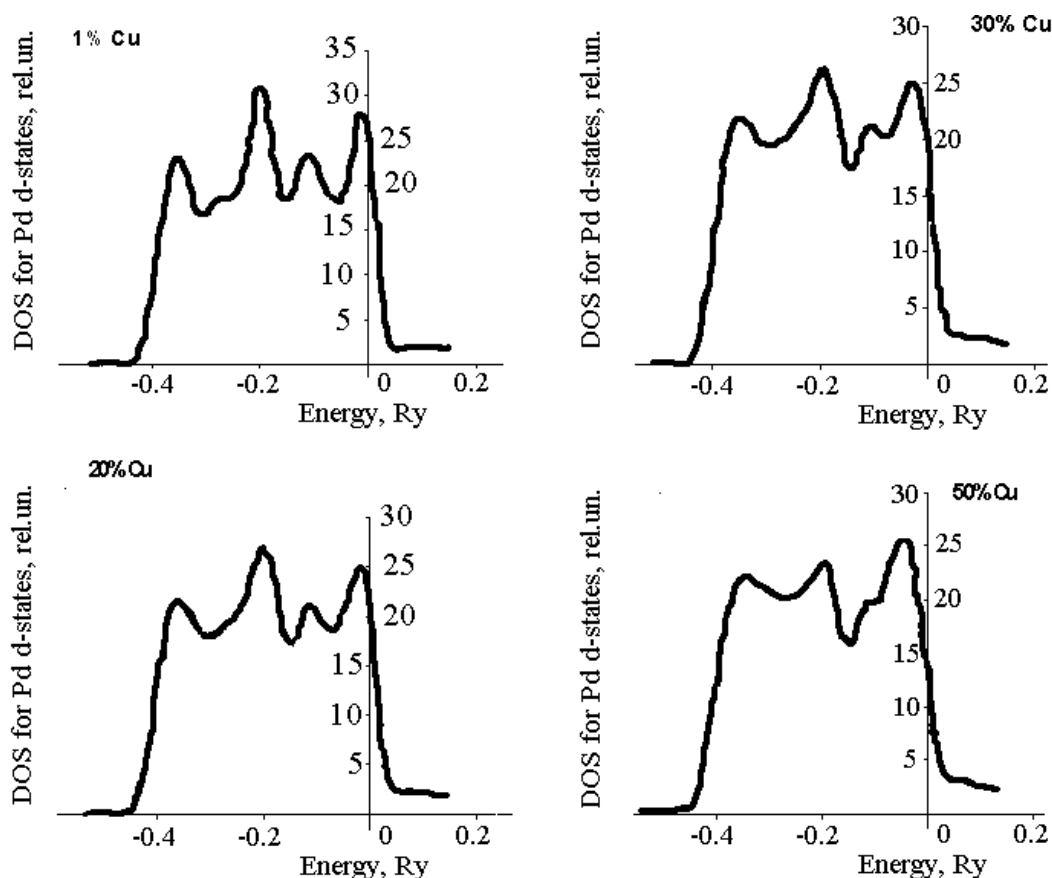


Figure 11. Calculated partial density of states for d-orbitals of palladium in $\text{Cu}_x\text{Pd}_{1-x}$: (a) 1% Cu, (b) 20% Cu, (c) 30% Cu, (d) 50% Cu.

5. Conclusions

The results obtained on Pd and Cu/Pd layers in two different series (TD spectra measurements under UHV and real ambient gas detection) of the experiments proved to be in good agreement.

The analysis of hydrogen TD on Pd_n/W and $\text{Cu}_m\text{Pd}_n/\text{W}$ structures allow us to reveal three types of adsorption: (1) surface chemisorption, (2) interface adsorption between the layer and the substrate, (3) absorption in the bulk of the film. The second and third types of sorption are responsible for gas sensitivity in MIS gas sensors.

Certain energetic parameters of adsorption centers for Pd (Cu/Pd) thin films were determined both from TD spectra and MIS sensor response isotherms. In

the latter case the parameter corresponds to Pd/dielectric interface adsorption. The adsorption heat per H atom in all cases correlates with the Pd-H (1.17 ± 0.01 eV) bond energy.

Structures containing palladium layer doped with Cu demonstrate significant decrease of the first component of adsorption suggesting an substantial reduction of the number of catalytically active surface centers. Therefore, it should increase the sensor response time. However, this is not observed due to the spillover effect, namely, surface transfer of atomic hydrogen from Pd to neighboring copper atoms and emptying of Pd related adsorption centers.

At the same time, a substantial increase in the amount of atomic hydrogen dissolved in the bulk of Pd films with Cu-modified surface takes place. This is qualitatively in agreement with the predicted changes and the results of experiments on MIS structures. Namely, the increase in the sensitivity of MIS structures with Cu/Pd electrodes to hydrogen is also observed. These facts may be explained by the reduction of the desorption rate constant of H_2 due to the hydrogen atoms trapping not only on Pd atoms, but due to the spillover effect on Cu atoms also. As a result, a great deal of atomic hydrogen trapped by copper cannot desorb associatively and is transferred to the bulk of the film.

A greater stability of composite Cu/Pd films to aging in oxygen atmosphere may be explained by selective interaction of oxygen probably with CuH complexes, that prevents poisoning of catalytically active centers associated with Pd. The local adsorption centers are thus protected against the action of oxygen. It is found that in the presence of oxygen the process of transfer of atomic hydrogen from the surface to the bulk of film is enhanced even more. In this case oxygen as well as copper will play the role of an “atomic pump” for hydrogen. This effect is important for the increase of efficiency of gas detection with MIS sensors.

Thus, in the present work it is shown that the surface reorganization caused by formation of a surface Cu_xPd composite (alloy) may be used to enhance the Pd surface catalytic activity with respect to dissociative adsorption with the subsequent dissolution of atomic hydrogen in the bulk. Microscopic parameters of adsorption centers are found to be identical for the films obtained with different techniques (ultra-thin layers and the surface of a metal film in MIS structures).

The mechanisms of enhanced hydrogen dissociation on Pd/Cu composite surface was analyzed by computer simulation in the framework of chemical kinetic approach. The method of molecular dynamics taking into account the stereochemical features of the interaction of absorption centers with the molecules of the gas environment, and *ab initio* calculations of the electronic structure of the Cu_xPd cluster were also used.

Acknowledgements

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