Catalysis of redox reactions is an important goal in photochemistry and photocatalysis because even small overvoltages diminish the efficiency of such systems immensely. Deposition of different metals (e.g., Pt, Ag, Pd) has often been employed to enhance the activity of semiconductor photocatalysts. Thus, the modification of semiconductor particles with the noble metals acting as a sink of photoinduced charge carriers and promoting interfacial charge-transfer processes, appears to be an essential factor for maximizing the efficiency of photocatalytic water splitting reactions as well as the processes of the photoinduced degradation of toxic organics. The deposition of metal particles possessing electrocatalytic activity also permits to realize photosynthetic reaction which are hardly feasible with the use of naked semiconductor photocatalyst. The enhancement of the performance of the photoelectrochemical cells as the result of modification of the photoelectrode surface with metal islets results not only from the mere elevation of electrocatalytic activity of the electrode surface but also from the suppression of the recombination due to changes in the structure of electronic states in a forbidden zone of the semiconductor produced by strongly adsorbing ad-atoms and metal clusters.

Notwithstanding to the fact that the modification of semiconductors with metal particles is widely used to improve the performance of different photocatalytic, photoelectrochemical and electrochemical systems, the interaction between metal nanoparticles and semiconductor support as well as an exact mechanism of operation of metal-loaded catalysts is not yet clearly understood. Thus, for example, still controversial remain: the exact role of electroactive (interfacial) states and Schottky barriers at the semiconductor/metal nanocontacts; the origin of the size dependence of catalytic activity of metal particles; the effect of the deposition conditions on the modifying activity of metal nanoparticles. To clarify these issues, the investigations rewired in this paper were carried out using well-identified thin-film oxide electrodes (mainly TiO$_2$ as a model photoelectrode material) modified with metal nanoparticles which were applied onto the semiconductor surface by different deposition techniques.
1. CHARACTERISTIC FEATURES OF OXIDE SEMICONDUCTORS AS THE ELECTRODE MATERIAL

The donor centers in the wide-bandgap heavily doped oxide semiconductors, such as amorphous and polycrystalline titanium dioxide, exhibit strong tendency to form associates. Depending on the semiconductor pre-history and doping level, the donor associates may have different sizes (from few nanometers to tens micrometers, representing, in the latter case, the microphase inclusions such as Magnéli phases or \( \text{Ti}_2\text{O}_3 \)). At sufficiently high concentrations of donor associates, they can overlap forming the percolation cluster which may act as an additional channels ensuring charge transfer through the semiconductor bulk to the electrode surface with the much higher efficiency as compared with the charge transfer via the semiconductor bands [1–3]. Such percolation clusters, exhibiting the properties of degenerated semiconductor or even metal, are characterized by hopping or metal-like conductivity and do not form Schottky barriers both at grain boundaries and in contact with electrolyte. On the other hand, when the donor clusters are sufficiently large to be considered as the microphase inclusions, it is inconceivable that the potential barriers may appear at the interfaces between the donor clusters and semiconductor matrix in which they are formed. In this case, the charge flows through the semiconductor bands and through the percolation cluster are to be completely independent. The donor clusters at the surface of semiconductor oxide electrode can be observed directly employing specially developed versions of photoelectrochemical microscopy (by measuring a local cathodic current at negative biases [4–5] or detecting the higher harmonics of the electrode ac-photoresponse to the periodic laser pulses which have been shown to be directly proportional to the donor density [6, 8]).

In terms of energetic diagram, the segregation of donor centers inherent in the heavily doped oxides can be described by the fluctuations of the energetic levels resulting in the formation of the potential relief at the electrode surface. In case of amorphous, amorphous-crystalline and polycrystalline \( \text{Ti}_2\text{O}_3 \) prepared by hydrolysis of titanium alcoxides these fluctuations appears to be large enough to make it possible almost unimpeded charge transfer in the heterojunctions «oxide-oxide» (\( \text{WO}_3/\text{TiO}_2, \text{Bi}_2\text{O}_3-\text{TiO}_2, \text{etc.} \)) [9, 10].

The formation of percolation cluster as the result of segregation of donor centers plays a valuable role in the formation of the dark anodic behaviour of thin-film \( \text{TiO}_2, \text{WO}_3, \text{Bi}_2\text{O}_3 \) electrodes [1–3]. In particular, the anodic current at the positively-biased highly-doped electrodes can be attributed to the electron transfer along percolation cluster rather then to the tunneling through the space charge region. This conclusion is confirmed by numerous experimental facts, including much higher values of anodic current than the calculated tunnel current, the characteristic shape of \( i, E \)-curves, and much higher sensitivity of dark current on the electrolyte composition than one would expect [3].
2. EFFECT OF DEPOSITION TECHNIQUE ON THE MORPHOLOGY OF METAL NANOPHASE GROWN ON THE SEMICONDUCTOR SURFACE

2.1. Contact deposition

The immersion of chemically-active semiconductors, such as silicon, germanium, Al_{III}B_{V} compounds in the solution containing the ions of metals (Au, Ag, Hg, Cu, etc.) which have more positive electrochemical potential than that of a semiconductor, leads to the formation of metal islets on the semiconductor surface. In this case, the surface concentration of deposited metal particles as well as the dispersity of growing nano- (micro-) phase appear to be dependent on numerous factors such as the concentration of metal ions in the solution, the deposition time, the porosity of the passive layer at the surface of the semiconductor, as well as the chemical properties of a metal and a semiconductor in use. On the other hand, one can also observe less evident phenomenon consisting in a spontaneous deposition of metal nanoparticles under the treatment of chemically inert semiconductors (such as titanium dioxide) with the metal ion-containing solution in the absence of the external bias, illumination, and reducing agents. During the contact deposition, the metal particles are formed as the result of interaction of metal ions with donor defects or donor associates in the semiconductor. In principle, this process may proceed both through the direct chemical reaction of donor centers with metal ions and via so-called electrochemical mec-

\[ a \]

\[ b \]

\[ c \]

\[ d \]

*Fig. 1. Size distribution of Ag particles grown on thin TiO_2 film. The particles were deposited by treating TiO_2 electrode with 0.001 M Ag_2SO_4.*
hahism involving a spatial separation of the reactions of oxidation of donor centers and growing of metal particles. With titanium dioxide and, probably, with many other oxide semiconductors, the electrochemical mechanism of spontaneous deposition of metal nanophase seems to be more credible than a pure chemical one. This is evidenced by the fact that the resulted metal particles have relatively large sizes and are positioned at the intervals much more (16–40 times) than the particle diameter [1,3]. Thus, during immersion of TiO$_2$ electrode, characterized by the concentration of ionized donors ($N_d$) of $10^{19}$ cm$^{-3}$, into $10^{-5}$–$10^{-3}$ M Ag$^+$-containing aqueous solutions, the average size of Ag nuclei increases from 0.8–0.9 to 9–10 nm as the time during which the electrode is immersed into solution increase from 1 to 10 min. Under the same conditions, the average size of Ag particles in the case of TiO$_2$ electrode with $N_d = 10^{18}$ cm$^{-3}$ rises from 0.7 to 3.2 nm (Fig. 1). Under more prolonged exposure of TiO$_2$ electrodes to the Ag$^+$-containing solutions, the size of the particles as well as their surface concentration rise moderately. It is characteristic that, in both cases, only a small portion of the electrode surface appears to be covered with silver (no more than 2–6 % in the case of TiO$_2$ electrode with $N_d = 10^{19}$ cm$^{-3}$).

The amount of deposited silver (in atoms/cm$^2$) on the surface of TiO$_2$ electrode can be readily determined by measuring the current passing during anodic oxidation of Ag particles at a linear potential sweep. At rather high concentrations of donor centers in the initial titanium dioxide ($N_d \sim 10^{19}$ cm$^{-3}$), a detectable background current is observed on the potentiodynamic $i$, $E$-curves obtained with these electrodes in indifferent electrolytes in the absence of redox additives, this current being attributed to the oxidation of donor centers in a semiconductor. After the treatment of the electrode with the Ag$^+$ ions, the background current dies out almost completely and, in its instead, the well-pronounced peak corresponding to the anodic oxidation of Ag particles appears (Fig. 2). The diminishing of the background current is associated with the consumption of donors in the reaction with Ag$^+$ ions as well as with the re-distribution of the potential drop from the free (uncovered) TiO$_2$ surface to the surface of Ag particles. High chemical reactivity of metal nanophase and a large surface-to-volume ratio for the deposited nanoparticles hinder the passivation processes, and a complete oxidation of Ag particles with the average size of 1–3 nm occurs at pH 5–7 even in the absence of depassivators. It should be noted that, when employing conventional potentiostatic setup for the determination of the surface concentration of Ag particles, the sensitivity of this method is no worse than 10$^{13}$ atoms/cm$^2$, i.e. about 0.01 of monolayer coating. Taking into account that the average size of Ag particles deposited by this technique lies in the range from 1 to 10 nm, one can estimate from the peak of anodic current on the potentiodynamic $i$, $E$-curves that the surface concentration of nanoparticles to be of $10^9$–$10^{12}$ cm$^{-2}$. It should be borne in mind that, when the average size of Ag particles exceeds 4–5 nm, the above method becomes less accurate because of the appearance of the passivation processes. The effect of these processes can be diminished by the introduction of depassivating additives (halide, rhodanate, and sulfide ions) into electrolyte (Fig. 2) provided that particular precautions (very careful removal of dissolved oxygen, etc.) are taken in order to prevent the loss of the chemically unstable smallest-sized fraction.
Using this approach, we have examined [11] the properties and concentration of electroactive (i.e., which are able to take part in the electrode processes) Pd nanoparticles formed by different methods: (i) combined pyrolysis of palladium chloride and titanium resinate (RTi) on air at 450 °C (1 h) and then annealed in hydrogen at 500 °C and 800 °C for 1 h, by vacuum deposition of Pd and by adsorption of Pd\(^{2+}\) ions on TiO\(_2\) film obtained by pyrolysis of titanium resinate.

**Table 1**

<table>
<thead>
<tr>
<th>Method of preparation of TiO(_2)-Pd film</th>
<th>500 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d, \text{ nm})</td>
<td>(d_a, \text{ nm})</td>
</tr>
<tr>
<td>Combined pyrolysis of PdCl(_2) and RTi</td>
<td>2–6</td>
<td>4.5</td>
</tr>
<tr>
<td>Vacuum deposition of Pd</td>
<td>2–20</td>
<td>9</td>
</tr>
<tr>
<td>Adsorption of Pd(^{2+}) ions on TiO(_2) film</td>
<td>2–120</td>
<td>17</td>
</tr>
</tbody>
</table>

Fig. 2. Potentiodynamic current-potential curves of oxidation of silver particles deposited on thin-film TiO\(_2\) electrode. The curves have been obtained in deaerated 0.1 M KCSN + 0.5 M K\(_2\)SO\(_4\) solution (curve 1), 0.1 M K\(_4\)Fe(CN)\(_6\) + 0.5 M K\(_2\)SO\(_4\) (curve 2), 0.5 M KOH (curve 3), and 0.5 M K\(_2\)SO\(_4\) (curve 4). The potential sweep rate is 40 mV/s.
chloride and titanium resinate (that is easily melting salts of resin acids – colophony derivatives), (ii) vacuum deposition of Pd on the TiO$_2$ surface, and (iii) adsorption of Pd$^{2+}$ ions at the TiO$_2$ surface (Fig. 3). In the course of this investigation it was shown that combined thermodecomposition of titanium resinate and PdCl$_2$, which brought about a concurrent formation of titania phase and Pd nanoparticles incorporated into it, permits to obtain smaller-sized and more monodisperse Pd particles in comparison with those produced by other methods (Table 1).

### 2.2. Galvanic deposition

In principle, the electrochemical deposition of metal particles on the surface of the semiconductor electrode is governed by the following factors: (i) the difference between the redox potential of Me/Me$^{n+}$ couple and the flatband potential of the semiconductor; (ii) the difference in work functions of the deposited metal and semiconductor substrate (that affects mainly the nucleation behaviour); (iii) the concentration and the nature of electroactive surface states.
Our investigations on the electrochemical behavior of thin-film titanium dioxide electrodes have shown that, with cathodically biased TiO₂ electrodes being in a contact with the solutions containing such metal ions as Ag, Pt, Pd, even a slight negative shift of the electrode potential from its stationary value causes the growth of metal nanoparticles. During this process, the growth of the particles already existing at the electrode surface predominantly occurs currently available particles take place, and the appearance of fresh species can be stimulated by the increase of the applied bias. At the deposition of Ag, Cu, Pd, Pt on the TiO₂ electrodes under the potentiostatic conditions, the increase of cathodic current with time is observed, the current-time dependencies being often linear in a wide range of potentials and currents. This linearity results from the combination of two factors: (i) the decay of nucleation efficiency with time and (ii) the diffusion-limited growth of the existing nuclei [1,12]. The TEM investigations has evidenced that the time dependence of the nucleation rate, \( \nu(\tau) \), can be approximated by the following relation (Fig. 4):

\[
\nu(\tau) = \frac{dN(\tau)}{d\tau} = \alpha \tau^{-1/2}; \quad \alpha = \text{const}
\]

Taking into account that under the diffusion control the current at a single hemispherical metal particle is governed by

\[
i = c \rho^{1/2} D^{3/2} \tau^{1/2} = k \tau^{1/2}; \quad k, c = \text{const}
\]

(where \( D \) is the diffusion coefficient, \( \tau \) is a time elapsing from the moment of appearance of metal nucleus, \( \rho \) is the density of metal phase, \( k \) and \( c \) are the constants), after \( t \) minutes, the current, \( I \), measured at an array of the growing silver microelectrodes on the semiconductor surface amounts:

\[
I = k \int_{\delta=0}^{t} \nu(\tau)(t-\tau)^{-1/2} d\tau = k \alpha \tau^{-1/2} \left[ \tau^{-1/2} d\tau - \frac{1}{2t} \int_{\delta=0}^{t} \tau^{1/2} d\tau \right] = \frac{5}{3} kat.
\]

Such current-time dependencies determine the peculiar type of potentiodynamic polarization \( i,E \)-curves, the characteristic feature of which is that the currents at the reverse potential sweep are essentially higher than those observed at the direct sweep, the effect of the potential sweep rate on the cathodic current being unusually strong (Fig. 4). Obviously, it is impossible to obtain the stationary potentiostatic \( i,E \)-curves because a progressive linear increase of cathodic current with time is observed the metal deposition onset potential is reached and the quasi-stationary current could be attained only after the complete covering of semiconductor surface with a metal layer. Characteristic of this process is practically unimpeded electron exchange between the metal particles growing under cathodic bias and the semiconductor c-band as evidenced by very small value of cathodic overvoltage (approximately the same as for the metal electrodes). This is not an ordinary fact because the process of metal deposition occurs at the electrode potentials \( 0.43 - 0.20 \) V, which are substantially higher than the flatband potential of TiO₂ \( -0.4 \) - \( -0.6 \) V; therefore, the deposition of metals proceeds under conditions where rather high \( 0.6 - 0.8 \) V Schottky barrier arises at the TiO₂/electrolyte.
Fig. 4. Cathodic deposition of silver particles onto titanium-dioxide electrodes:
a) time dependence of the surface concentration of silver particles in the potentiostatic conditions at +0.4 V (vs. sat. Ag|AgCl); b) typical view of cyclic polarization curve obtained under cathodic deposition of silver; c) current-time dependences for rotating disk TiO₂ electrodes with \( N_d \approx 10^{19} \) cm⁻³ (curves 1, 3, 4) and \( 10^{18} \) cm⁻³ (curve 2); rotation speed was 900 (curve 1), 300 (curve 2, 3) and 180 rpm (curve 4); d) typical current vs. electrode potential sweep rate curve.
junction. The existence of a distinct Schottky barrier on the surface of TiO2 electrode free of the metal particles is confirmed by the impedance measurements (the linear Mott-Schottky plots [3]) and by the high photovoltage \( V_{oc} = 0.5 - 0.6 \) V

2.3. Photoinduced (photocatalytic) deposition

The photocatalytic deposition of metal from contacting solutions can be used for the removing of metal ions (especially, the toxic ones, such as Hg\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Cr\(^{3+}\)) and for the improving the activity of semiconductor photocatalysts and photoelectrodes [1,3,13]. The photoselective version of this process has been investigated for the potential application in the fabrication of microelectronic circuits and devices [2,3] and for the development of novel silver-halide and non-silver imaging systems [2,3,14,15]. A special case of the formation of metal nanophase under illumination is a direct photolysis of the semiconductor matrix that is inherent, e.g., for bismuth oxihalides [16–18].

The mechanism and kinetics of the process of nucleation of small metal particles on the semiconductor surface have been studied with the use of silver ion photoreduction on the titania surface as a model reaction [2,3]. In these researches the consideration has been given to the photogeneration of the electron-hole pairs in titanium dioxide with subsequent interaction of photogenerated holes with adsorbed water molecules, OH\(^-\) ions, or hole-accepting species and trapping of the electrons with the surface states followed by the reduction of Ag\(^+\) ions. In the presence of Ag\(^+\) ions, the charge exchange between Ag particles on the electrode surface and Ag\(^+\) ions in the solution appears to be very efficient so that the action of UV irradiation under the open circuit conditions causes only a slight negative shift of the electrode potential (Fig. 5).

This shift corresponds to the establishment of the equilibrium between two half-reactions involved in the photocatalytic process. The first half-reaction is the reduction of silver on the semiconductor surface (the cathodic partial process in which the majority charge carriers are involved), while the second one is the conjugated anodic partial process related to the generation and consumption of photoholes. Under illumination of the electrode, the parameters of the electronic surface states may exhibit a slight change; moreover, in the case of the lightly-doped semiconductors, the intense illumination may offer a substantial increase of the concentration of majority charge carriers. Hence some differences may exist between the kinetic characteristics of the dark reaction of metal ion reduction and the cathodic half-reaction involved in the overall photocatalytic process in spite of the participation of majority charge carriers in the both processes. Nevertheless, according to our experimental results [1,3], the effect of the illumination on the parameters of the cathodic half-reaction is actually insignificant in many cases including the reaction of the photocatalytic deposition of Cu and noble metals onto the surface of titanium dioxide and other wide-bandgap semiconductors. Taking this into account, the dark cathodic part of the net polarization curve can be reasonably used for simulation of the reductive half-reaction involved in the overall photocatalytic process.

The above features of the cathodic growth of metal particles on the surface of semiconductor TiO\(_2\) electrode surface are best consistent with the behavior of titanium dioxide characterized by the moderate concentrations of ionized donors \( N_d \approx 10^{18} \) cm\(^{-3}\). In this case, the electrochemical and photocatalytic behaviour of
the TiO$_2$ electrode modified by the metal nanoparticles can be simulated by the equivalent circuit consisting of two parallel-connected independent parts: a set of metal nanoelectrodes, on the one hand, and a semiconductor surface free of metal particles, on the other hand.

**Fig. 5.** Energy diagrams of TiO$_2$ in contact with the electrolyte containing Ag$^+$ ions under open circuit conditions in the dark (solid lines) and under illuminations (dashed line):

- **a** – moderately doped TiO$_2$ ($N_d \sim 10^{16} - 10^{18}$ cm$^{-3}$);
- **b** – heavily doped TiO$_2$ ($N_d \sim (1-5)\times10^{19}$ cm$^{-3}$);
- **c** – Time dependence of TiO$_2$ electrode potential under UV illumination in 0.2 M K$_2$SO$_4$: without additives (curves 2, 3), in presence of 0.05 M Ag$^+$ (curves 1, 4). Concentration of ionized donors in TiO$_2$ was $10^{19}$ cm$^{-3}$ (curves 1, 2) and $5 \times 10^{17}$ cm$^{-3}$ (curves 3, 4)
With substantially decreased doping of titanium dioxide (up to $N_d = 10^{16} - 10^{17}$ cm$^{-3}$), the deposited Ag particles offer the essentially less values of the exchange current in contact with the electrolyte contained Ag$^+$ ions as well as the less surface concentration of the metal nanophase (calculated in atoms/cm$^2$). As the result, the effect of metal nanoparticles is reduced mainly to the modification of the structure of existing electronic surface states rather than to the introduction of new ones that, in particular, enables high open-circuit photovoltage to be generated under UV illumination (Fig. 5). For such electrode, we should also introduce into the equivalent electric circuit an additional resistance or «diode» element that mimic the metal-semiconductor junction, as well as an impedance element corresponding to the electronic surface states on the free semiconductor surface and that covered by metal nanoparticles.

We have established that for more refined understanding of the process of Ag deposition onto TiO$_2$ it is necessary also to take into account the role of the electronic surface states induced by the chemisorbed Ag$^+$ ions and growing Ag nanoclusters, the characteristic features of the interaction of silver ions and particles with donor defects and their associates in the oxide, the changes in the structure of a double electric layer localized at the sites of metal particle deposition, the variations of the electrode electrocatalytic properties originated from the appearance of nano- and microphase, etc. [2, 3, 19–21].

The difference in the modification action of metal islets of comparable sizes deposited by different methods can be attributed to the fluctuations of energy levels arising as the result of the inhomogeneity of the semiconductor surface. Due to this, the metal particles deposited by photocatalytic and electrochemical methods align themselves on distinct areas of the semiconductor surface which differ as to the $N_d$ and corresponds to the different portions of potential relief. Thus, the cathodic deposition occurs in the most pronounced minima in this relief (which are the most likely corresponding to the donor associates), while the photocatalytic deposition is induced by photoelectrons generated under illumination at the moderately doped areas on the semiconductor surface, these nonequilibrium electrons then flowing downslope to the nearest minimum where the reduction of me-

---

Fig. 6. Macrofluctuations of the energy levels at the semiconductor surface: (a) of the covariant type; (b) of the contravariant type (b).

The arrows show the places where the electrochemical (1) and photocatalytic (2) reduction of metal ions occurs.
tal ions takes place. The potential fluctuations thus facilitate the lateral separation of photogenerated charges, the electron and hole reactions being localized at the separate at the illuminated semiconductor surface. Alongside with the charge separation events, some flattening of the potential relief occurs under illumination (in similar manner to the photoinduced band unbending under open circuit conditions). As the result, a number of places at the electrode surface which have the potential negative enough to induce the reduction of metal ions increases. This provide an explanation of the fact that the photocatalytically-deposited metal appears to be much more dispersed as compared to the galvanic deposit; by the same token the increase of the light intensity, which should ensure the further flattening of the surface potential relief, results in the increase of concentration of Ag nuclei.

3. ELECTRONIC SURFACE STATES IN THE FORBIDDEN ZONE OF SEMICONDUCTOR INDUCED AS A RESULT OF DEPOSITION OF METAL PARTICLES ON SEMICONDUCTOR SURFACE

Electrolyte electroreflectance (EER) spectroscopy is a powerful tool for the in situ investigation of band structure of semiconductor electrodes contacting with the electrolyte solution. In the EER experiments, a periodically modulated electric field is applied to the semiconductor electrode, which causes small changes in the reflectivity and the absorbance. When the modulated electric field is sufficiently low, the lineshape of the EER spectrum of non-degenerate semiconductor is determined by the modulation-induced effect of population-depopulation of the electronic surface states (in the sub-bandgap absorption range) or is closely related to the third derivative of the dielectric function (in the bandgap absorption range). This spectroscopic technique has sown a promise in determining the potential distribution inside the nanocrystalline films and between the space charge and Helmholtz (or surface oxide) layer, studying the evolution of space charge region in the degenerated semiconductors contacting with the electrolyte solution, measuring the flatband potentials, and obtaining information on the degree of inhomogeneity of electrode surface. High sensitivity of EER technique (it is possible to detect the $\Delta R/R$ values of about $10^{-5}$–$10^{-7}$) permits to detect not only the bulk electronic levels but also to evaluate the concentration and energy distribution of energy states at the surface of naked and metal-modified semiconductor in contact with aqueous solution [1–3,19–27].

It is seen from Fig. 7 that in case of amorphous TiO$_2$ film only the bandgap transitions contribute to a EER spectrum which appears to be closely similar to that of single crystalline oxide. The analogous EER spectra observed for amorphous and monocrystalline TiO$_2$ point to the fact that in both cases the semiconductor surface is almost clean from energy states capable of contributing to EER response. The annealing of amorphous TiO$_2$ films accompanied with the formation of crystalline phase, gives rise to an intense EER signal peaking in the sub-bandgap region (Fig. 7). This sub-bandgap EER response can be attributed to the localized electronic states (presumably not only pure surface states but also those residing in grain boundaries as well). The electroative states created upon crystallisation
are also apt to screen the electric field from electrode bulk thus substantially affecting the band-gap EER response.

As can be seen from Fig. 8, the deposition of noble metals (Ag, Pt, Pd) and Cu particles on the surface of TiO$_2$ electrodes gives rise to the EER peaks in the sub-bandgap region. These signals indicate the creation of the surface electronic states, the population of which may undergo perturbations under the modulation of electrode potential. These peaks appear to be the most pronounced in the case of cathodically-biased electrodes, i.e., under circumstances where the Fermi level of semiconductor falls within the region of the energy distribution of the electronic surface states (Fig. 8). The energies of these electronic states are dependent on the properties of a semiconductor as well as on the nature of deposited metal and the average size of metal particles. For instance, the EER signal from the Ag-modified heavily-doped TiO$_2$ electrode ($N_d = 10^{19}$ cm$^{-3}$) exhibits shift to the lower energies (from 2.50 to 2.38 eV) when the average size of Ag particles increases from 0.8 to 1.8 nm (Fig. 9). This corresponds to the increase of the depth of energy levels,
formed by the Ag nanoparticles and to the diminishing of their electric interaction with the c-band. In the limiting case, when the average size of Ag particles rises up to 30–50 nm, the metal nanophase on the semiconductor surface becomes «quasi-isolated» and does not contribute into the EER response. For the metal particles of compatible sizes, the diminishing of donor concentration in TiO₂ leads to somewhat increase of energy of the surface electronic states, which thus appear to be more «shallow» with respect to the conduction band. In the same time, the peak half-width decreases (for instance, from 0.38–0.41 eV for the Ag-modified TiO₂ electrode with \( N_d = 10^{19} \text{ cm}^{-3} \) to 0.21 eV for that with \( N_d = 5 \times 10^{17} \text{ cm}^{-3} \)). The origin of such shift of the surface energy states, which is additionally masked by the effect of the donor defect sub-system on the morphology and other properties of depositing metal particles, is not clearly understood. However, the obtained results point to the fact that there exists a pronounced tendency towards the increase of the interaction between metal nanophase and semiconductor matrix with lowering a matrix doping.
On the other hand, the size distribution of metal particles grown on the semiconductor surface is strongly influenced by conditions of deposition process (such as the shift of surface potential from its equilibrium value, the photon energy and/or charge carriers density, peculiarities of the ionic adsorption and mass-transfer, surface diffusion coefficient for metal ad-atoms, etc.) strongly influence the size distribution of the resulting species. This plague the direct correlation of the electronic surface state parameters for the metal particles obtained by the different methods so that only general tendencies can be revealed. In particular, when the surface concentrations of metal nanophase deposited by different methods are comparable, the nanoparticles obtained galvanostatically (under low cathodic bias) induce, as a rule, the highest-energy levels in the semiconductor matrix (i.e. the most «shallow» levels with respect to the c-band edge). The vacuum-deposited metal particles form the states of minimal energy, while the nuclei obtained photocatalytically under open circuit conditions induce the levels possessing intermediate energies. It is clear that, in spite of the similar surface concentrations of deposited particles, the size distribution of these nuclei and the energetic distribution of metal-induced electronic states in the forbidden zone can vary essentially for different deposition methods (Fig. 10), and even a similarity of the average particle sizes does not yet ensure a resemblance of the properties of metal nanophase. It is especially difficult to compare the energies of electronic states induced as the result of deposition of different metals. As a whole, as to the «depth» of electronic states with respect to the edge of c-band, the metals can by arranged in the following order: Ag≤Pd<Pt<<Cu. It should be noted that the differences

Fig. 9. EER spectra of TiO2 (Nd = 10^{18} cm^{-3}, electrode potential −0.8 V) modified by Ag nanoparticles with different size distribution illustrated by histograms.
between the energies of electronic surface states formed by the different metals on the oxide with a given doping have been found to be less then the differences between the states formed by the same metal on the oxides with different doping. 

Contrary to the Ag, Pd, and Pt nanoparticles, which form the «shallow» electronic surface states, the Cu particles create essentially «deeper» levels with energy of about 2.1–2.2 eV (Fig. 10).

It should be noted that all above-mentioned results have been obtained using polycrystalline titanium dioxide (anatase, rutile) [1, 3]; on the whole, the same regularities are observed during the control experiments with the monocrystalline rutile. When going from poly- to nanocrystalline TiO₂ obtained by sol-gel method, the EER spectrum of the oxide substantially changes [23]. In contrary to this, the EER response attributed to the electronic surface states induced, for instance, by the deposition of Cu nanoparticles on the nanocrystalline TiO₂ appears to be very similar to that obtained in the case of the same deposition on the polycrystalline TiO₂ matrix (Fig. 11).

The EER investigations thus evidences that the electroactive electronic states (i.e., those which are able to change their population with electrode potential) are
induced in the forbidden zone of both poly- and nanocrystalline TiO$_2$ as the result of deposition of Ag, Pt, Pd, and Cu nanoparticles. Of special interest is the fact that the energies of these surface states exhibit decrease with increasing the size of the deposited metal particles, all other factors being equal. It is very likely that the resulting «deep» electroactive levels may act as the recombination centers decreasing the efficiency of the photochemical and photoelectrochemical processes. On the other hand, the electronic surface states formed by the smallest-sized particles are located just below the edge of conduction that facilitate the establish-

Fig. 11. EER spectra of untreated (a) and copper modified (b) nanostructured TiO$_2$ film electrodes under the negative polarization in 0.1 M acetic buffer solution (pH = 6)
The electron equilibrium between metal particles and conduction band. Hence, it is very probable that such particles would function as modifying agent improving the electrocatalytic properties of a semiconductor in dark processes.

4. EFFECT OF THE DEPOSITION OF METAL NANOPARTICLES ON THE ELECTROCATALYTIC ACTIVITY OF SEMICONDUCTOR ELECTRODES

The wide-bandgap semiconductors typically possess very low electrocatalytic activity [3,20,26]. Thus, at the electrode potentials higher than the flat-band potential \( E_{fb} \), TiO\(_2\) electrodes with ordinary doping \( (N_d = 10^{17} - 10^{19} \text{ cm}^{-3}) \) are characterized by the extremely small current densities \( (0.1 - 10 \mu\text{A/cm}^2) \) even in the presence of such strong reducing agents as sodium boron hydride, hypophosphite, and formaldehyde (Fig. 12). The deposition of metal nanoparticles (Pt, Pd, Ag, Au, Cu, Co, Ni) leads to the multiple increase of the anodic current density with the peculiarities of this electrocatalytic effect being substantially different for the noble metals and for Cu, Ni, Co, and Cd. For instance, after cathodic deposition of rather small amounts of Cu nanoparticles \( (1\times10^{15} - 5\times10^{15} \text{ atoms/cm}^2) \) on the surface of TiO\(_2\) electrode with \( N_d = 10^{19} \text{ cm}^{-3} \), the typical view of \( i,E \)-curves for the resulting electrode in the process of the anodic oxidation of BH\(_4^-\) ions (curves 4–6, Fig. 12) differs considerably from those obtained with the use of metal Cu electrode (curve 1) and initial TiO\(_2\) electrode (curves 7,8). The appearance of two peaks in \( i,E \)-curve for metal Cu electrode can be attributed to the oxidation of Cu and increasing the electrocatalytic activity of the electrode caused by the resulted oxidized species followed by the depassivation and passivation processes. In the case of this electrode, the inherent anodic current densities are several orders of magnitude greater than in the case of Cu-modified TiO\(_2\) electrode in spite of the fact that the total surface area of Cu particles is no more than 2–5 times higher than the specific surface area of bulk Cu electrode. The most important feature of the electrochemical behavior of Cu-modified TiO\(_2\) electrodes in the processes under investigation is the appearance of the well-pronounced limiting currents in a wide range of electrode potentials. It is seen from Fig. 12 that the values of these limiting currents are dependent on the concentration of the deposited Cu nanoparticles. With high surface concentrations of Cu particles \( (2\times10^{17} - 10^{18} \text{ atoms/cm}^2) \), when the deposit constitutes not an island layer but a particulate film possessing 2D conductivity, the shape of \( i,E \)-curve exhibits drastic change: one can observe a typical peak attributed to the oxidation-passivation of Cu coating (-0.4 – -0.6 V) followed by the current noise resulted from the disruptions of electric conductivity in a degrading Cu layer.

Of special interest is the fact of appearance of the limiting current in the \( i,E \) curve for the Cu-modified TiO\(_2\) electrode, especially taking into account that this current is not dependent on the stirring of electrolyte and cannot be considered as a consequence of any diffusion limitation. At the same time, this limiting current is very sensitive to the heating of the electrolyte as well as to the IR illumination of the electrode.
By contrast to Cu particles, noble metal particles deposited onto the surface of TiO$_2$ electrode exhibit strong electrocatalytic effect. With similar concentrations of deposited metals, the current values are 50–200 times higher in the case of noble metals than for Cu-modified TiO$_2$ electrode. Moreover, in case of TiO$_2$ electrode modified with noble metals, the above mentioned limiting current does not appear on the $i,E$-curves (Fig. 13). The current exhibits decrease at high electrode potentials where even the bulk metal electrodes undergo passivation; besides this, under high anodic current densities the usual diffusion limitations begin to play role. The electrochemical properties of TiO$_2$ electrodes modified with Ni, Co, Cd, Bi, and Pb are intermediate between Pt-modified and Cu-modified ones, being strongly dependent strongly on the surface concentration of metal nanophase and on the nature of reducing agent. For instance, the electrocatalytic action of Ni nanoparticles approaches that of Pt and Pd species in the oxidation processes limited by the dehydrogenation stage.

To understand the above peculiarities of the electrocatalytic activity of metal nanophase in dark oxidation processes on the TiO$_2$ electrodes, one should take into ac-
count the differences in the electrocatalytic properties inherent in the deposited metals, on the one hand, and the data on the energy distribution of electronic states induced by the nanoparticles of these metals in a forbidden zone of TiO₂ electrode, on the other hand. A peculiar shape of i,E-curves obtained for the Cu-modified TiO₂ electrodes and the appearance of the limiting currents can be attributed to the formation and properties of Schottky barrier at the TiO₂/Cu interface [1, 22, 26]. The «deep» (with respect to the c-band edge) electronic surface states formed by the Cu nanoparticles are unable to increase the permeability of Schottky barrier to the tunneling electrons. Since such a barrier is not completely perfect, there always exist leaking currents, this results in the increased electrocatalytic activity of the Cu-modified TiO₂ electrodes in comparison with the naked ones. However, the attained increase of activity is essentially less than in the case of TiO₂ electrodes modified by the deposition of noble metals particles. In the latter case, the «shallow» electronic surface states formed by metal nanoparticles, when their concentration is sufficiently high, provide the typical «soft breakdown» of Schottky barrier. The nanoparticles of metal fappears to be in an immediate electric contact with the semiconductor bulk, the electrochemical behavior of the electrode being governed predominantly by the electrocatalytic properties of these particles.

From the above reasoning one could expect that the pre-deposition of small amounts of noble metals on the TiO₂ surface in a form of the intermediate sub-layer capable of inducing the «shallow» electronic surface states in the forbidden zone of TiO₂, may enhance the electrocatalytic effect of subsequently deposited Cu

Fig. 14. Anodic current vs. potential curves for the process of BH₄⁻ ions oxidation on the TiO₂ electrodes surface modified by Pd:
5×10¹⁵ atoms/cm² – curve 1;
10¹⁵ atoms/cm² – curve 2;
Ag: 10¹⁵ atoms/cm² – curve 3; and by successive electrodeposition of Ag (10¹⁴ atoms/cm²) and Cu (10¹⁵ atoms/cm²) – curve 4.
The values of N_d for TiO₂ were 10¹⁸ cm⁻³ (curve 5) and 10¹⁹ cm⁻³ (curves 3, 4, 6).
Electrolyte: 0.1 M NaBH₄ + 0.1 M NaOH.
The potential sweep rate is 5 mV/s.
particles. Actually, the photocatalytic deposition of silver particles in amount of $5 \times 10^{14}$ atoms/cm$^2$, which on its own only slightly increases the electrocatalytic activity of TiO$_2$ electrode, leads to 2–3-fold enhancement of the electrocatalytic activity of Cu deposited in a relatively high concentration ($10^{16} – 10^{17}$ atoms/cm$^2$) [22].

Notwithstanding to the fact that the efficiency of the anodic electrochemical reaction in the case of metal-modified TiO$_2$ electrode is limited by the value of the leakage current for the reverse-biased Schottky diodes corresponding to the «metal/oxide» microjunctions, there exists a pronounced correlation between the electrocatalytic activity of TiO$_2$-Me and bulk metal electrodes, with the efficiency of BH$_4^-$ oxidation increasing in the following manner: Cu < Ag < Ni < Pt. Such a behaviour can be attributed to the fact that the higher catalytic activity of the metal, the lower values of the potential drop in the Helmholtz layer reaching in case of different TiO$_2$-Me electrodes at the same current densities, that, in its turn, results in larger potential drop in the space charge layer. Such potential redistribution, which can be described in terms of some kind of feedback, leads to the corresponding increase of the efficiency of the electrochemical reaction on the metal-modified semiconductor surface.

5. IMPEDANCE OF SEMICONDUCTOR OXIDE ELECTRODES MODIFIED WITH METAL PARTICLES

The effect of fine metal particles deposited onto the surface of semiconductor electrodes on the frequency and potential dependencies of the electrochemical capacity of metal-modified semiconductor electrode is mainly due to the appearance of the capacitance corresponding to the surface (interfacial) states ($C_{ss}$) and the capacitance of the Helmholtz layer at the metal/electrolyte interface. The latter factor is well-pronounced only in the condition of effective electron exchange between metal particles and semiconductor bands, as with the noble metals cathodically-deposited onto the surface of film TiO$_2$ electrodes. In the simplest case, the equivalent circuit which mimic the behaviour of such electrode system can be represented by two arms, connected in parallel, which correspond to free semiconductor surface contacted with electrolyte and the surface of metal particles, respectively. If especial precautions in order to exclude the presence of reducing metal ions in the solution are not taken, the substantial changes in the electronic states on the uncovered semiconductor surface represented by the corresponding changes in the equivalent circuit may take place.

It is evident that the adequate description of electrode impedance in the case of the actual contact between the surface-modified semiconductor and electrolyte represents a very complicated problem due to the appearance of some hardly measured parameters associated with the particle size effects and the contributions of surface and interfacial electronic states. Because of this, we shall restrict our consideration to the simplest situation, when metal particles act as a set of metal microelectrodes electrically connected with the bulk of a semiconductor without the formation of Schottky barrier at the metal/semiconductor interface, assuming that the average size of these particles is sufficiently large to leave the properties of the contact unaffected.
The Mott-Schottky plots obtained for the Ag-modified TiO₂ electrode differ from those for the necked electrode as the slope value, with the potential corresponding to the intersection of the plot with the potential axis remain almost unaffected (Fig. 15). Since the heavily-doped TiO₂ electrodes were used, when describing Mott-Schottky dependence it is worthwhile to take account of the Helmholtz-layer capacitance ($C_H$) connected in series with the space charge capacity:

$$C^{-2} = C_H^{-2} + 2\left[ E - E_{fb} - kT / e \right] / \varepsilon \varepsilon_0 e N_d$$

(1)

As a first approximation, the $C_H$ value can be assumed to be not dependent on the electrode potential. When the fine metal particles are present on a semiconductor surface, the capacitance of Helmholtz layer at the metal particles, connected in parallel with the $\approx C_{ac}C_H \approx$ segment, and contribute to the total electro-chemical capacity:

$$C = mC_M + n\left[ C_H^{-2} + 2\left[ E - E_{fb} - kT / e \right] / \varepsilon \varepsilon_0 e N_d \right]^{-1/2}$$

(2)

where $m$ and $n$ are, respectively, the portions of the electrode surface covered by metal particles and free of them. The results of the numerical calculations made

Fig. 15. Mott-Schottky dependences for non-modified (curves 1–5) and modified by Ag nanoparticles (curves 6–10) TiO₂ electrodes. The frequency of alternative current was 10 kHz (1, 6); 1 kHz (2, 7); 700 Hz (3, 8); 500 Hz (4, 9); 100 Hz (5, 10). Electrolyte: 0.25 M Na₂SO₄
with the use of the above equation suggest that the introduction of the capacitance of the metal particles into the equivalent circuit of the electrode system leads to the changes in a slope of Mott-Schottky plots corresponding to the formal increase of $N_d$ value (Fig. 16). Thus a correction derived from the capacity of metal microelectrodes on a semiconductor surface should be introduced into the commonly accepted determination of $N_d$ value from the slope of Mott-Schottky curves:

$$N_d' = N_d \left\{ \frac{mC_M + n \left[ C_H^{-2} + 2 \left( \frac{E - E_{fb} - kT}{e} \right) / \varepsilon \varepsilon_0 eN_d \right]^{-1/2}}{n \left[ C_H^{-2} + 2 \left( \frac{E - E_{fb} - kT}{e} \right) / \varepsilon \varepsilon_0 eN_d \right]^{-1/2}} \right\}^{3/2}$$

Fig. 16. Equivalent circuit representing the electrode system «TiO$_2$ -Ag nanoparticles- electrolyte» and calculated Mott-Schottky curves for different portions of the electrode surface covered by metal particles ($m$):

- 0 (curve 1);
- 0.02 (curve 2);
- 0.2 (curve 3).

$C_H = 10 \mu F/cm^2$;
$C_M = 20 \mu F/cm^2$; $N_d = 1.5 \times 10^{18} \text{ cm}^{-3}$

The above ratio is dependent on the electrode potential, this dependence becoming more pronounced with the increase of both $m$ value and the difference between the electrode potential and $E_{fb}$ (Figs. 15, 16).

Describing the Mott-Schottky dependences of semiconductor electrodes modified with fine metal particles, it is reasonable to take into account the contribution of the capacitance of the electronic surface state induced by the chemisorption/reduction of ions and formation of metal ad-atoms and clusters. Taking into account the charge of these electronic states ($Q_{ss}$) one can draw inference about the shift of the extrapolation point of the Mott-Schottky plot by the following value:

$$E' = E_{fb} + kT/e + Q_{ss}/C_H - \frac{\varepsilon \varepsilon_0 eN_d}{2C_H^2}$$
In the case of the system "TiO₂ – metal nanoparticles", the role of surface states becoming negligible at sufficiently high frequencies (≥5–8 kHz) and under bias by 4–5 kT/e more positive than $E_{fb}$. The analysis of Mott-Schottky plots (Fig. 15) shows that the appearance of the capacitance of the Helmholtz layer at the metal nanoparticles actually causes the marked changes in the slope of the plot. As the result, the $N_d$ values calculated by the equation (1) appear to be substantially higher than $N_d$ value for the initial TiO₂. To take an illustration, the $N_d$ value determined from the Mott-Schottky plots for the TiO₂ electrode modified by Ag particles 1–5 nm in size with the surface concentration of about $10^{12}$ cm⁻³ is 6.2±0.3 times higher than that of the naked TiO₂. This correlates well with the value $N_d^*/N_d = 5.9±0.2$ calculated by the equation (3) with the use of the estimate for consideration for the total surface area of metal particles obtained by the electron microscopy [3, 29].

In the case of TiO₂-Me electrode, the newly formed surface states also affects the frequency dependence of electrode capacitance. Under anodic biases this dependence exhibits linear behaviour in $C$ vs $\omega^{1/2}$ plots (Fig. 17) that is consistent with low mobility of charge carriers (the Warburg impedance). Assuming that the change in the concentration of the majority charge carriers in the semiconductor, $\Delta n$, exhibits the harmonic variations during the impedance measurements, one could obtain:

$$j\omega \Delta n \equiv \frac{\mu_{eff} kT d^2 \Delta n_z}{e}$$

Fig. 17. Frequency dependence of (1) surface states and (2) electrode capacity for TiO₂ electrode ($N_d=2\times10^{18}$ cm⁻³).
C² vs $\omega$ plots for (3) TiO₂, (4) TiO₂-Ag electrodes

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where \( \mu_{\text{eff}} \) is an effective mobility of charge carriers, the other symbols have their traditional meaning. Taking into account the boundary condition

\[
\lim_{x \to 0} \Delta n_x = 0
\]

one could obtain the following solution of this equation:

\[
\Delta n_x = \Delta n_x \exp \left[ -x \left( \frac{j \omega k T \mu_{\text{eff}}}{e} \right)^{1/2} \right], \quad \text{where} \quad \Delta n_x = \frac{e E_{\text{sc}}}{k T} \ln \frac{e}{k T E_{\text{sc}}} - 1,
\]

where \( \Delta E_{\text{sc}} \) is potential drop in the space charge layer. The differentiation with respect of \( x \) yields the following equation for electrode impedance:

\[
Z = k T \frac{n_e}{e^2} \sqrt{\frac{j \omega k T \mu_{\text{eff}}}{e}}.
\]

As the result, the electrode capacity appears to be governed by:

\[
C^{-2} = \frac{k T \omega}{2 e^3 n_e^2 \mu_{\text{eff}}}.
\]

The decreased slope of the \( C \) vs. \( \omega^{-1/2} \) dependence in case of TiO\(_2\)-Ag electrode (Fig. 17) is formally consistent with higher mobility of charge carriers as compared to the naked electrode that points to the increased permeability of the space charge layer in the presence of silver nanoparticles (0.5–2.5 nm in size) on the TiO\(_2\) surface. In other words, upon Ag deposition additional channels of charge transfer appears to be activated, in particular, due to the redistribution of the potential drop among the Helmholtz layer and space charge layer facilitates the soft breakdown of the Schottky barrier.

6. INTERACTION OF METAL NANOPARTICLES WITH THE ASSOCIATES OF DONOR DEFECTS IN THE OXIDE SEMICONDUCTORS

The peculiarities of the interactions in the system «metal nanoparticles-semiconductor oxide» makes the deposition of metals a very sensitive tool permitting to probe the semiconductor surface and to obtain a valuable information on the segregation of donor centers typical of moderately and heavily doped semiconductors. It is clear that during the contact deposition of metals the nucleation on the TiO\(_2\) surface occurs at the sites of donor location, especially at the donor clusters. The process of oxidation of donor centers due to their interaction with metal ions do not propagate interior the semiconductor bulk to the depth larger than several oxide lattice constants because of limitations due the diffusion of oxygen accompanying the oxidation of donor centers. To explain the experimentally observed appearance of a rather small concentration of large Ag particles on the TiO\(_2\) electrodes, account must be given to the possibility of lateral electron transfer from
neighboring donor centers via the mechanism typical to the electroless deposition of metals. In any case, metal nanoparticles deposited as the result of the interaction of semiconductor donor centers with metal ions prove to be localized at the sites corresponding to the donor clusters. In a similar manner, during the deposition of metal particles onto the cathodically-biased TiO₂ electrode in a solution containing metal ions, the growth of metal phase will be also localized at the sites of the surface exposure of the donor clusters. Just these sites possess the enhanced electrocatalytic activity as compared with the surface of stoichiometric oxide and are responsible for the formation of the additional channels providing the unimpeded charge transfer through the space charge region. Actually, a peculiar «decoration» of donor centers and donor clusters by metal nanoparticles occurs as the result of the contact deposition of metal nanoparticles. The increased electrocatalytic activity of the wide-band-gap semiconductor electrodes resulted from the deposition of metal nanoparticles on their surface may be also regarded as a «decoration» of special type. In case of oxide semiconductors (e.g., WO₃), the role of donor clusters in the formation of the electrocatalytical behaviour of electrode can be revealed by the selective electrochemical deposition of dielectric polymer, such as poly-o-phenylenediamine permitting to blockade the abruptions of donor clusters at the electrode surface [30].

As a whole, the discussed results evidences that the charge transfer through the oxide semiconductor / electrolyte interface is governed by the local electrochemical processes at the surface of «microelectrodes» corresponding to the donor clusters, rather than by tunneling of electrons through the semiconductor space charge region.

CONCLUSIONS

The morphology of metal nanophase formed on the surface of wide-bandgap semiconductor oxides via the contact, photocatalytic, or photoelectrochemical deposition is substantially dependent on concentration, bulk distribution, and energy characteristics of donor defects in the semiconductor substrate. As a rule, the necessary condition for the formation of the smallest-sized particles in the highest surface concentration is the maximum shift of the surface potential of semiconductor from its equilibrium value during metal deposition. This is part of the reason for the experimentally observed fact that the particles formed in the condition of photocatalytic deposition are characterized by less average size and cover superior portion of surface than those obtained under cathodic deposition, all other factors being equal.

The generation of electronic surface states in a forbidden zone of the semiconductor by the deposition of metal nanoparticles is the major factor determining the efficiency of electron exchange between metal particles and semiconductor bulk and the efficiency of electrocatalytic process as a whole. According to the electrolyte electroreflectance spectroscopic measurements, Ag, Pd, and Pt nanoparticles induce the «shallow» (with respect to the c-band edge) surface states in the forbidden zone of TiO₂, which provide near-unimpeded electron exchange bet-
ween metal particles and semiconductor c-band. As the size of metal particles increases, the surface state levels in TiO₂ become more «deep» in relation to the edge of c-band. Thus the modification of the energy structure of surface states, e.g. by depositing metal nanophase of definite morphology or using the successive deposition of different metals opens the fresh opportunities in exerting an effective control over the electrocatalytic, photocatalytic, and photoelectrochemical properties of metal-loaded semiconductors.

REFERENCES