

ELECTRONIC PROPERTIES OF PALLADIUM-DOPED POROUS SILICON AND ITS APPLICATION FOR WATER DECOMPOSITION WITHOUT APPLYING ELECTRIC VOLTAGE

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The por-Si/*p*-Si and por-Si/*n*-Si structures fabricated with the use of an internal current source have been examined by measuring the temperature dependences of their capacitance photovoltage in the temperature interval 100–300 K. The same structures were examined after their doping with Pd in PdCl₂ aqueous solutions. The energy bands in the *n*- and *p*-Si boundary layers were bent down before doping and became bent up after it. Pd-doping increases the concentration of boundary electronic states (BESs) below the midpoint E_i of the energy gap and decreases it above E_i . It also decreases the hole trap concentration at the por-Si/*n*-Si interface. The examination of the time dependences of a current, which flows – without application of external voltage – between Pd-doped (or undoped) structures under investigation and a Yb (or Pt) electrode immersed into water, has revealed the water decomposition into OH⁻ and H⁺ ions, which becomes possible owing to the catalytic activity of the Yb and por-Si(Pd)/*n*-Si electrodes.

1. Introduction

Porous silicon (por-Si) and its modifications comprise a good basis for implementing the processes of heterogeneous catalysis [1, 2]. There are various methods for the por-Si fabrication; in particular, the most often used are the methods of anodic etching by applying an external voltage at various compositions of the etchant, as well as the method of “stain” etching. In this work, we studied porous silicon that was obtained following the method described in work [3], namely, making use of an internal current source that arises owing to the difference between the electrochemical potentials of single-crystal silicon and a platinum electrode immersed into the etching solution. Single-crystalline wafers of *p*- and *n*-silicon were used. The electronic properties of por-Si/*p*-Si and por-Si/*n*-Si systems obtained in such a way, as well as the properties of those systems doped with palladium in the aqueous solutions of a PdCl₂ salt, were studied by measuring the temperature dependences of the capacitor photovoltage [1, 2]. This method has

not been applied earlier for researching the systems concerned.

In this work, we also studied, for the first time, the current flow caused by the contact potential difference between electrodes of various kinds and por-Si structures immersed into distilled water. In a number of cases, we found that the current through the investigated system grew as long as the system remained immersed in water, and this phenomenon was accompanied by the hydrogen and oxygen release at electrodes and por-Si structures. Therefore, a decomposition of water into hydrogen and oxygen without applying an external voltage has been executed for the first time; hydrogen and oxygen obtained in such a way can be further used – by allowing them to interact with each other – for the energy generation.

The analysis of the experimental results testifies that the current flow through water is practically independent of the external illumination; this means that the energy gain obtained at the water decomposition is not related to the use of the energy of light quanta of the external illumination. The effect results from different values of the electrochemical potential (the work function) in the electrodes with a non-zero electrical potential difference between them; the latter phenomenon arises owing, first of all, to electrochemical reactions which run at the electrodes and, probably, to the consumption of the thermal energy from the environment.

2. Experimental Methods of Researches

Layers of porous silicon 1–3 μm in thickness were deposited onto mechanically polished (100) surfaces of *p*-Si (the specific conductance of 10 Ω · cm) or *n*-Si (2 Ω · cm) specimens following the method proposed in work [3]. Porous silicon was formed owing to the current of 5–6 mA/cm², which flowed for 15–20 min

between a platinum electrode and a silicon specimen, both immersed into a 1:1 electrochemical mixture of HF and C_2H_2OH with the addition of 0.7 M H_2O_2 . For the fabrication of por-Si layers on n -Si specimens, the illumination by an ordinary 150-W electric incandescent lamp was used. Aluminum contacts had been preliminarily deposited on the back sides of specimens and annealed at 400 °C. Before anodizing the specimens, the contacts were lacquered, and the specimens were first treated in HF for a short term and then washed in distilled water.

The undoped specimens of por-Si/ p -Si and por-Si/ n -Si, as well as these structures doped with palladium during 60 min in $PdCl_2$ aqueous solutions with the concentrations of 10^{-4} and 10^{-3} M, were studied. Such a doping procedure results in the formation of palladium nanocrystals in the por-Si layer [4].

For the measurements of the temperature dependences of the photovoltage generated across those structures, a mica plate was pressed to the porous layer; on the other side of that plate, a translucent conducting $SnO_2(Sb)$ layer was deposited. In so doing, we obtained a capacitor SnO_2 -mica plate-por-Si/Si-Al. The method for measuring the photovoltage, which emerges across this capacitor at the illumination of the latter by light pulses, was described in detail in a number of our works (see, e.g., works [5–7]).

The photovoltage signal registered for the first pulse of light can differ by amplitude from the signals registered for the second or other following pulses in the train. This phenomenon is associated with the capture of nonequilibrium charge carriers onto the traps located either at the interface por-Si-Si or in the por-Si layer. When red light was used for illumination, the specimens were heated up after every measurement to a temperature, at which traps became released from the captured charge carriers; then, the specimens were cooled down again to the temperature of the next photovoltage measurement carried out for the first and second pulses. Note that photovoltage signals, starting from the second pulse, did not differ from one another as a rule, which testifies that even the action of the first pulse of light made traps saturated with nonequilibrium charge carriers.

The temperature dependences of the photovoltage were measured in a cryostat, where the vacuum of 10^{-4} Pa was maintained, at the decrease of the temperature from 300 to 100 K. After the photovoltage having been measured, the specimens were used as electrodes, together with platinum (or ytterbium) counterelectrodes, in an electrochemical system for the

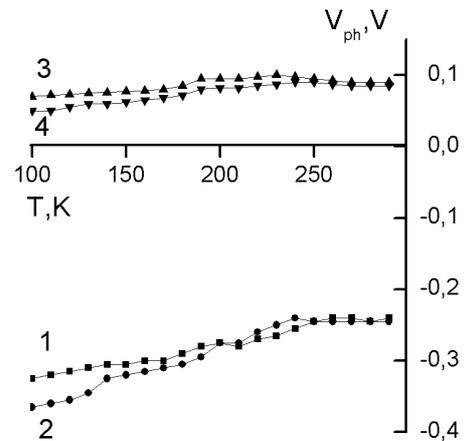


Fig. 1. Temperature dependences of the photovoltage V_{ph} across the structures por-Si/ p -Si (curves 1 and 2) and por-Si(Pd)/ p -Si (curves 3 and 4). Measurements were made using red- (curves 1 and 3) and white-light pulses (curves 2 and 4)

water decomposition into oxygen and hydrogen. The decomposition started, when the electric circuit that included the electrodes became closed. The electron work functions of electrodes with respect to the platinum electrode were determined preliminarily.

3. Experimental Results of Photovoltage Researches and their Discussion

In Fig. 1, the dependences of the photovoltage amplitudes V_{ph} across por-Si/ p -Si (curves 1 and 2) and por-Si(Pd, 10^{-4} M)/ p -Si (curves 3 and 4) structures at the illumination of the latter with red- (curves 1 and 3) and white- (curves 2 and 4) light pulses are depicted. The measurements were carried out, when the temperature was reduced from 300 to 100 K. It is evident from this figure that the dependences $V_{ph}(T)$ for red- and white-light pulses weakly differ from each other. This circumstance testifies that the amplitude of photovoltage, which arises directly in por-Si and por-Si(Pd) layers, is insignificant. The main contribution to the V_{ph} amplitude is made by the photovoltage generated in the near-surface layer of the silicon wafer. It follows from the values of this photovoltage obtained at red-light illumination that the near-surface p -Si layer in an undoped structure is hole-depleted, and the values of the boundary potential $\varphi_s = -V_{ph}$ at the interface p -Si-por-Si change from 0.225 to 0.325 V, if the temperature diminishes from 300 to 100 K. Doping the structure with Pd brings about the variation of the magnitude and the sign of the boundary potential (curves 3 and 4). Its

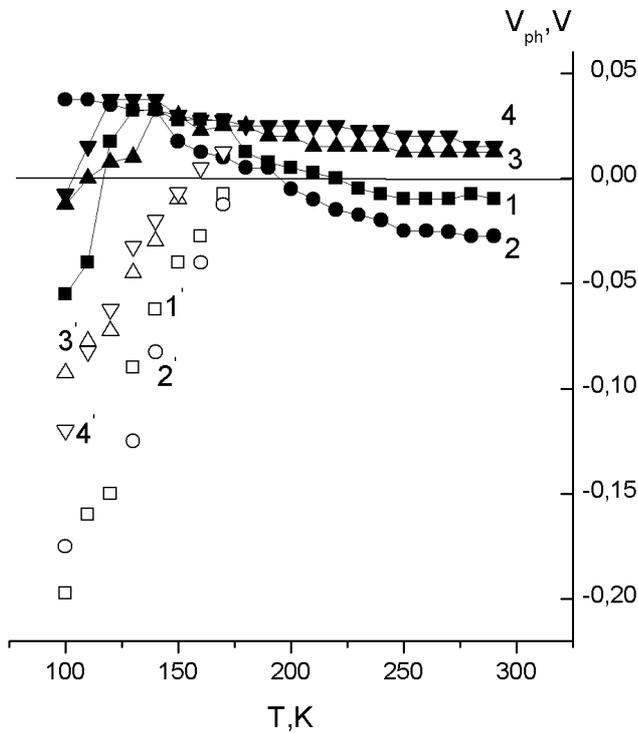


Fig. 2. Temperature dependences of the photovoltage V_{ph} across the structures por-Si/ n -Si (dependences 1, 1', 2, and 2') and por-Si(Pd)/ n -Si (dependences 3, 3', 4, and 4'). Dependences 1 and 3 correspond to red-light pulses, and dependences 2 and 4 to white-light pulses. The unprimed dependences correspond to the first, while the primed ones to the second pulse in the train

amplitude varies within the interval $\varphi_s = -0.098 \div -0.067$ V as the temperature decreases, which evidences for the availability of a hole-enriched boundary p -Si layer at the interface with por-Si(Pd).

We emphasize that, while measuring the dependences $V_{ph}(T)$, the phenomenon of photomemory with respect to V_{ph} was not noticed for p -Si-based structures, i.e. the V_{ph} amplitudes were identical for the first and following light pulses in the train. This testifies that electron traps in por-Si and por-Si(Pd) layers, as well as at their interfaces with p -Si, do not manifest themselves in the whole temperature interval 100–300 K. The dependences $V_{ph}(T)$ also evidence for the absence of a reconstruction in the system of boundary electron states (BESs) in the p -Si wafer under varying the temperature [6].

As the temperature decreases from 300 to 100 K, the Fermi level in the p -Si bulk becomes shifted towards the v -band position in Si. In so doing, the BESs that were located below the Fermi level become empty of electrons. Similarly to what was done in a number of our

works – in particular, in work [7] – we can calculate the BES concentration distribution in the energy interval of the forbidden gap at the p -Si boundary, which is traversed by the Fermi level as the temperature varies. It turned out that, for the structure undoped with Pd, the BES concentration was almost constant and equal to $N_s = 1.6 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ within the interval located by 0.07–0.2 eV below the energy-gap midpoint. After Pd-doping, the BES concentration considerably increased. The calculations show that two ranges with different BES concentrations manifest themselves in the energy gap of p -Si contacting with por-Si(Pd): the BES concentration amounts to $N_s = 1.1 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ in the interval located by 0.38–0.46 eV below E_i and to $N_s = 3.1 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ in the interval located by 0.50–0.56 eV below E_i .

The temperature dependences $V_{ph}(T)$ for por-Si/ n -Si and por-Si(Pd, 10^{-3} M)/ n -Si structures (see Fig. 2) substantially differ from those obtained in the case of p -Si wafer. First, a considerable contribution to the V_{ph} magnitude in the case of white-light illumination (dependences 2 and 4) is given – both for undoped and Pd-doped structures on n -Si wafer – not only by the photovoltage generated in the interface region of n -Si (it can be measured making use of red-light pulses; see dependences 1 and 3), but also by the photovoltage generated in the por-Si and por-Si(Pd) layers. Second, the dependences $V_{ph}(T)$, which change their sign in the temperature interval 110–100 K, testify that, as the temperature reduces, a reconstruction of the BES system occurs both in the undoped and Pd-doped structures, starting from the temperature of 135 K. In addition, at $T \leq 160$ K, the phenomenon of V_{ph} photomemory is observed for both red- and white-light pulses and for both undoped and doped structures. All those characteristic features of the structures on n -Si wafers are associated, in our opinion, with more nonequilibrium conditions for the por-Si layer formation on n -Si wafers, because holes, which are necessary for that, are generated by the illumination of the electric lamp, whereas there are enough holes in p -Si wafers (they are majority charge carriers there) even without illumination.

As is seen from Fig. 2 (dependence 1), the boundary n -Si region in the undoped por-Si/ n -Si structure is somewhat enriched with electrons at $T > 220$ K ($\varphi_s \approx 0.012$ V); at 130 K $< T < 220$ K, it becomes electron-depleted and, at $T < 130$ K, once more electron-enriched. These variations in the n -Si boundary layer, which accompany the temperature decrease, are associated with the

occupation of BESs by electrons at $T > 130$ K and the reconstruction of BES system at $T < 130$ K. The results of calculations show that the BES concentration in the interval located by 0.32–0.44 eV above E_i does not exceed $4 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. The doping of the por-Si/ n -Si structure with palladium leads to the depletion of the electron-enriched n -Si boundary region (φ_s changes from 0.012 to -0.012 V) (see Fig. 2, dependence 3). If the temperature of the Pd-doped structure decreases down to $T \approx 140$ K, the electron depletion in the n -Si boundary region increases (φ_s changes from -0.012 to -0.027 V). The corresponding calculations demonstrate that, in this case, those BESs which are located by 0.30–0.44 eV above E_i become occupied with electrons. Their concentration changes from 3×10^{10} to $1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ in the direction away from E_i . Therefore, doping the por-Si/ n -Si structure with palladium reduces the BES concentration. The reconstruction of this BES system in the doped structure takes place at $T < 140$ K (Fig. 2, dependence 3).

The smaller values of V_{ph} for the second red- and white-light pulses, which were obtained while studying the undoped and Pd-doped structures on n -Si wafers at temperatures $T \leq 170$ K (dependences 1'–4'), evidence for the capture of nonequilibrium charge carriers (holes) into structure traps. The difference between $V_{\text{ph}}(T)$ values registered for the first and second red-light pulse makes it possible to calculate the number of holes N_{ti} captured into the traps located at the interface por-Si/ n -Si [5–7]. In Fig. 3, the dependences $N_{\text{ti}}(T)$ for the undoped (dependence 1) and Pd-doped (dependence 2) structures are exhibited. It is evident that the values of N_{ti} strongly increase as the temperature decreases. This is related to engaging the more shallow (with respect to the v -band) traps into the process of hole capture and retention at lower temperatures. Since the traps become saturated with holes even during the first light pulse, the dependences $N_{\text{ti}}(T)$ also depend on the concentration of traps, which capture holes. From Fig. 3, it is evident that the Pd-doping reduces the hole trap concentration at the interface por-Si/ n -Si.

The analysis of the values of $V_{\text{ph}}(T)$ obtained for the first and second white-light pulses (Fig. 2), which takes hole capture at the interface into account, gave rise to the conclusion that hole traps are practically absent from the por-Si layer of the undoped structure, and that the trap concentration in the por-Si(Pd) layer is not higher than $3 \times 10^{10} \text{ cm}^{-2}$ after Pd-doping (in the temperature interval from 160 to 130 K).

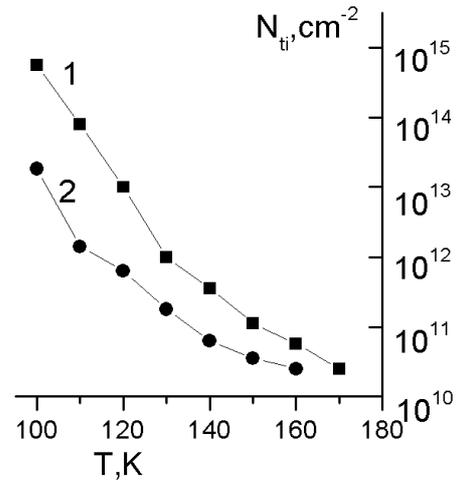


Fig. 3. Temperature dependences of the concentration of holes captured onto the traps located at the interface of the por-Si/ n -Si (1) or por-Si(Pd)/ n -Si (2) structure

4. Water Decomposition Using Undoped and Pd-doped Structures with Porous Silicon

In our work [1], it was pointed out that porous silicon – especially with nano-crystalline metal impurities – can be used as an effective catalyst in heterogeneous reactions. In this work, we aimed at finding whether porous silicon with nanocrystalline palladium impurities can be used as a catalyst in such a specific reaction as the water decomposition into hydrogen and oxygen.

For the water decomposition, we used the electrodes por-Si/ p -Si, por-Si/ n -Si, por-Si(Pd)/ p -Si, por-Si(Pd)/ n -Si, as well as platinum (Pt) and ytterbium (Yb) ones. First of all, we determined their electron work function with respect to a Pt electrode, whose work function is well-known ($\varphi = 5.32$ eV). For this purpose, the voltage V with an amplitude of 9.7 V but with variable sign was applied between the Pt and another electrodes which were both immersed into distilled water. The currents were measured after their relatively quick electronic stabilization (no later than in 5 s after the voltage V had been applied), i.e. when electrochemical reactions, which change electrode polarization, had not started yet. On the basis of the equations

$$J_1 = (V - \Delta\varphi/q)/R$$

and

$$J_2 = (V + \Delta\varphi/q)/R,$$

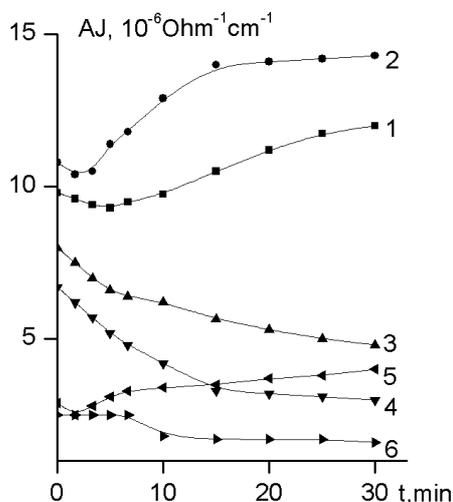


Fig. 4. Time dependences of the conductance in the as-polished Yb-Pt (1), aged Yb-Pt (2), Yb-por-Si/n-Si (3), Yb-por-Si/p-Si (4), Pt-por-Si/n-Si (5), and Pt-por-Si/p-Si (6) structures

where $\Delta\varphi$ is the work function difference between the Pt and the other electrode, R the resistance of electrochemical system, and q the electron charge, the quantity

$$\Delta\varphi = V[(J_2 - J_1)/(J_2 + J_1)]$$

was determined, which made it possible to find the value of φ for the given electrode. In the same manner, the values of φ for all other electrodes were determined. It turned out that the value of φ for the ytterbium electrode depends on the state of its surface: it amounts to $\varphi(\text{Yb}_{\text{ox}}) = 3.70$ eV for a surface that has been subjected to the long-term oxidation and to $\varphi(\text{Yb}_{\text{pol.}}) = 3.05$ eV for an as-polished (mechanically) one. After the Yb electrode had been kept in air for a month, the value of $\varphi(\text{Yb})$ returned back to the value of 3.58 eV. For the other electrodes, the following values of the work functions were determined: 4.53 eV for por-Si/p-Si, 4.58 eV for por-Si/n-Si, 4.83 eV for por-Si(Pd)/p-Si, and 4.91 eV for por-Si(Pd)/n-Si.

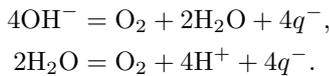
It is well-known [8, 9] that the immersion of an electrode into water (the latter contains OH^- and H^+ ions, each type has a concentration of $1.2 \times 10^{14} \text{ cm}^{-3}$ at 25 °C, and H^+ ions form H_5O_2^+ complexes [10]) stimulates the electron-ion exchange between the electrode and water. As a result, a potential jump (the so-called contact Galvani potential difference) is established between them, which, in its turn, is composed of at least three components: the potential drop across the diffusion ionic layer of the electrolyte (water); the potential drop across

a thin (about 10^{-8} cm) Helmholtz layer formed by ions immediately adjacent to the electrode, and the drop of potential across the electrode. The latter component can be substantial, if the electrode is a semiconductor rather than a metal (in the former case, there exists a region of near-surface charge in the electrode). In addition, if the oxide layer on the electrode is characterized by a considerable thickness and a high electric resistance, it can make a large contribution to the Galvani potential difference. In our researches, the drop of potential took also place across por-Si layers, even if the latter were saturated with water.

While carrying out the experiments, two disconnected electrodes located at a distance of 1.0–1.5 cm from each other were simultaneously immersed into water. We assume that, in a short time (1–2 min) after the immersion, an equilibrium between the electrodes becomes established; owing to different values of electrochemical potentials (or the work functions) in electrodes, there appears an electric potential difference between them. Some portion of electrons transfer from the electrode with a higher electrochemical potential (with a lower work function) to the electrode with a lower electrochemical potential (with a higher work function). As a result, the former electrode becomes charged positively (it becomes an anode), while the latter negatively (it becomes a cathode). Provided that the external electric circuit is closed, an electric current runs through it, with electrons moving from the electrode-anode to the electrode-cathode, because – in water – OH^- ions move towards the anode and H^+ (H_5O_2^+) ones towards the cathode. We emphasize that the initial potential difference ΔV between electrodes was always smaller than the difference $\Delta\varphi/q$ between the electrode work functions.

We experimentally measured the value of ΔV (at the beginning of the experiment) and the time dependence of the current J which ran between electrodes. Since the electrode surface area S , the interelectrode distance L , and ΔV were different for different electrode pairs, we plotted, in order to compare the efficiency of various electrode pairs, the time dependences of the effective specific conductivity of the electrochemical system, $\sigma_{\text{eff}} = AJ$, where the factor $A = (L/\Delta VS)$. As counterelectrodes for por-Si, the Pt and Yb electrodes were used; therefore, it was interesting to study the dependence $AJ(t)$ for the electrode pair Yb-Pt which was characterized by the maximal value of $\Delta\varphi$ in our experiments. The results obtained are presented in Fig. 4 (curves 1 and 2).

Platinum is known to be the most chemically resistant metal, which is covered by a superthin oxide film. Moreover, as our further researches demonstrated, Pt, when being in pair with other metals, does not produce such strong variations of $AJ(t)$ which are observed in Fig. 4. Therefore, the dependences $AJ(t)$ should be discussed on the basis of examining the processes which take place near the Yb electrode (the anode). It is known [10] that the following reactions can run at the anode in neutral environments ($\text{pH} \approx 7$):



Really, when a current ran between Yb and Pt electrodes, we always observed the oxygen bubbling onto the Yb electrode. Nevertheless, the decomposition $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$ proceeds at the Yb electrode even without the current flow, but owing to a catalytic action of Yb and its oxide Yb_2O_3 which have unoccupied $5d5f$ electron shells; this property is inherent to the catalysts of redox processes [11]. This circumstance explains an insignificant initial reduction of the quantity AJ – within the first 5 min for the as-polished Yb electrode (curve 3) and within 1.5 min for the aged one (curve 2). In our opinion, this effect was caused by the separation of H^+ and OH^- ions, which had been available in H_2O before the electric circuit was closed, between the cathode (Pt) and the anode (Yb). A further saturation of the growth of AJ in time was observed. This behavior can be explained as a manifestation of the decomposition of water molecules at the Yb electrode, which is non-uniformly covered with Yb_2O_3 oxide, and the enhanced catalytic ability of Yb and Yb_2O_3 induced by a significant electric field on the surface originating from atomic-scale surface inhomogeneities.

Figure 4 also exhibits the dependences $AJ(t)$ for structures with undoped por-Si layers on n - and p -type Si, when Yb (curves 3 and 4) and Pt (curves 5 and 6) were used as counterelectrodes. In the former case, Yb is an anode, and a structure with a por-Si layer is a cathode; in the latter, a structure with por-Si is an anode, and Pt is a cathode. As is seen from Fig. 4, the quantity AJ and the character of its dependences on time essentially differ in those two cases. When Yb was used as an electrode, the initial values of AJ were larger, although being, at the same time, smaller than that in the case of the Yb–Pt systems. But the main distinction is that different characters of the dependence $AJ(t)$ are observed for the Yb–Pt system and for the Yb–por-Si(n,p) one. The current – i.e. the decomposition

rate of H_2O molecules – increases in time in the case of the Yb–Pt system; at the same time, it decreases if the system is Yb–por-Si(n,p). The latter phenomenon can be associated with the penetration of hydrogens ($\text{H}^+ + q^- \rightarrow \text{H}$) into por-Si/ (n,p) structures, so that the electrical resistance of the latter appreciably increases. The difference between curves 3 (n -Si) and 4 (p -Si) becomes obvious, if n - and p -Si are used as cathodes.

The initial values of AJ at $t = 0$ are considerably smaller for systems with the Pt electrode (curves 5 and 6) than with the Yb one. One of the reasons is some lower decomposition of H_2O molecules on the Pt electrode, which also possesses catalytic properties, in comparison with their decomposition on the Yb one; in the latter case, the decomposition starts before the electric circuit becomes closed. Moreover, the behaviors of the dependence $AJ(t)$ for Yb and Pt electrodes are substantially different. In the case of the Yb electrode, the magnitude of $AJ(t)$ decreases in time; at the same time, the pair Pt–por-Si(n) demonstrates the dependence $AJ(t)$ (curve 5) similar to that observed for the pair Yb–Pt; while, for the pair Pt–por-Si(p), the amplitude of $AJ(t)$ does not almost change (curve 6). These differences are associated, first, with the circumstance that the Yb electrode is an anode and the Pt one is a cathode, so that the por-Si(n,p) structures become either a cathode or an anode, respectively. Second, the different – by amplitude – values of the potential difference $\Delta\varphi$ between electrodes are of importance, as well as the type of por-Si conductivity, namely, the availability of electrons or holes in por-Si electrodes for the electrochemical reactions to run. Third, the electrochemical reactions at both the anode and the cathode are accompanied by the oxidation of the electrode or the penetration of hydrogen atoms into it [8, 11], which eventually modifies almost all electrode's properties and the further course of the water decomposition reaction, i.e. the $AJ(t)$ dependence.

The dependences $AJ(t)$ are changed essentially after the structures por-Si/ n -Si and por-Si/ p -Si are doped with Pd (Fig. 5). First of all, note the variation of the dependence character in the case with an Yb electrode-anode. After the Pd-doping, the “decaying” dependences $AJ(t)$ (Fig. 4, curves 3 and 4) became “growing” (Fig. 5, curves 1 and 2) and similar to that obtained in the case of the Yb–Pt pair. This evidences for a considerable catalytic decomposition of water at cathodes, the initiators of which are Pd nano-crystals. The catalytic activity of transition metals (Pt, Pd) is known to increase if the latter are in the nanocrystalline state [1,2,11]. Substantially larger values of $AJ(t)$ for

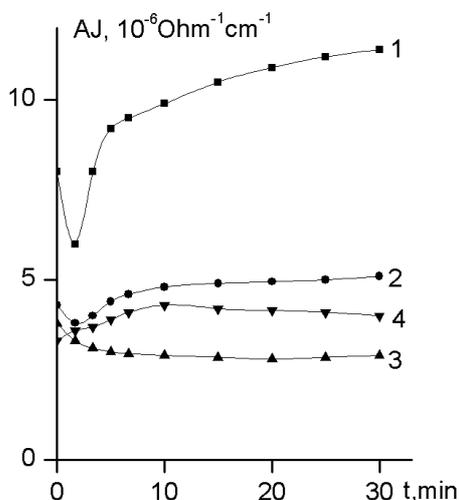


Fig. 5. Time dependences of the conductance in the Yb-por-Si(Pd)/n-Si (1), Yb-por-Si(Pd)/p-Si (2), Pt-por-Si(Pd)/n-Si (3), and Pt-por-Si(Pd)/p-Si (4) systems

por-Si(*n*)⟨Pd⟩, as compared to those for por-Si(*p*)⟨Pd⟩, are caused by a high concentration of electrons in the *n*-Si which are necessary for the H⁺ ions to be discharged.

In the case of a Pt electrode-cathode, the character of the dependences $AJ(t)$ also changed after doping with Pd. The amplitudes of $AJ(t)$ for these dependences remained small (within $(2 \div 4) \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$), but their time dependence differed drastically after doping (cf. curve 5 in Fig. 4 with curve 3 in Fig. 5 and curve 6 in Fig. 4 with curve 4 in Fig. 5). All those variations can be explained by the same reasons which were considered above.

Note that the current $J(t)$ practically does not depend on the background illumination level (from bright solar light to twilight) for all studied pairs of electrodes, which testifies that photochemical reactions play no essential role in the water decomposition. As the time grew and the magnitude of the current J became larger, the current oscillations within 2–5%, accompanied by the formation and floating-up of bubbles near the Yb electrode, were observed. Practically no hydrogen bubbles emerged on the Pt and por-Si(Pd)/*n*-Si electrodes, which testifies to the prevailing diffusion of hydrogen atoms into the depth of those electrodes (it is known that hydrogen is well soluble in Pt and Pd [11]).

According to the Faraday law, the mass m of a substance (here, OH and H) produced at an electrode is $m = kJt = kQ$, where k is the electrochemical equivalent of the substance ($k = 0.01$ for H and 0.176 for OH), and Q is a charge transferred by the current

J during the time t [12]. The calculations show that, in the case of the Yb-por-Si(Pd)/*n*-Si system, 1.06×10^{15} particles (OH or H) per cm^2 are discharged on a corresponding electrode during 30 min. According to work [13], every reaction event $\text{H}_2\text{O} \leftrightarrow \text{OH} + \text{H}$ consumes (or releases) an energy of 5.1 eV. Then, the general energy balance for the system functioning for 30 min amounts to $5.4 \times 10^{15} \text{ eV} = 8.6 \times 10^{-4} \text{ J}$. This energy gain was obtained, first of all, due to the difference between the electrochemical potentials of the electrodes in use, as well as owing to the energy balance of electrochemical reactions at electrodes and, probably, the environment heat, which support the difference between electrode potentials.

Really, the results of photovoltage V_{ph} measurements (in vacuum) testify that, after doping the por-Si/Si structures with palladium, the energy bands in *n*- and *p*-Si become bent up, which is in a good agreement with the growth of the work function φ (determined in water) for por-Si(Pd)/*p*-Si and por-Si(Pd)/*n*-Si structures in general. The growth of φ for these structures provides a larger potential difference ΔV between one of them and an Yb electrode. At the water decomposition, when OH⁻ ions are discharged at the anode (Yb) and H⁺ ones at the cathode (por-Si(Pd)), the value of ΔV has to diminish, in principle, and eventually vanish. But it is not the case, because the externally closed electric circuit, where there are no jump-like potential barriers between electrode connections owing to good ohmic contacts, supplies the cathode with electrons, thus restoring the difference ΔV . It is this process, which consumes the energy released at electrochemical reactions and, probably, the thermal energy of the environment.

5. Conclusions

1. The method of measuring the temperature dependences of the photovoltage was used to find that porous silicon fabricated on a *p*-Si wafer following the method of work [3], which provides higher equilibrium conditions in the course of *p*-Si etching process, has a perfect structure. This perfectness manifests itself in the absence of electron traps in the por-Si and por-Si(Pd) layers and at their interfaces with *p*-Si, as well as in the absence of a reconstruction in the BES system when the temperature varies. These favorable qualities of porous silicon are absent, as a rule, if it is manufactured by the method of “stain” etching or the method of anode etching by an external voltage.

2. Porous silicon fabricated in the same way but on a *n*-Si wafer has no favorable properties mentioned in item 1, because the por-Si layer is formed under nonequilibrium conditions and making use of illumination. Doping the por-Si/*n*-Si structures with palladium reduces, to some extent, the BES concentration and the concentration of traps for nonequilibrium holes at the interface between por-Si and an *n*-Si wafer.

3. The phenomenon of the water decomposition, $H_2O \rightarrow H^+ + OH^-$, occurring in the absence of any external voltage applied to the electrodes, has been revealed in the case where one of the electrodes is made of porous silicon and the counterelectrode is made of Pt or Yb. This decomposition is caused by a difference between the electrochemical potentials of the electrodes and their catalytic activity. If we compare various electrode pairs where porous silicon is included as a component, the most effective water decomposition, the yield of which grew in time, was observed for the Yb (anode)–por-Si(Pd)/*n*-Si (cathode) pair.

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ЕЛЕКТРОННІ ВЛАСТИВОСТІ ЛЕГОВАНОГО ПАЛАДІЄМ ПОРИСТОГО КРЕМНІЮ І РОЗКЛАДАННЯ НА ЙОГО ОСНОВІ ВОДИ БЕЗ ЗОВНІШНЬОЇ ЕЛЕКТРИЧНОЇ НАПРУГИ

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Резюме

Методом температурних (300–100 К) залежностей конденсаторної фото-ерс досліджено структури пористого кремнію на підкладках *p*-Si і *n*-Si, виготовлені із використанням внутрішнього джерела струму. Ці ж структури досліджували після їх легування паладієм Pd із водних розчинів PdCl₂. Якщо до легування межові шари *n*- і *p*-Si мали вигин енергетичних зон вниз, то після легування – вгору. Легування Pd збільшує концентрацію межових електронних станів (МЕС) нижче середини забороненої зони E_i і зменшує її вище E_i , а також зменшує концентрацію пасток для дірок на межі *por*-Si/*n*-Si. Досліджуючи часові залежності струму у воді між легованими Pd (або нелегованими) структурами і Yb(або Pt)-електродами, без прикладання зовнішньої напруги було виявлено ефективне розкладання води на іони OH^- і H^+ при реалізації каталітичної активності електродів Yb і *por*-Si(Pd)/*n*-Si.