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Current generation in Pd/InP structures in hydrogen medium

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The electrical properties of Pd/InP Schottky diodes and Pd-layers deposited on glass substrate by thermal evaporation in vacuum, and placed in hydrogen medium containing 10−100 vol.% of hydrogen, were studied. The current generation in Pd/InP Schottky diodes, as well as the decrease in resistance of Pd layers were observed in hydrogen medium. It is proposed that the current generation in the structures under study is due to free electrons as result of hydrogen atoms ionization. The current induced by these electrons exists in electric circuit until hydrogen is present in the environment. It is shown that the hydrogen current generators can be created based on the Pd/InP diode structure.

Keywords: palladium, Pd/InP, hydrogen, ionization, hydrogen current generator.

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1. Introduction

Palladium (Pd) is a platinum-group metal that has a unique feature in its capacity for absorption of prodigious amounts of hydrogen. Although a considerable number of research papers have been published, only the volume of hydrogen absorbed by a unit volume of palladium is normally indicated in them. Numerical values vary from one study to another, falling within the range from 350 to 2400; in most cases, the experimental conditions are not detailed [1–3]. Notably, the amount of hydrogen absorbed by palladium depends on the state of Pd (bulk crystalline, polycrystalline, or amorphous). As palladium grows more disperse (i.e., as crystallites in a polycrystal become smaller), the solubility of hydrogen in it decreases. Palladium hydrides (α-phase and β-phase, which is superconducting at a temperature of 9 K and normal pressure [6,7]) form in crystalline palladium as the amount of dissolved hydrogen increases [4,5]. These hydrides do not form in amorphous palladium and in the case when particles in polycrystalline palladium are smaller than 2.6 nm in size [8].

Discrepant (and primarily theoretical) data on the variation of electrical resistance of palladium in a hydrogen medium are found in literature. The authors of [9] argued that the overlapping of bands 4d and 5s and a high density of states in the vicinity of the Fermi level lead to predominant carrier scattering off optical phonons in palladium and, consequently, to an increase in its electrical resistance. At the same time, an increase in the density of states in the vicinity of the Fermi level should result in an elevated concentration of electrons in palladium in a hydrogen medium, and this, in turn, should induce an enhancement of conductivity and a corresponding drop in resistance. It was demonstrated theoretically in [10] that the resistance of palladium hydride PdH_x increases up to $x = 0.75$ and drops sharply after that. The electrical resistance of palladium in hydrogen may grow in both bulk samples and films due to an enhancement of the lattice constant in palladium hydrides and to the formation of microcracks in the process. It was demonstrated in [11] that microcracks form in palladium layers thicker than 40 nm on glass in a hydrogen-containing medium; when the thickness exceeded 100 nm, layers disintegrated in hydrogen under the influence of severe internal mechanical stresses.

The authors of almost all studies into the effect of hydrogen on the properties of structures with a palladium layer assume or state that hydrogen atoms ionize when H dissolves in palladium [12–16]; according to theoretical predictions, the ionization energy of hydrogen in palladium drops to zero if the distance between their atoms is on the order of the Bohr radius of hydrogen [17].

The present study is a continuation of [18] and is focused on current generation in Pd/InP structures and the conductivity of palladium layers on glass in a gaseous hydrogen-containing medium.

2. Objects under study

Two types of samples were examined: Pd/InP structures and palladium layers on glass. Palladium layers were fabricated by thermal evaporation in vacuum. The process conditions for glass and InP were identical [18,19]. The palladium layer in Pd/InP structures (Figure 1) was 1×1 mm in size and had a thickness of 250 Å. InP crystals were n-type with an electron concentration of 10^{16} cm^{-3}. Electrical contacts were deposited onto the palladium layer and the back side of the InP substrate. Samples on glass had the shape of rectangular parallelepipeds with a thickness of

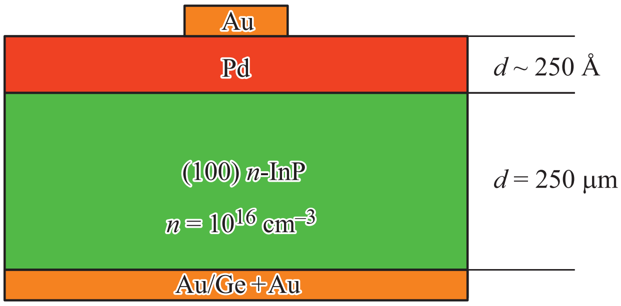

Figure 1. Diagram of the Pd/InP structure. (A color version of the figure is provided in the online version of the paper).

350 Å, a length of 20 mm, and a width of 1.5, 2.0, or 5 mm with gold contacts along the narrow faces of parallelepipeds.

The electrical conductivity of palladium layers fabricated on glass substrates was examined at a temperature of 300 K in vacuum and under atmospheric pressure in air and in gaseous mixtures of hydrogen and nitrogen with the hydrogen concentration varying from 10 to 100 vol%.

The generation of current in Pd/InP structures was studied in gaseous media containing 10–100 vol% of hydrogen at a temperature of 300 K and atmospheric pressure in the dark and under illumination by a light-emitting diode (LED) with the maximum-intensity wavelength in its spectrum being 0.9 μm, which corresponds to the absorption edge in InP.

3. Experimental results

Let us examine the magnitude of electron current emerging in a short-circuited Pd/InP structure (with zero external bias) introduced into a cuvette with a gaseous medium: 10 vol% of hydrogen in nitrogen. The cuvette was evacuated to a residual pressure of 10^{-3} mm Hg and filled with a mixture of hydrogen and nitrogen. Figure 2 presents the kinetics of currents in the studied Pd/InP structure in the dark and under various intensities of LED illumination. The band diagram of the Pd/InP structure in a hydrogen-containing medium is shown in Figure 3 to clarify the processes occurring in the electrical circuit.

When the hydrogen mixture is introduced into the cuvette, a detectable short-circuit current (3–4 μA in different studied structures; see current *1* in Figures 2 and 3) emerges in the electrical circuit with the Pd/InP structure even under zero illumination. We call this current the „hydrogen“ one, since it is produced only in a hydrogen-containing medium. When the Pd/InP structure surface is illuminated by the light-emitting diode operating at 0.9 μm, a photocurrent of non-equilibrium carriers, which has a negative direction and increases in proportion to the LED emission intensity, is produced in the shorted circuit. It follows from Figure 2 that both the photocurrent and the „hydrogen current“ through the structure have a negative direction. Thus, electrons of the „hydrogen current“ cross a potential barrier at the Pd–InP interface from palladium to indium phosphide (Figure 3). It is assumed here (just as in [18]) that the positive direction of current corresponds to

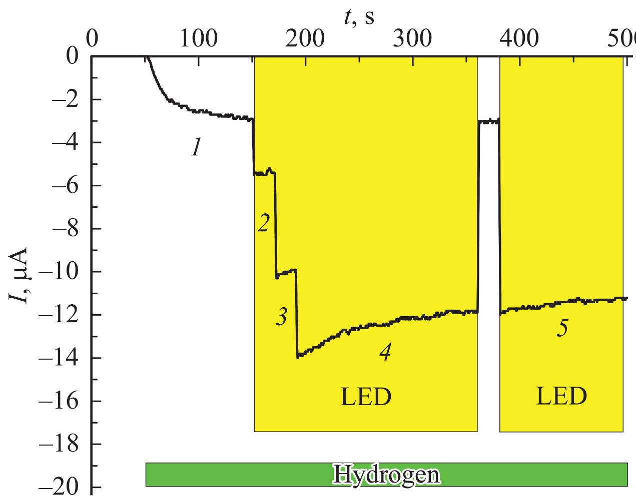

Figure 2. Kinetics of current generation in the Pd/InP structure at 300 K in a gaseous mixture with 10 vol% of hydrogen under various intensities of illumination at a wavelength of 0.9 μm by a light-emitting diode; *1* — „hydrogen current“ and *2–5* — sum of the „hydrogen current“ and the photocurrent. „LED“ areas mark the periods of time when the structure is illuminated (LED current: *1* — 0, *2* — 10, *3* — 30, and *4* and *5* — 50 mA); the „Hydrogen“ rectangle denotes the period of time when the structure is immersed in a hydrogen-containing medium.

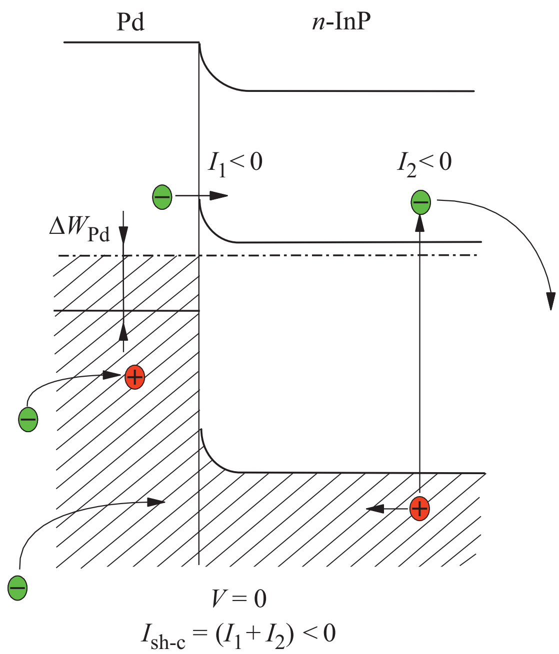

Figure 3. Band diagram of the Pd/InP structure in a hydrogen-containing gaseous medium. Zero bias is applied to the sample, and the electrical circuit is shorted. I_1 — current of electrons produced in the course of ionization of hydrogen atoms in Pd („hydrogen current“); I_2 — current of non-equilibrium electrons produced in the sample under LED illumination; and ΔW_{Pd} — variation of the work function of Pd in a hydrogen medium.

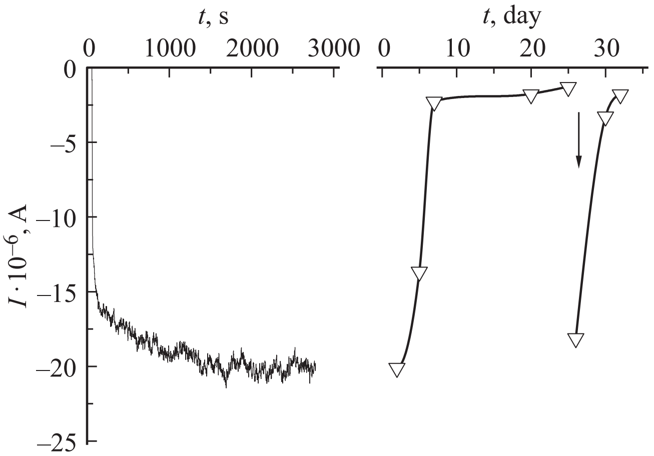

Figure 4. Lifetime of current in Pd/InP structures in a gaseous hydrogen-containing medium; the arrow denotes the moment of repeat introduction of hydrogen into the cuvette with samples on the 26th day of tests.

a positive palladium potential in measurements of current–voltage curves (forward I-V curve branch).

The current in studied structures introduced into the cuvette with a nitrogen–hydrogen mixture remains unchanged for 24 h in the dark and then drops to zero within 6−7 days. If hydrogen is fed again into the cuvette, the former level of current is reestablished with subsequent delayed (by 24 h) gradual reduction to zero within 6−7 days.

An electrical circuit of five identical Pd/InP diodes (with an overall area of $5\,mm^2$) connected in parallel was prepared in order to determine the lifetime of „hydrogen current". The test results are presented in Figure 4.

As expected, the current in the circuit retained its negative direction and increased by a factor of ~ 5 to $20\,\mu A$, while the curve of current variation in time remained the same as the one for individual diodes. The result also remained unchanged when hydrogen was fed again into the cuvette on the 26th day. This suggests that the current in the shorted Pd/InP structure circuit remains unchanged as long as a sufficient amount of hydrogen is present in the system.

The electrical properties of palladium layers deposited onto glass were examined in a hydrogen-containing medium with the aim of verifying the hypothesis regarding ionization of hydrogen atoms dissolved in palladium (and, consequently, the driving force behind the generation of „hydrogen current" in Pd/InP structures). In order to exclude the possibility of formation of microcracks affecting the resistance of palladium, the thickness of Pd layers in all the studied samples was kept below 35 nm. At such thickness levels, microcracks do not form in palladium [19].

Samples with palladium layers on glass were introduced into the cuvette that was first evacuated to 10^{-3} mm Hg and then filled with hydrogen. The current through the samples and their resistance were measured. The resistance of samples in air was normally (0.2−0.5)% higher than the corresponding values in vacuum, while the resistance of samples in a hydrogen medium decreased at all times. Notably, the observed variations in a gaseous medium with 10 and 100 vol% of hydrogen were similar. This confirms previous reports that palladium gest saturated with hydrogen to a certain level regardless of the concentration of hydrogen in the surrounding medium within the 10−100 vol% range [18,19]. Only the rate of saturation of palladium with hydrogen increased with increasing hydrogen concentration in the surrounding medium.

Figure 5 presents the variation of resistance of the examined sample of palladium on glass in a medium with 100 vol% of hydrogen. When hydrogen was fed into the cuvette, the resistance of the sample $2\,cm \cdot 0.2\,cm \cdot 3.5 \cdot 10^{-6}\,cm = 1.4 \cdot 10^{-6}\,cm^3$ in size decreased by $1260\,\Omega$ at a voltage across the sample of 0.1 V. In our view, this pronounced change in resistance of a thin Pd film is attributable to ionization of hydrogen atoms dissolved in the palladium layer. The emergence of additional electrons in the circuit probably leads to a dramatic (five-fold) reduction in resistance of the Pd layer.

A sustained current flow in a short-circuited Pd/InP system implies the presence of an external energy source. Hydrogen acts as such a source. It is our understanding that the interaction of hydrogen with the Pd layer may be split tentatively into two phases. The first one is the saturation of palladium with hydrogen molecules (when H_2 is fed into the evacuated sealed chamber). The duration of this phase is 1−3 s, and a constant current is established in the short-circuited system within the same time frame. The second phase is the reaction of hydrogen with the palladium layer (production of hydrides PdH_x, α- and β-phase [20]).

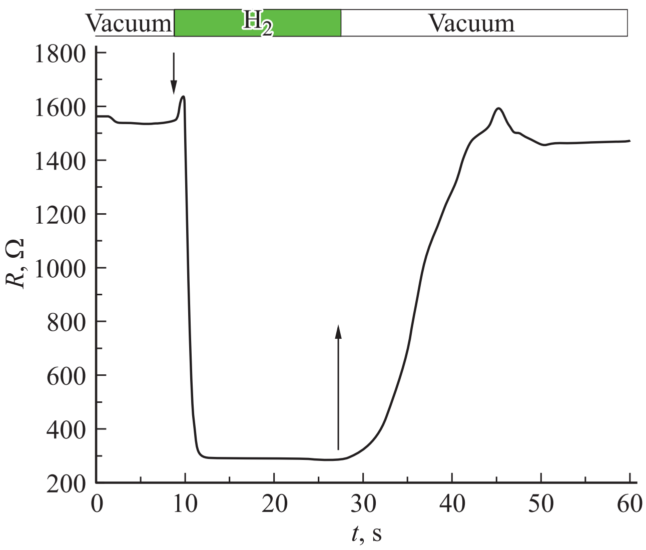

Figure 5. Variation of the resistance of a palladium layer on glass in a medium with 100 vol% of hydrogen. The sample size is 20 mm × 2 mm × 350 Å, and the voltage across the sample is 0.1 V. The green rectangle marks the period of time when the sample was exposed to hydrogen; arrows denote the moments of introduction and pumping-out of hydrogen. (A color version of the figure is provided in the online version of the paper).

This is an exothermal (energy-releasing) reaction [21–23]). The formation of PdH_x crystallites was verified by X-ray data in [24]. The onset of formation of PdH_x crystallites coincides with the moment of contact between H_2 and the Pd layer. Thus, hydrogen from the gas phase should migrate gradually into the solid phase of palladium hydride. The amount of hydrogen in the gas phase will decrease gradually, and we will observe a reduction in current in the system (in addition, the leakage of hydrogen through rubber seals of the measurement chamber also reduces the amount of hydrogen in the measurement system). If the system is sealed hermetically, the number of hydrogen atoms will remain constant and only the ratio of hydrogen amounts in solid and gas phases will change. In a Pd/InP Schottky diode with a thin Pd layer, electrons and protons produced upon contact between hydrogen and the Pd layer will be separated at the Schottky barrier and produce electromotive force. If a Pd/InP Schottky diode is short-circuited, an electrical current depending on the concentration of hydrogen will be produced in the system.

4. Conclusion

The generation of current in Pd/InP diodes and the variation of resistance of palladium layers on glass substrates in a hydrogen-containing gaseous medium were examined.

In our view, hydrogen atoms ionize upon contact between hydrogen and the palladium layer, producing protons and electrons and inducing a change in the palladium layer resistance. In a Pd/InP Schottky diode, these newly produced electrons and protons are separated at the Schottky barrier and generate electrical current in a short-circuited system. The magnitude of this current depends on the concentration of hydrogen in the system.

Conflict of interest

The authors declare that they have no conflict of interest.

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