Current generation in Pd/InP structures in hydrogen medium

© V.A. Shutaev[1], E.A. Grebenshchikova[1], V.G. Sidorov[2], Yu.P. Yakovlev[1]

[1] Ioffe Institute,
194021 St. Petersburg, Russia
[2] LLC „Independent Business & Scientific Group",
194021 St. Petersburg, Russia
E-mail: vadimshutaev@mail.ru

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The current generation mechanism in Pd/InP Schottky diodes has been studied in the range of $90-300$ K in vacuum, hydrogen-nitrogen mixture of concentration from 4 to 100 vol.%, and under illuminating of the structures by LED with the wavelength of $0.9\,\mu$m, corresponding to the absorption edge in InP. It was shown that at low temperature ($T = 90$ K) $I-V$ characteristics of the structures in vacuum have rectifying character with the barrier height of $130-150$ meV. In hydrogen-nitrogen medium the barrier height decreases almost to zero with increasing the temperature to 300 K due to palladium work function decreasing. It was demonstrated that under simultaneous impact of illumination ($\lambda = 0.9\,\mu$m) and hydrogen-nitrogen mixture there are two opposite directed electron flows in the structures, one of which is related to the LED illumination and the other one to hydrogen absorption in palladium layer.

Keywords: palladium, Pd/InP, hydrogen, work function, potential barrier.

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1. Introduction

Palladium (Pd) has a unique capacity for absorption of large amounts of hydrogen (a certain unit Pd volume may absorb up to a thousand unit volumes of hydrogen [1,2]). What is more, palladium absorbs hydrogen selectively from a mixture of gases, which is why it is used in various types of hydrogen sensors to detect hydrogen or measure its concentration in the ambient environment [3,4].

Palladium saturated with hydrogen has been studied for a long time and fairly extensively. It was found that several characteristics of palladium change in the process of hydrogen absorption: the work function decreases [5]; the structure is altered (palladium hydrides form [6,7], thus causing a significant increase in lattice constant [8]); the electric resistance changes (superconductivity may emerge [9–11]); the optical properties become modified [12,13].

At the same time, the mechanisms of interaction between hydrogen and palladium evidently require further study. It is assumed that hydrogen molecules in palladium dissociate into atoms [7], which are then supposedly ionized with the emergence of free electrons and free or bound protons [14]. However it be, theory allows for reduction of the hydrogen ionization energy in Pd to zero [15]. Although direct experimental evidence of hydrogen ionization in Pd are lacking, ionization is assumed fairly often in the interpretation of properties of structures containing a Pd layer [16,17].

The present study is focused on the examination of mechanisms of current generation in Pd/InP structures at different temperatures in vacuum and in a gaseous environment with hydrogen, under an electrical bias and without it, and in darkness and under illumination.

2. Experiment

The studied Pd/InP structures were fabricated in accordance with the procedure outlined in [3,4]. The substrates for these structures were n-InP crystals with an electron density of $10^{16}\,\mathrm{cm}^{-3}$. Palladium layers with thickness $d_{\mathrm{Pd}} = 25$ nm were deposited onto InP by thermal evaporation in vacuum. The current–voltage curves (CVCs) of structures were measured in the temperature interval of $90-300$ K in vacuum and in gas mixtures of hydrogen with nitrogen at hydrogen concentrations of $4-100$ vol% in a tightly sealed cryostat, which blocked external light, and under illumination with LED radiation with a wavelength of $0.9\,\mu$m that corresponds to the InP absorption edge. The generation of currents under zero external electrical bias was studied in complete darkness and under illumination with a constant supply of nitrogen–hydrogen mixtures into a cryostat with structures that was evacuated to a residual pressure of 10^{-3} Torr. A KEITHLEY-2600A (Keithley Instruments, Inc.) sourcemeter was used in the measurement of electrical and photovoltaic characteristics of Pd/InP structures. The obtained data were fed to a computer.

Figure 1 presents the current–voltage curves for a typical Pd/InP structure measured under different conditions: black CVCs were measured in darkness and in vacuum (curves *1, 3*); green CVCs were measured in darkness and in hydrogen atmosphere (curves *2, 5*); red CVCs were measured under illumination with LED radiation with a wavelength of $0.9\,\mu$m (curves *4, 6*, where *4* and *6* correspond to experiments in vacuum and in hydrogen, respectively).

Figure 2 shows the current kinetics in the Pd/InP structure in an environment with 10 vol% of hydrogen

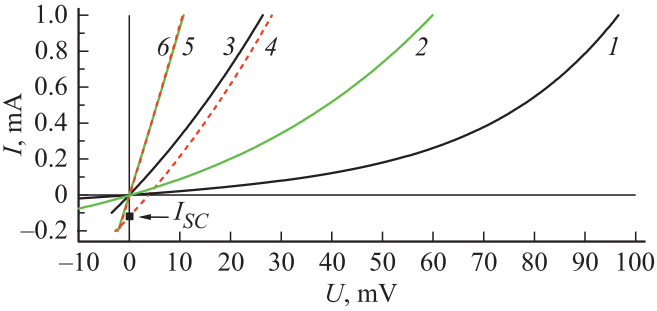

Figure 1. Current–voltage curves for the Pd/InP structure: *1* and *2* — at 210 K in darkness (*1* — in vacuum; *2* — in hydrogen); *3, 4, 5,* and *6* — at 300 K (*3* — in vacuum in darkness; *4* — in vacuum under illumination with LED radiation with a wavelength of 0.9 μm at an LED current of 50 mA; *5* — in a gas mixture with 10 vol% of hydrogen in darkness; *6* — in a gas mixture with 10 vol% of hydrogen under illumination with LED radiation with a wavelength of 0.9 μm at an LED current of 50 mA). (A color version of the figure is provided in the online version of the paper).

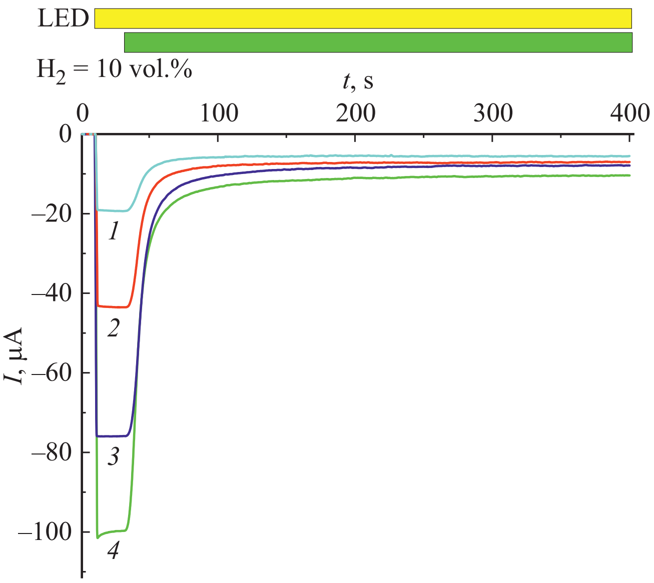

Figure 2. Kinetics of current generation at 300 K in the Pd/InP structure in a gas mixture with 10 vol% of hydrogen under different intensities of illumination with LED radiation with a wavelength of 0.9 μm. The yellow bar indicates the time interval of LED illumination (LED current, mA: *1* — 10, *2* — 20, *3* — 30, *4* — 50); the green bar denotes the time interval within which the structure was kept in a gaseous environment with hydrogen.

in darkness and under different intensities of illumination. When hydrogen was fed into the cryostat, the Pd/InP structure currents under any illumination conditions reached saturation in a time on the order of a minute and persisted until hydrogen remained in the cryostat. Notably, the currents increased proportionally to the LED illumination intensity. Without hydrogen, the currents returned to their former values.

3. Analysis of results

A close-up of the features of curves measured in hydrogen in darkness (*5*) and under illumination (*6*) is shown in Fig. 3. These CVCs are specific in that they intersect (the intersection point is denoted with a black square and an arrow) as the forward bias increases. This implies that two currents flowing in opposite directions are present in the structure. When the external voltage is adjusted, the ratio of these currents changes.

Figure 4 presents the schematic band diagrams of the Pd/InP structure that provide an explanation for the measured CVCs. Let us track the electron flows in the structure. The positive direction of flow of electrons is assumed to represent their motion through the barrier from InP to Pd (current I_1 in the band diagrams in Fig. 4) that corresponds to a forward electrical bias applied to the structure (positive potential at Pd). Current I_2 in the band diagrams corresponds to the current of non-equilibrium electrons emerging in InP under illumination with edge radiation.

At a low temperature of 210 K, the CVCs both in vacuum and in hydrogen (Fig. 1, curves *1* and (*2*) are rectifying in nature with a barrier height of ~ 50 and ~ 30 meV, respectively. At 90 K, the barrier height reaches 150 and 130 meV. At room temperature, the CVC measured in vacuum in darkness (Fig. 1, curve *3*) becomes almost linear. The potential barrier becomes substantially transparent, but does not vanish completely, since it separates non-equilibrium carriers generated in InP under illumination (Fig. 4, *a*, current I_2 is negative and equal to short-circuit current I_{SC}, Fig. 1). Under forward bias, non-equilibrium electron current I_2 is directed opposite to forward diode bias current I_1 (Fig. 4, *b*). The net current through the structure is $I = I_1 - |I_2|$, the CVC shifts toward lower currents, and the CVC measured under illumination (Fig. 1, curve *4*) becomes closer to the CVC measured in darkness (Fig. 1,

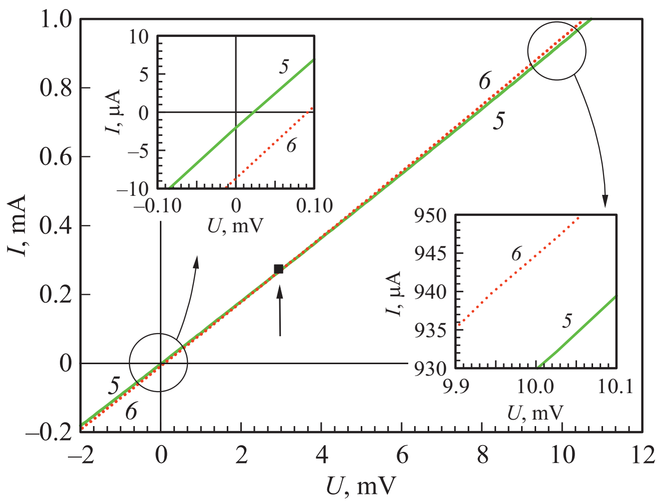

Figure 3. Current–voltage curves of the Pd/InP structure measured in a gas mixture with 10 vol% of hydrogen in darkness (*5*) and under illumination (*6*); the numbering and coloring of curves is preserved from Fig. 1.

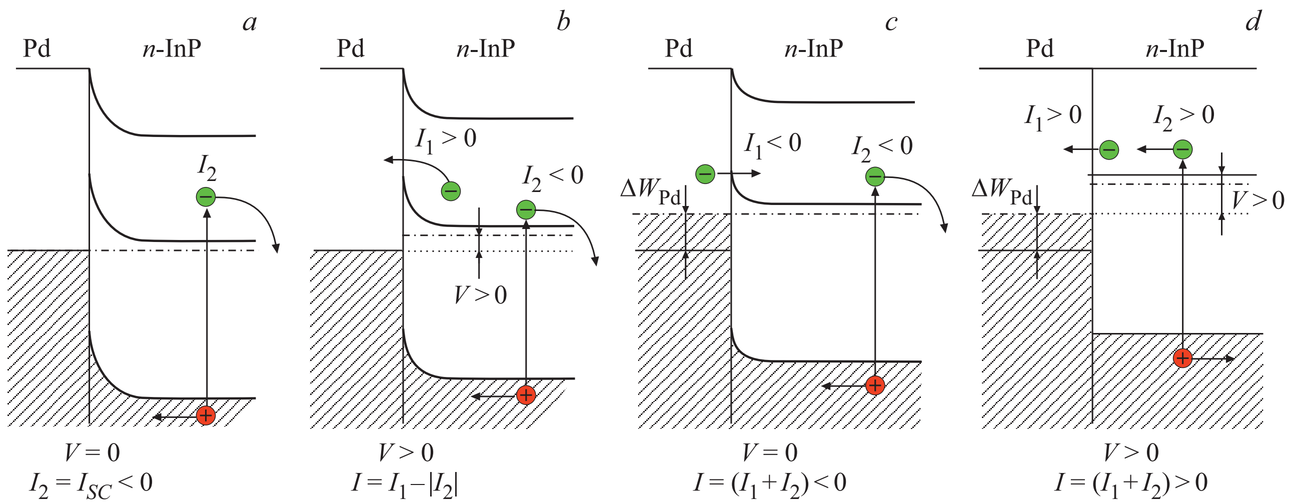

Figure 4. Schematic band diagrams and diagrams of electron currents in the Pd/InP structure: *a* and *b* — in vacuum (*a* — external voltage $V = 0$ is applied to the structure; *b* — external voltage $V > 0$); *c* and *d* — in hydrogen (*c* — $V = 0$; *d* — $V > 0$); I_1 is the current of equilibrium electrons; I_2 is the current of non-equilibrium electrons generated by LED radiation.

curve *3*) as the forward bias increases, since a fraction non-equilibrium electrons is entrained by the forward bias field and transported through the barrier from InP to Pd.

In a hydrogen environment, the work function of palladium decreases (Figs. 4, *c* and *d*, ΔW_{Pd}), the potential barrier at the Pd/InP interface vanishes almost completely, and the CVCs measured in darkness and under illumination become linear and almost coincident (Fig. 1, curves *5* and *6*). A thorough examination of the close-up of these CVCs (Fig. 3) revealed that a low barrier still persists at the interface, since the non-equilibrium electron current under zero bias is negative (Fig. 2, curve *6*, Fig. 4, *c*, current I_2). Under forward bias, the potential barrier at the Pd/InP interface vanishes completely, the external field turns electron currents I_1 and I_2 in the positive direction (Fig. 4, *d*), and the CVCs measured in darkness and under illumination (*5* and *6*) intersect. The current produced under illumination (Fig. 3, curve *6*) becomes higher than the dark current (Fig. 3, curve *5*).

It should be noted that the observed values of currents in Pd/InP structures depended only weakly on the hydrogen concentration in the ambient environment, which varied within the range from 4 to 100 vol%. This implies that palladium is saturated with hydrogen to a certain specific extent under any conditions, and the concentration of hydrogen in the ambient environment affects only the rate of this process. This also suggests that hydrogen absorbed by palladium is in the bound state. If this were not the case, a clear relation between the concentration of hydrogen in the ambient environment and its concentration in palladium would be observed. The following experimental fact provides another indication that hydrogen in palladium is in the bound state: palladium gets saturated with hydrogen within a time ranging from several microseconds to seconds, while the release of absorbed hydrogen from palladium proceeds within several minutes (or even tens of minutes).

In addition, the abrupt change of Pd properties in a hydrogen atmosphere points at the formation of palladium hydride (PdH_x), which differs in its characteristics from pure palladium. However, the properties of a palladium layer are restored following hydrogen desorption [12].

4. Conclusion

Pd/InP structures were fabricated, and their current–voltage curves were examined in the temperature interval of 90–300 K in vacuum and in nitrogen–hydrogen mixtures (with a hydrogen concentration of 4–100 vol%) in darkness and under illumination with LED radiation with a wavelength of 0.9 μm that corresponds to the InP absorption edge.

At a low temperature of 90 K, the current–voltage curves of these Pd/InP structures both in vacuum and in a hydrogen environment are rectifying in nature with a barrier height of 150 and 130 meV, respectively. Since the work function of palladium saturated with hydrogen decreases, the barrier height drops almost to zero at higher temperatures in a hydrogen environment.

The photocurrent produced in the Pd/InP structure under illumination with radiation with a wavelength corresponding to the InP absorption edge decreases sharply in a hydrogen environment to a value proportional to the illumination intensity. This effect is related to the reduction in height of the potential barrier at the Pd/InP interface, which, in turn, is caused by the fact that the work function of palladium decreases in a hydrogen environment.

The weak dependence of currents observed in the Pd/InP structure on the concentration of hydrogen in the ambient environment suggests that the process of saturation of palladium with hydrogen stops at a certain specific level and that hydrogen absorbed by Pd is in the bound state.

Conflict of interest

The authors declare that they have no conflict of interest.

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