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Hydrogen current generator based on palladium nanofilms

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A hydrogen current generator based on palladium nanofilms obtained by thermal-vacuum sputtering on a glass slide has been proposed and created for the first time. Constructively, the nanofilms are divided into two parts. The first part is the nanofilm open surface for interaction with hydrogen, and the other one is covered with a protective layer preventing direct interaction with hydrogen. It was found that in the 100 % hydrogen atmosphere the open-circuit voltage of 10 μV is generated in the structure, while the short-circuit current reaches $\sim$ 300 nA. It is supposed that the hydrogen current generation is related to formation of palladium hydride (PdH_x) on the Pd nanofilm open area and emergence of a potential barrier on the Pd/PdH_x interface.

Keywords: hydrogen, palladium, palladium hydride, ionization, hydrogen current generator.

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For the first time we have reported creation of a hydrogen current generator based on the Pd/InP Schottky diode in [1] where the element sensitive to hydrogen was a palladium layer. To our mind, when hydrogen interacts with the palladium nanofilm, hydrogen atoms get ionized with formation of protons and electrons which get separated at the Pd/InP Schottky barrier. Separation of charge carriers at the barrier results in generation of short-circuit electric current.

As is known, the hydrogen-palladium interaction gives rise to palladium hydride PdH_x [2–10]. The palladium hydride properties differ from those of pure palladium. For instance, when hydrogen is absorbed by palladium, variations in its optical transparency [2.7], magnetic susceptibility [6.7], plasticity [4.8.10], and electron work function [8.11] take place. Some theoretical papers discuss the possibility of high-temperature superconductivity of PdH_x [3,6]. In addition, the literature often presents an assumption about hydrogen ionization in palladium during the Pd $\rightarrow$ PdH phase transition [4,9]; however, the presence of this phenomenon in the Pd$-$H system has not been confirmed experimentally up to date. In this study, we decided to use the effect of the palladium hydride formation in the hydrogen atmosphere to develop the hydrogen current generator based on the palladium nanofilm.

To create the hydrogen current generator, Pd nanofilms 20$-$40 nm thick were created by thermal-vacuum sputtering on glass substrates 1.5 mm thick (glass slides). The palladium film surface area was 1×2 cm. At the sample butt ends, Au layers 0.2$-$0.3 μm thick were applied to the Pd film surface to ensure electrical contact with copper leads of the measuring device. Half of the sample area 1×1 cm in size was tightly covered with a protective Scotch-tape-based polymer film (Fig. 1).

The prepared generator specimen was placed in a sealed cell. The I-V characteristics were studied in vacuum (10^{-2} Torr) and in hydrogen (100 % H_2) using source-measure unit Keithley 2601A. In the hydrogen atmosphere, molecular hydrogen directly contacted with the Pd film open surface; at the same time, the covered part of the Pd film did not contact with hydrogen. All the measurements were performed at 300 K.

Consider time variations in current (Fig. 2, *a*) and electromotive force (EMF) (Fig. 2, *b*) in the sample placed first in vacuum and then in hydrogen. In vacuum, no generation of electric current or EMF was observed in the structure. After feeding 100 % hydrogen into the vacuum cell, electric current begins increasing at the 30th second; EMF increases simultaneously. In the current growth curve, two sections may be distinguished: a section of rapid current growth (0 to 150 nA) over a time period of 30 to 50 s, and a section of slow growth (150 to 300 nA) over a period of 150 to 1000 s. EMF increases from 0 to $\sim$ 10 μV over 30 s. The existence of two current growth sections is probably associated with the phase transition in palladium hydride from the α- to β-phase (while hydrogen is being absorbed in palladium).

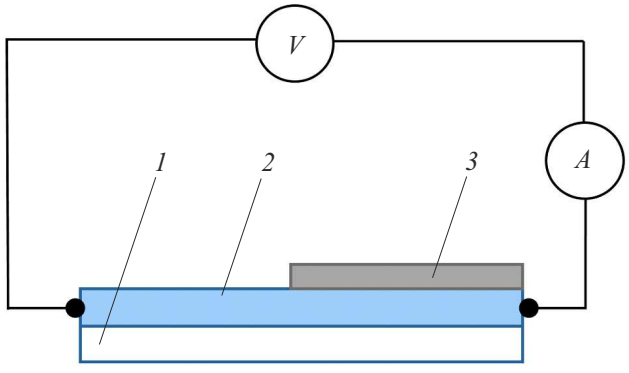

Figure 1. Schematic diagram of the experiment. *1* — glass slide, *2* — palladium, *3* — protective coating.

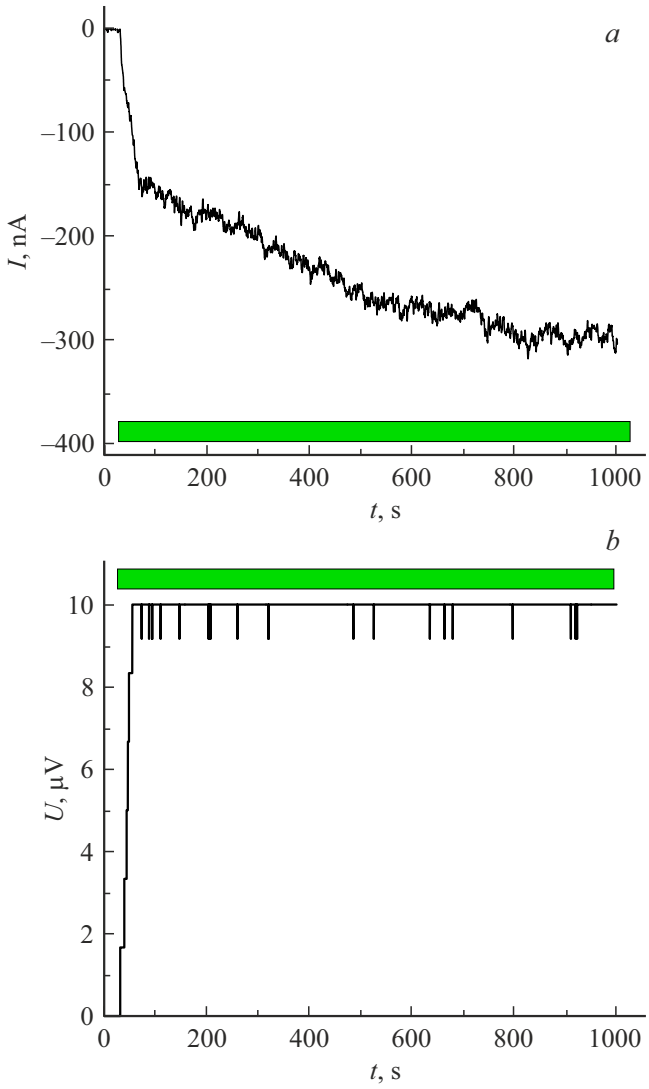

Figure 2. Generation of current (*a*) and open-circuit EMF (*b*) in the Pd/PdH system. The colored area indicates that the structure is in the hydrogen atmosphere.

The current and EMF generation continues as long as the hydrogen amount in the system remains sufficient.

Consider the I-V characteristic of the structure under study in vacuum and hydrogen (Fig. 3). Assume the positive direction of current of electrons to be that of their motion from the unprotected part of palladium towards the palladium film part under protective coating (the positive potential is on the palladium film under protective coating). In vacuum, the I-V curve is of the linear (ohmic) character (Fig. 3, *1*). When hydrogen is supplied to the cell, the I-V characteristic shape transforms from the linear (Fig. 3,*1*) to diode-type one (Fig. 3, *2*). The I-V curve obtains the diode-type character at the 30th second and slowly changes with time towards an increase in open-circuit EMF.

The inset shows the open-circuit EMF (V_{oc}) and short-circuit current (I_{sc}) on an enlarged scale. When 100 % hydrogen is supplied to the cell, EMF and current arise in the structure shown in Fig. 1. EMF is $\sim 30\,\mu$V, while short-circuit current is ~ 400 nA. These values are comparable in order of magnitude with those in Fig. 2 for the period when the sample is in the hydrogen atmosphere.

The EMF and current emergence in the palladium nanofilm may be connected with two factors. The first one is Pd interaction with molecular hydrogen; the second one is the Pd film subdivision into two parts, namely, that with the open surface for contacting with H_2 and that with protective coating preventing contacting with H_2. As is known, the hydrogen contact with the Pd layer gives rise to palladium hydride (PdH_x) whose work function is $\sim 0.3-0.5$ eV lower than that of palladium [11,12]. Thus, at the interface between the palladium open surface and surface with protective coating, a potential barrier may arise as a result of contact between two materials with different work functions. In our case, the barrier emerges between the palladium part under the protective coating and the rest part exposed to hydrogen and being transformed to palladium hydride. The potential barrier formation manifests itself in changing the sample I-V curve type from ohmic one in vacuum (*1* in Fig. 3) to diode one in hydrogen (*2* in Fig. 3). We believe that the molecular hydrogen interaction with the palladium nanofilm open surface promotes hydrogen ionization with formation of protons and electrons which get separated at the Pd/PdH_x barrier. Note that, when the cell gets unsealed, hydrogen is desorbed from the palladium hydride with simultaneous decay of the potential barrier and attenuation of the current and EMF.

Thus, it is possible to create on the base of palladium nanofilms passive hydrogen sensors on the one hand and new-generation hydrogen current generators on the other hand.

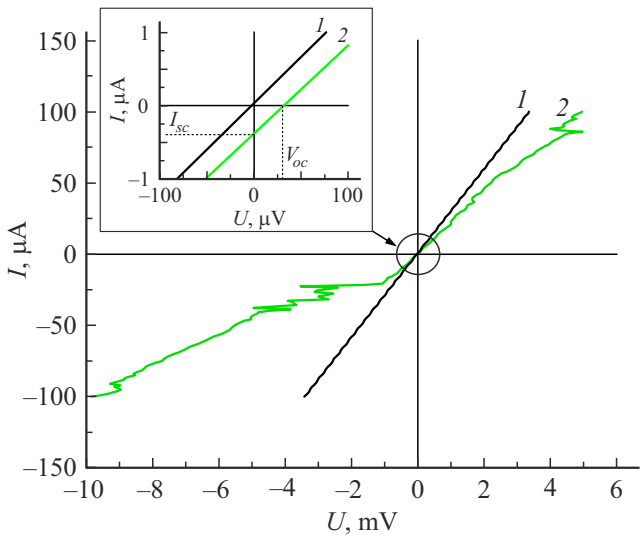

Figure 3. I-V characteristics of Pd *1* and Pd/PdH_x *2*. The inset shows the I-V curve on an enlarged scale (V_{oc} — open-circuit EMF, I_{sc} — short-circuit current).

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] V.A. Shutaev, V.G. Sidorov, E.A. Grebenshchikova, Yu.P. Yakovlev, Semiconductors, **58** (1), 34 (2024). DOI: 10.61011/SC.2024.01.58119.4740.
[2] V.A. Shutaev, E.A. Grebenshchikova, V.A. Matveev, N.N. Gubanova, Yu.P. Yakovlev, Opt. Spectrosc., **131** (3), 391 (2023). DOI: 10.61011/EOS.2023.03.56191.4368-22.
[3] Q. Wang, S. Zhang, J. Guo, P. Chen, Front. Mater., **11**, 01 (2024). DOI: 10.3389/fmats.2024.1365526
[4] A. Kawasaki, S. Itoh, K. Shima, T. Yamazaki, Mater. Sci. Eng. A, **551**, 231 (2012). DOI: 10.1016/j.msea.2012.05.011
[5] T. Ube, S. Hasegawa, T. Horie, T. Ishiguro, J. Mater. Sci., **56**, 3336 (2021). DOI: 10.1007/s10853-020-05419-3
[6] S.S. Setayandeh, C.J. Webb, E. MacA. Gray, Prog. Solid State Chem., **60**, 100285 (2020). DOI: 10.1016/j.progsolidstchem.2020.100285
[7] J.I. Avila, R.J. Matelon, R. Trabol, M. Favre, D. Lederman, U.G. Volkmann, A.L. Cabrera, J. Appl. Phys., **107**, 023504 (2010). DOI: 10.1063/1.3272047
[8] C.C. Ndaya, N. Javahiraly, A. Brioude, Sensors, **19** (20), 4478 (2019). DOI: 10.3390/s19204478
[9] Yu.M. Koroteev, O.V. Gimranova, I.P. Chernov, Phys. Solid State, **53** (5), 896 (2011). DOI: 10.1134/S1063783411050143.
[10] G.I. Zhirov, Fizika i tekhnika vysokikh davleniy, **13**, (2), 71 (2003). (in Russian)
[11] K. Okuyama, N. Takinami, Y. Chiba, S. Ohshima, S. Kambe, J. Appl. Phys., **76** (1), 231 (1994). DOI: 10.1063/1.357132
[12] V.A. Shutaev, V.G. Sidorov, E.A. Grebenshchikova, L.K. Vlasov, A.A. Pivovarova, Yu.P. Yakovlev, Semiconductors, **53** (10), 1389 (2019). DOI: 10.1134/S106378261910018X.

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