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Hydrogen Influence on Electrical and Photoelectrical Properties of InP/Pd Thin-film Structures obtained by Sol-Gel Method

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The current-voltage characteristics and photoelectric properties of semiconductor structures containing Pd nanoparticles in thin films synthesized by the sol-gel method on an *n*-InP substrate have been investigated. The experimental results show that in presence of hydrogen the cut-off voltage changes. The photovoltage and photocurrent upon illumination of the structure with an LED ($\lambda = 0.9\,\mu$m) and pulsed exposure to hydrogen change, that was observed earlier for hydrogen-sensitive Pd/*n*-InP Schottky diodes. The prospects of using the structures under study as a sensitive element for hydrogen sensor are discussed.

Keywords: Pd nanoparticles, sol-gel method, hydrogen, Schottky diode, hydrogen sensor.

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At present, structures containing palladium in thin films on the surface of semiconductors are actively studied as sensitive elements of hydrogen sensors. The most widespread are solid-state sensors with metal oxides as a gas-sensitive layer on a silicon or ceramic substrate with a thin catalytic layer of palladium nanoparticles deposited directly on the metal oxide layer. This group of sensors is characterized by a low detection threshold, a mostly short response time of the order $t = 1-10$ s and long recovery. Recovery time varies from 10 s to 20 min depending on manufacturing techniques. The disadvantages include the need to heat the sensing element to 300−550°C [1].

Another group of sensors is based on semiconductors with a sensitive palladium layer (metal–dielectric–semiconductor structures, field-effect transistors or Schottky barrier structures). The main advantages of these sensors are the ability to detect hydrogen at room temperature, the high sensitivity to hydrogen and the low power consumption.

The sensors operation is based on various physical phenomena. Most hydrogen sensors are based on detecting changes in their electrical characteristics in the presence of hydrogen [1–3] or photovoltaic characteristics [4–6]. The significant advantage for practical applications of using photovoltaic characteristics to detect hydrogen in the environment is shown in [4] (see also references therein). The palladium layer in such gas-sensor devices is generally formed by various methods.

One promising area of materials technology is the sol-gel technology, which can relatively easily synthesize nanocomposite materials and modify the surface of sensitive layers. For the deposition of nanoscale films on the surface of semiconductor materials, specially prepared sols such as those based on tetraethoxysilane are used. Silicon tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS) is the main traditional component used in sol-gel technology. TEOS is a relatively inexpensive reagent and has been successfully used as a precursor in the silica matrix formation, in which metallic nanoparticles are evenly distributed. TEOS-based sols can be easily modified with different compounds. Using this method makes it possible to obtain planar film structures in which Pd nanoparticles are evenly distributed in the silica matrix (SiO_2@Pd) [7]. The use of sol-gel technology opens up the possibility of increasing the specific surface area of the sensor element, varying the palladium content in the catalytic layer by dosing Pd compounds in silica as well as allowing the formation of gas-sensitive layers on substrates of different geometries.

In works [4,5], we studied the photovoltaic characteristics of Pd/InP and Pd−oxide−InP structures, in which Pd layer was deposited by thermal vacuum deposition. The purpose of this work is to investigate the electrical and photovoltaic characteristics of structures containing Pd nanoparticles in silica films produced by sol-gel synthesis on *n*-InP substrate.

The sol was synthesized by slow acidic (in the presence of HCl) hydrolysis of tetraethoxysilane $Si(OC_2H_5)_4$, its volume fraction in the sol was 3 vol.%. The palladium chloride $PdCl_2$ was pre-transformed into H_2PdCl_4 by dissolving in ethanol acidified with HCl [8]. The desired amount of this solution was then added to the TEOS solution, using a mixture of ethanol and butanol-1 as solvents. The resulting sol aged to a state of reproducible film formation over several weeks. The sol was applied to the InP substrate by spinning rate of 1700 rpm for 30 s to form thin films (spin-on-glass), after which they „heat setting“

by annealing at 130°C for 50 min in an air environment. After heat treatment, the polysiloxane film was mechanically hardened as it transformed into a silica matrix [9] containing palladium nanoparticles with a molar ratio of 20 mol Pd to 100 mol SiO_2. These samples are designation by simbol n-InP/SiO_2@20Pd. The film thickness after heat treatment was determined based on X-ray reflectometry results. X-ray studies were carried out using a Rigaku SmartLab diffractometric complex (PNPI, Gatchina), equipped with a set of optics and a goniometer allowing for reflectometry studies. A rotating copper anode (CuK_α, 45 kV, 200 mA) was used as the X-ray source for the diffractometer. The thickness of the synthesized films, according to X-ray reflectometry, was 46.8 ± 0.3 nm.

The phase composition of the films was determined from diffraction patterns obtained in grazing incident X-ray beam geometry (GiXRD). It was found that the doping impurity (palladium compounds) was evenly distributed in the polysiloxane film as nano-inclusions already at the deposition stage [10,11]. With the influence of alcohols, Pd^{2+} to Pd^0 is reduced, and X-ray-visible metallic palladium nanoparticles form during heat treatment. It was observed that after thermofixation at $T = 130$°C, the diffraction patterns show peaks of a face-centered cubic lattice of palladium. The array parameter derived from X-ray diffraction data was $a = 3.89 \pm 0.01$ Å, which agrees well with the ICDD crystallographic database: $a = 3.890$ Å(card N 00-005-0681). The crystallite size was related to the size of the coherent scattering region, which was calculated using the Debye–Sherrer formula [12,13]. The crystallite size in the films (SiO_2@20Pd), according to the data obtained from the broadening of the Bragg peaks, was ~ 8 nm.

The samples under study are made on n-InP substrate ($n \approx 10^{16}\,\mathrm{cm}^{-3}$), substrate thickness $d \approx 300\,\mu$m. Before applying the film, the substrate was degreased by boiling in organic solvents and washed in deionized water. Contacts (Au) in the shape of a square with side $100\,\mu$m to the SiO_2@20Pd film and contacts (Cr/AuGe/Au) to the back side of the substrate were made by thermal-vacuum deposition method in vacuum. The n-InP/SiO_2@20Pd structure was divided into individual 1.4×1.7 mm chips, which were mounted on standard TO-18 houses. Current-voltage characteristics (CVC) of fabricated diodes were studied in air and hydrogen atmosphere (10 vol.% in nitrogen-hydrogen gas mixture) at 300 K (positive potential applied to Pd film) using a KEITHLEY-2600A source/measurer (Keithley Instruments, Inc.). The photovoltaic properties were studied by illuminating the structure with LED emission at a wavelength $\lambda = 0.9\,\mu$m, corresponding to the absorption edge in InP, and by pulsed hydrogen supply.

Ten diode structures were made from the n-InP/SiO_2@20Pd structure and their CVCs were subsequently measured. The characteristics of two typical diodes are shown in Fig. 1.

The figure shows that the studied diodes have a rectifying character of CVC with a cut-off voltage of 0.3 V (1) and 0.45 V (2). Experimentally, the height of the potential barrier in metal–semiconductor and metal–dielectric–semiconductor structures is usually identified with the value of the cut-off voltage $U_{cut-off}$ (expressed in eV), determined by extrapolating to zero current the linear section of the CVC at large forward bias on the structure [5]. We also studied the hydrogen effect on the CVC of n-InP/SiO_2@20Pd diode structures (dashed lines in Fig. 1). Fig. 1 shows that the structure characteristics change in the presence of hydrogen: the cut-off voltage of the studied diodes decreases by ~ 0.2–0.35 V. We attribute this result to a decrease in work function of Pd, which leads to a decrease in the height of the potential barrier in the structure [5].

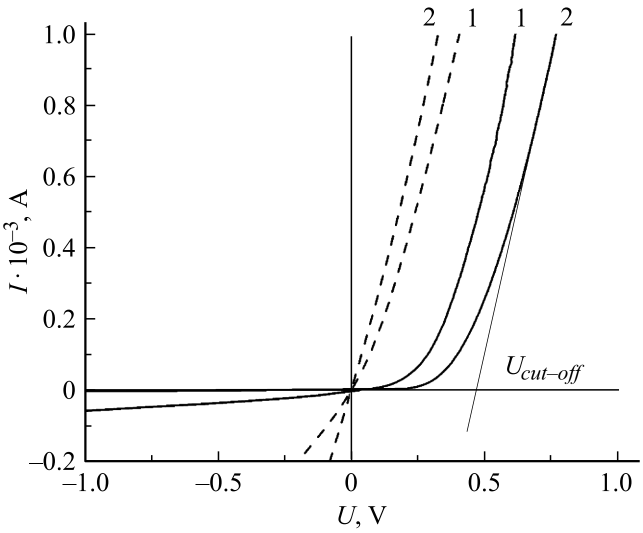

Figure 1. Current-voltage characteristics of the n-InP/SiO_2@20Pd structure measured at $T = 300$ K in an air atmosphere (solid lines) and in a nitrogen-hydrogen gas mixture atmosphere with hydrogen content 10 vol.% (dashed lines).

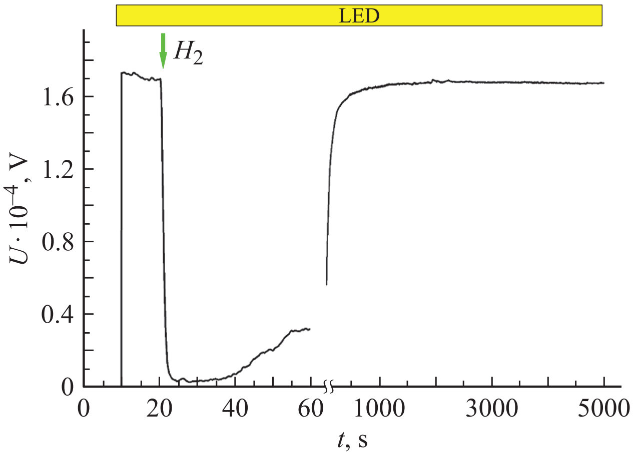

Figure 2. Kinetic variations of photovoltage of the structure n-InP/SiO_2@20Pd when illuminated by LED emission ($\lambda = 0.9\,\mu$m) and pulsed hydrogen supply.

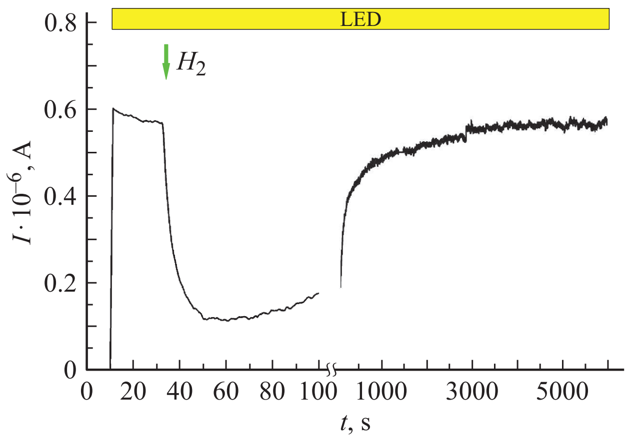

Figure 3. Kinetic variations of the photocurrent of the structure n-InP/SiO$_2$@20Pd when illuminated by LED emission ($\lambda = 0.9\,\mu$m) and pulsed hydrogen supply.

The kinetic variations of photovoltage and photocurrent for typical samples from n-InP/SiO$_2$@20Pd structure are shown in Figs 2 and 3. Measurements were made in a cryostat ($T = 300$ K) in both air and hydrogen atmospheres (in a 90 vol.% N_2 + 10 vol.% H_2 gaseous verification mixture). The cryostat was filled with a nitrogen-hydrogen mixture after it had been vacuumed. Pulsed hydrogen supply was carried out as follows: after vacuuming the cryostat, in which the investigated structure was placed, hydrogen was injected into the cryostat. After holding the structure in the cryostat for $t = 1{-}3$ s a forced cryostat depressurization was carried out, followed by a purging with air.

Once the LED is switched on, the photovoltage appear for fractions of a second and remain almost unchanged until hydrogen is supplied. After pulsed hydrogen exposure, there is a sharp drop in photovoltage (for ~ 1 s) and then, after 10 s a slow return of the photo-response signal to the original level begins (Fig. 2).

The photocurrent also decreases after hydrogen pulsing by $\sim 80\%$ of the original value. The photocurrent then returns to its baseline (Fig. 3).

Thus, for the first time, semiconductor structures n-InP/SiO$_2$@20Pd were created, in which thin silica films containing palladium nanoparticles are formed by sol-gel technology. The palladium crystallite size in the obtained films was ~ 8 nm. Preliminary tests of the created structures showed the results comparable to those obtained for previously developed sensors based on Pd/InP and Pd–oxide–InP structures, in which Pd was deposited by thermal-vacuum deposition. Consequently, the thin-film structures created using sol-gel technology are promising for the development of hydrogen sensors based thereon.

Conflict of interest

The authors declare that they have no conflict of interest.

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