JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **6** No 4, 04022(4pp) (2014)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **6** № 4, 04022(4cc) (2014)

Electrical and Photoelectrical Properties of Porous Silicon Modified by Cobalt Nanoparticles

I.B. Olenych*

Ivan Franko National University of Lviv, 50, Dragomanov Str., 79005 Lviv, Ukraine

(Received 19 May 2014; published online 29 November 2014)

In this work, the electrical and photovoltaic properties of sandwich structures based on porous silicon modified by cobalt nanoparticles were investigated. The increase of electrical conductivity, photovoltage and photocurrent of experimental structures was detected for the case of introduction of cobalt into the porous silicon matrix. The spectral characteristics of photoresponse of the barrier structures in the 450-1100 nm wavelength range were studied. The temperature dependences of photovoltage and energy characteristics of the structures based on porous silicon modified by cobalt nanoparticles were measured. The results extend the perspectives of porous silicon in photoelectronics and sensor electronics.

Keywords: Porous silicon, Cobalt nanoparticles, Current-voltage characteristics, Photoresponse, Spectral characteristics.

PACS numbers: 73.63. – b, 73.50.Pz

1. INTRODUCTION

Formation of nanomaterials with unique physical, electrochemical, catalytic properties is one of the priority directions of the development of science and technology which opens wide possibilities for the creation of new effective catalysts, sensor systems and photoelectric converters. Porous silicon (PS) belongs to such nanostructured materials. Small sizes of PS nanocrystals, large area of their surface, increased band gap in comparison with bulk silicon condition wide application perspectives of this material in micro-, nano- and optoelectronics, sensorics and energetics [1-5].

Moreover, PS can be used as a matrix for the introduction of different nanoparticles that allows to create on its basis nanocomposites with controlled functional properties. In particular, it was established that deposition on the PS surface or introduction into pores of metal (gold, palladium, nickel, copper, etc.) nanoparticles promotes the enhancement of manifestation effectiveness of the optical, luminescence, catalytic properties of the material [6-9]. Collective excitations of the conduction electrons in metal nanoparticles (surface plasmon resonance) under the action of electromagnetic radiation condition the amplification of the optical effects of composite environment.

Low-dimensional systems based on PS with incorporated nanoparticles of ferromagnetic metal which possess interesting magneto-optical characteristics attract scientific and practical interest [10, 11]. Moreover, information about electrophysical properties of "magnetic" nanocomposites based on silicon is actual.

Therefore, the aim of the work was to modify the surface of PS nanocrystals by electrochemically deposited cobalt nanoparticles and study the electric and photovoltaic properties of modified PS-based structures. We should note that method of electrochemical deposition of metals has undeniable advantages, since it is comparatively simple, cheap and compatible with ordinary PS technology.

2. EXPERIMENTAL TECHNIQUE

PS layers were formed by the method of electrochemical anodizing of the monocrystalline silicon plates of the thickness of 400 μm of electron conduction with the resistivity of 4.5 Ohm·cm of the crystallographic (100) orientation in an ethanol solution of hydrofluoric acid with the volume component ratio of HF : C_2H_5OH = 1 : 1. In order to obtain a uniform porous layer, a gold film, which also served as a contact for further measurements, was pre-deposited on the back surface of silicon substrate by the thermal-vacuum method and annealed at the temperature of 450 °C during 20 minutes. Anode current density and etching time were equal, respectively, to 30 mA/cm^2 and 5 min. To provide the presence in the near-surface *n*-Si layer of positive charge carriers, which are necessary for the anode reactions and formation of PS [12], working surface of the plate was irradiated by white light during the whole process of electrochemical etching. The obtained structures were divided into samples of the area of ≈ 1 cm^2.

Introduction of cobalt fragments into the PS matrix was carried out by the electrochemical method from 20 % solution of cobalt acetate ($Co(CH_3COO)_2$) at the direct current flow of 20 mA during 10 min. Control of the introduction of metal nanoparticles into a porous layer was performed using the scanning electron microscope Selmi REMMA-102

Electrical contact to a porous layer of the diameter of 6 mm was formed by the method of thermal-vacuum deposition of a semitransparent silver film. Angle between the direction of the flux of evaporated Ag atoms and the normal to the PS surface was equal to 60 ° that provided the formation of electric contact on the surface of porous layer avoiding Ag penetration into pore depth.

Measurements of the current-voltage characteristics (CVC) were performed according to the standard techniques with the step of 50 mV at the current passing through the structures along the direction perpendicular to the surface. Photovoltaic phenomena were investigated under the condition of irradiation of the structures from the side of a porous layer by the radiation of

* iolenych@gmail.com

light-emitting diode FYLP-1W-UWB-A with the power of 1 W, luminous flux of 76 lm. Measurements of the spectral dependences of the photovoltage and photocurrent were performed on the standard optical equipment using diffraction monochromator and incandescent lamp (2800 K). Photoresponse spectra were normalized on the black-body curve with the temperature of 2800 K (the Plank curve) and corrected taking into account the spectral sensitivity of the device.

Study of the energy characteristics of the structures Au – *n*-Si – PS – Ag was carried out using light emitting diode, whose radiation intensity is directly proportional to the current. In the case of the investigation of the temperature dependences of the photovoltage, experimental samples were placed into cryostat, in which vacuum was maintained on the level of residual pressure of about 10^{-3} mm Hg, and were pre-cooled in dark. Measurements were performed under the conditions of linear heating of the samples from the temperature of 80 K to 325 K with the rate of 0.1 K/s.

3. RESULTS AND DISCUSSION

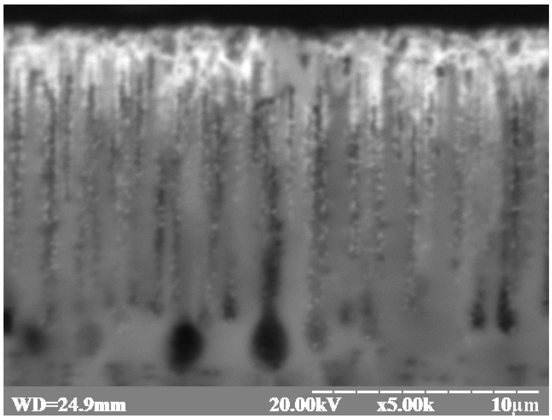
Analysis of the PS surface and cross-section of the experimental samples by scanning electron microscopy (SEM) methods in the regimes of elastically reflected electrons and X-ray microanalysis allowed to establish that significant amount of electrically deposited cobalt was located in the near-surface PS layer. In the regime of elastically reflected electrons, SEM-image sections with larger brightness are identified as formed metal clusters (see Fig. 1). In depth of a porous layer cobalt was placed on the walls between pores in the form of nanoparticles, whose sizes reached some tens of nanometers.

Regime of the X-ray spectral microanalysis allows to determine the phase composition of composite structure. Peaks in the energy ranges of 0.8 keV, 6.95 keV and 7.65 keV, which correspond to the cobalt atoms, were observed besides the peak with the energy of 1.7 keV which is typical for silicon.

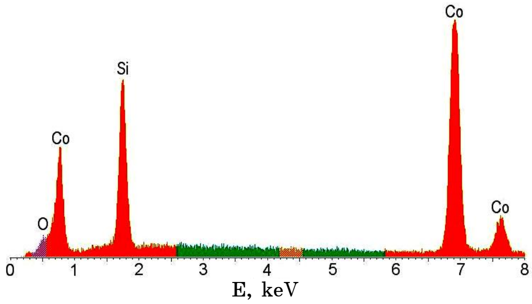
CVC of the sandwich structures Au – *n*-Si – PS – Ag measured in the dark at room temperature possessed rectifying behavior that is, probably, conditioned by the Schottky barrier (Fig. 2). Forward branch of the CVC corresponded to the positive potential on the silicon substrate with respect to Ag contact on the porous layer. We have to note that rectification factor was larger in the case of the structures modified by cobalt nanoparticles. This can be conditioned by both larger metal/silicon contact area and modification of the electron parameters of PS nanocrystals due to the interaction of silicon with a metal. Moreover, we have also observed the increase in the electrical conductivity of the investigated structures with incorporated cobalt nanoparticles that can be connected with the formation of additional channels for the current passing through a porous layer.

Under the influence of the light-emitting diode irradiation with the luminous flux of 76 lm on the PS surface, CVC of the experimental samples were changed similarly to the photodiode structures. Appearance of the negative photovoltage on the semitransparent Ag contact was observed in the photogalvanic mode.

The values of the photovoltage and photocurrent were larger for Au – *n*-Si – PS – Ag structures modified by



a



b

Fig. 1 – SEM-images (a) and X-ray microanalysis diagram (b) of the PS cross-section with incorporated cobalt nanoparticles

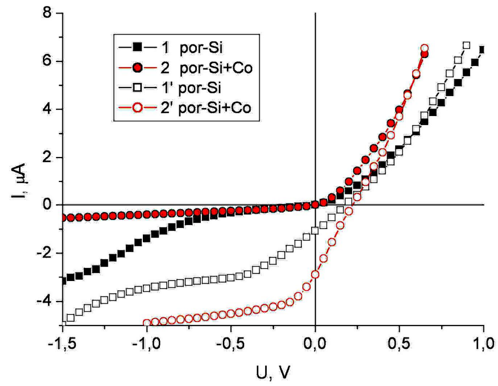


Fig. 2 – CVC of the initial Au – *n*-Si – PS – Ag structure (1, 1') and modified by cobalt nanoparticles (2, 2'): 1, 2 – in the dark; 1', 2' – under the action of the light-emitting diode (FYLP-1W-UWB-A) irradiation of the PS surface

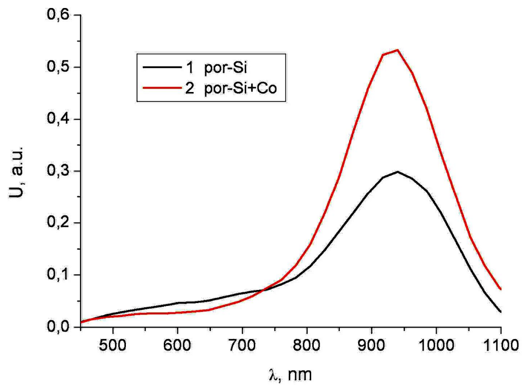


Fig. 3 – Spectral dependence of the photovoltage of the structure Au – *n*-Si – PS – Ag (1) and modified by cobalt nanoparticles (2)

cobalt nanoparticles that can be connected with larger metal/semiconductor contact area.

Spectral dependences of the photovoltage of the barrier Au – *n*-Si – PS – Ag structures are shown in Fig. 3. Photovoltage spectra in the idling mode were similar to the photoresponse spectrum of PS/silicon heterojunctions [13, 14] and characterized by a wide maximum in the range of 950 nm. Moreover, decrease in the spectral photosensitivity of the PS-based structures modified by cobalt was observed in the short-wave region. This can be connected with shunting of quantum-sized PS nanocrystals by incorporated cobalt particles. During the transition to the short-circuit mode, behavior of the spectral dependence of the photocurrent corresponded to the photovoltage spectra.

Temperature dependences of the photovoltage of the investigated structures in the range of 80-300 K have a nonmonotonic behavior with the maximum at the temperature of about 200 K (Fig. 4). An additional maximum of the photovoltage at the temperature of about 100 K was observed for Au – *n*-Si – PS – Ag structure modified by cobalt nanoparticles.

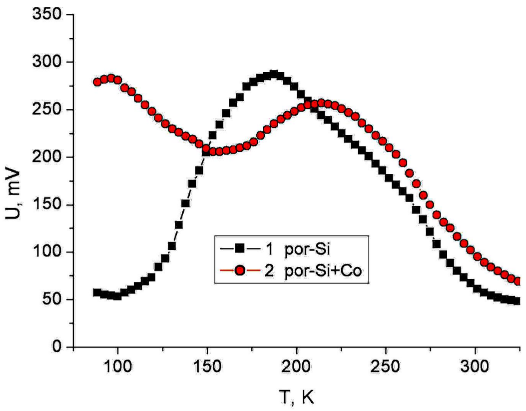


Fig. 4 – Temperature dependences of the photovoltage of the Au – *n*-Si – PS – Ag structure (1) and modified by cobalt nanoparticles (2) under the action of the light-emitting diode (FYLP-1W-UWB-A) irradiation of the PS surface

The observed nonmonotonic behavior of the obtained temperature dependences can be defined by a number of reasons, in particular, by the change in the position of the Fermi level with temperature, by the presence of trapping levels of non-equilibrium charge carriers both on the surface of silicon nanocrystals and at the porous layer/substrate interface, etc. [8, 15]. In particular, different in nature and activation energy trapping levels were revealed during the investigations of thermostimulated conductivity and PS depolarization [16, 17]. The value of photosignal depended on the carrier confinement time at trapping levels which increased with the decrease in temperature.

In order to obtain additional information about the photoelectron processes in Au – *n*-Si – PS – Ag structures, their energy characteristics are studied. Character of the dependences of the photovoltage on the irradiation intensity was similar to the photodiode signal, however, deviation from linearity of the energy dependences of the fhotocurrent (Fig. 5) was observed.

Such sublinear dependence of the photocurrent on the irradiation intensity also can be connected with trapping of carriers by traps. The obtained results imply a more complex, than diode, structure of the investigated systems.

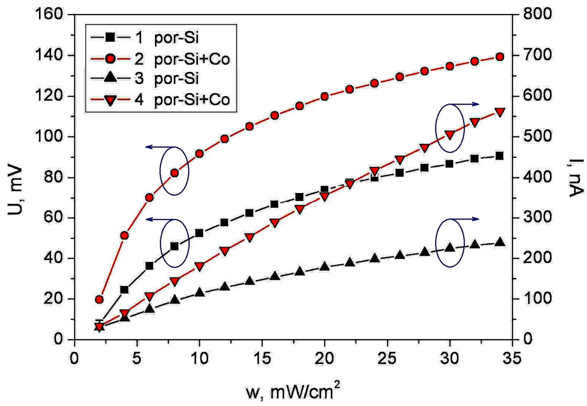


Fig. 5 – Dependence of the photovoltage (1, 2) and photocurrent (3, 4) of the Au – *n*-Si – PS – Ag structure (1, 3) and modified by cobalt nanoparticles (2, 4) on the irradiation intensity

4. CONCLUSIONS

In the work, it is experimentally established that application of the electrochemical method ensures an effective incorporation of cobalt into PS layers, and, as a result, formation on the walls between pores of metal nanoparticles, whose sizes reached several tens of nanometers, was observed. Analysis of the CVC of photosensitive Au – *n*-Si – PS – Ag barrier structures has shown that incorporation into a porous layer of cobalt nanoparticles conditions the increase in the electrical conduction of sandwich structures and enhancement of the photosignal value that can be connected with a larger metal/semiconductor contact area and the formation of additional channels of current passing through a porous layer.

Based on the temperature dependences of the photovoltage and energy characteristics of the experimental Au – *n*-Si – PS – Ag structures, it was revealed the existence of trapping levels of non-equilibrium charge carriers which considerably influence the electron processes in PS nanostructures. High sensitivity of the structures Au – *n*-Si – PS – Ag in the visible and the near infrared spectral regions broadens the perspective of PS application in photodetectors. The obtained results also can be used in sensorics and power engineering for the effective formation of nanocatalysts in porous materials.

REFERENCES

1. K.Q. Peng, S.T. Lee, *Adv. Mater.* **23**, 198 (2011).
2. B. Ünal, A.N. Parbukov, S.C. Bayliss, *Opt. Mater.* **17**, 79 (2001).
3. C. Baratto, G. Faglia, G. Sberveglieri, Z. Gaburro, L. Pancheri, C. Oton, L. Pavesi, *Sensors* **2**, 121 (2002).
4. S. Ozdemir, J. Gole, *Curr. Opin. Solid State Mater. Sci.* **11**, 92 (2007).
5. T. Pichonat, B. Gauthier-Manuel, *J. Power Sources* **154**, 198 (2006).
6. N.V. Sotskaya, O.V. Dolgikh, V.M. Kashkarov, A.S. Len'shin,

E.A. Kotlyarova, S.V. Makarov, *Sorbtsionnye i khromatograficheskie protsessy* **9**, 643 (2009).
7. T.S. Amran, M.R. Hashim, N.K. Al-Obaidi, H. Yazid, R. Adnan, *Nanoscale Res. Lett.* **8**, 35 (2013).
8. E.F. Venger, S.I. Kirillova, I.M. Kizyak, É.G. Manoilov, V.E. Primachenko, *Semiconductors* **38**, 113 (2004).
9. N.A. Yashtulov, S.S. Gavrin, A.A. Revina, V.R. Flid, *Izv. RAN. Ser. khim.* No8, 1450 (2010).
10. E.A. Gan'shina, M.Yu. Kochneva, D.A. Podgornyi, P.N. Shcherbak, G.B. Demidovich, S.N. Kozlov, *Phys. Solid State* **47**, 1383 (2005).
11. F.A. Korolev, E.A. Gan'shina, G.B. Demidovich, S.N. Kozlov, *Phys. Solid State* **49**, 528 (2007).
12. A.G. Cullis, L.T. Canham, P.D.J. Calcott, *J. Appl. Phys.* **82**, 909 (1997).
13. I.B. Olenych, L.S. Monastyrskii, O.I. Aksiment'eva, B.S. Sokolovskii, *FKhTT* **13**, 1011 (2012).
14. I.B. Olenych, L.S. Monastyrskii, B.S. Sokolovskii, *J. Nano-Electron. Phys.* **4** No3, 25 (2012).
15. E.F. Venger, T.Ya. Gorbach, S.I. Kirillova, V.E. Primachenko, V.A. Chernobai, *Semiconductors* **36**, 330 (2002).
16. L. Monastyrskii, M. Panasyuk, I. Olenych, *Visnyk Lviv. untu. Seriya fizychna* **35**, 54 (2002).
17. L.V. Grigor'ev, I.M. Grigor'ev, M.V. Zamoryanskaya, V.I. Sokolov, L.M. Sorokin, *Tech. Phys. Lett.* **32**, 750 (2006).