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Photodetectors on the Basis of Porous Silicon

I.B. Olenych*, L.S. Monastyrskii, B.S. Sokolovskii

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

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The paper studies the electrical characteristics of photodiode structures porous silicon/silicon substrates modified by the molecules of iodine. Changes in the behavior of the current-voltage characteristics of the obtained structures from symmetrical to straightening because of the iodine adsorption are revealed. The spectral characteristics of photoresponse in the 450-1100 nm wavelength range, its temperature dependence in the 125-325 K range, and energy characteristics of photovoltaic structures based on porous silicon are studied. A possible mechanism of influence of iodine adsorption on the electrical and photoelectrical properties of the structures porous silicon/silicon substrates is proposed. The obtained results extend the perspectives of porous silicon application in photoelectronics.

Keywords: Porous silicon, Adsorption, Photodetector, Photoresponse, Spectral characteristics, Current-voltage characteristics.

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1. INTRODUCTION

Significant attention is currently devoted to the study of the properties of semiconductor nanostructures in connection with the tendency of miniaturization of the elements of modern electronics. In particular, porous silicon (PS) is the promising material of optoelectronics, sensorics, nanoelectronics [1-3]. Unique properties of PS layers allow to create on their basis devices of different application, namely, radiators, photodetectors, chemical and biological sensors, photon crystals, etc. Small sizes of PS nanocrystals, large area of their surface, reflection coefficient, which is less in comparison with bulk silicon, provide considerable sensitivity of the electrophysical properties of PS to both the conditions of the environment and electromagnetic radiation in a wide spectral range.

Modification of PS layers induced by the adsorption-electrical effects attracts scientific and practical interest. It is established that adsorption of chemically active or polar molecules (NO_2, NH_3, C_2H_5OH, H_2O, I_2, etc.) conditions a significant change in the concentration of free charge carriers in PS and its electrophysical parameters [4-7]. Moreover, due to the adsorption of I_2 molecules with acceptor properties, inversion of the electron conduction of meso-PS nanocrystals to the hole conduction [8] was observed as well as the inversion of the hole conduction to the electron one under the influence of adsorption of NH_3 molecules with donor properties [9]. However, the possibility of the control of the electronic properties of silicon nanostructures by means of the change in their molecular environment has not been studied in full.

Inversion of the conduction type of silicon nanocrystals can be used for the formation of potential barriers in the structures based on PS. Therefore, the aim of the present work was the creation of photovoltaic structures PS/*n*-Si by the modification of porous layer by adsorbed iodine molecules and study of their electrical and photoelectrical properties.

2. EXPERIMENTAL TECHNIQUE

As-prepared PS samples whose surface was not yet covered by a thick film of natural oxide were used for the experimental investigations. Such selection of the samples is conditioned by the fact that influence of molecule adsorption on the luminescent properties of PS decreased with the growth of the oxide layer thickness which separates silicon nanocrystals and adsorbed elements [10].

PS layers were formed by the method of electrochemical anodizing of monocrystalline silicon plates of the thickness of 400 μm of the electron conduction with the resistivity of 4,5 Ohm·cm in an ethanol solution of hydrofluoric acid with the volume component ratio of $HF:C_2H_5OH$ = 1:1. Back surface of the silicon substrate was preliminarily metalized by thermal vacuum deposition of silver film of the thickness of about 1 μm, which also acted as a contact for further measurements, in order to obtain uniform porous layer. Current density and anodizing time were equal to 20-30 mA/cm^2 and 3 min, respectively. To provide the presence in the near-surface *n*-Si layer of positive charge carriers necessary for anode reactions and formation of PS [11], working surface of the plate was irradiated by a white light during the whole process of electrochemical etching. Meso-PS layers are formed with the porosity of about 60-70% under these technological conditions [11, 12]. Thickness of the PS layer determined using the scanning electron microscope was about 10 μm. Obtained structures were divided into samples with the area of ≈ 1 cm^2.

Adsorption of I_2 molecules was performed from 1,5 and 10% ethanol solution of iodine for different samples by their short-term dipping into solution. After drying of the samples during 30 min at the room temperature, contacts of the diameter of ≈ 2 mm were deposited on the PS surface by using colloidal carbon. To provide time stability of the photoelectrical characteristics, PS surface was covered by transparent protective film of zapon (solution of celluloid in ether) which prevent desorption of iodine from PS.

* iolenych@gmail.com

Investigation of the electrical and photoelectrical properties of the experimental samples was carried out according to the standard techniques during current passage through the structures in the direction perpendicular to the surface. Current-voltage characteristics (CVC) were measured at the voltage change from – 1 V to 1 V with the step of 50 mV.

Photoelectrical phenomena were studied under irradiation of the structures on the part of porous He-Ne layer by laser (λ = 0,63 μm) with the radiation power of 2 mW. Measurements of the spectral dependences of the photo-emf and photocurrent were performed on the standard optical equipment using incandescent lamp (2800 K). Spectra of photoresponse of the studied samples were normalized on the radiation curve of a blackbody with the temperature of 2800 K, corrected with taking into account the spectral sensitivity of the device, and compared with the spectral characteristic of silicon photopdiode FD-7.

For measurement of the temperature dependences of the photo-emf and photocurrent, adsorption-modified PS/*n*-Si structures were placed in cryostat with vacuum of the residual pressure of 10^{-3} mm Hg and pre-cooled both in dark and at illumination. Measurements were performed under the conditions of linear heating of the samples from the temperature of 125 K to 325 K with the rate of 0,1 K/s at radiation by He-Ne laser with the intensity of 60 mW/s. Study of the energy characteristics of the studied structures was carried out using light-emitting diode FYL-3014 UWC whose radiation intensity is directly proportional to the current.

3. RESULTS AND DISCUSSION

Investigations of the electrical parameters of the obtained PS/*n*-Si structures have revealed a considerable influence of the adsorption of iodine acceptor molecules on the CVC of the samples. In comparison with the control sample (without adsorbed iodine) which had symmetrical but non-linear CVC, for the structures with PS layers, modified by I_2 molecules, a straightening behavior of the dependences $I(V)$ was observed (Fig. 1). Direct branch of the CVC corresponded to a positive potential on porous layer.

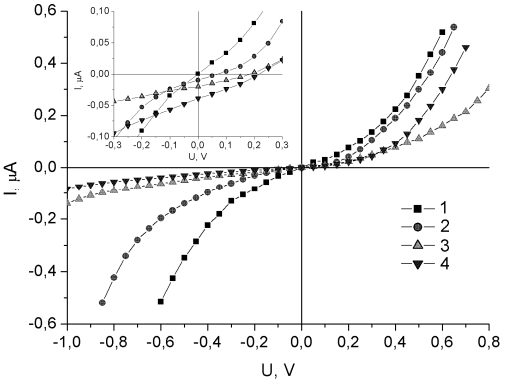

Fig. 1 – Dark CVC of PS/*n*-Si structures: 1 – without adsorption of I_2; 2 – adsorption of I_2 occurred from 1% iodine solution in ethanol; 3 – 5%; 4 – 10%. On the inset: CVC of these structures under the influence of irradiation by He-Ne laser with the intensity of 60 mW/cm^2

Under the action of illumination of PS surface by He-Ne laser with the intensity of 60 mW/cm^2, CVC of the experimental samples, which are modified by iodine, were changed similarly to the photodiode structures (see the inset in Fig. 1). These facts imply the appearance of a new or dominance of one of the existing electrical barriers in the PS/*n*-Si structure under the action of adsorption of iodine molecules. We should note that the increase in the concentration of I_2 in the solution, from which adsorption occurred, conditioned the increase in the rectification factor of CVC of the PS/*n*-Si structures, as well as the values of the photo-emf and photocurrent in the photogalvanic measurement mode.

Inversion of the electron conduction of PS nanocrystals to the hole one due to the adsorption of I_2 was the probable reason of the appearance of photosensitive potential barriers. It is known that adsorption by silicon surface of acceptor molecules leads to the formation of surface levels of the acceptor type and the corresponding bending of energy zones. This conditions free carrier depletion of the near-surface region of *n*-type semiconductor. Even inversion of the conduction type of the near-surface layer is possible in the case of a weakly-doped *n*-Si [13]. Taking into account significant specific surface of PS nanocrystals, inversion of the electron conduction to the hole one due to the adsorption of I_2 can be expected in a whole nanocrystal volume. As a result, photosensitive electrical barriers were formed on the PS/*n*-Si boundary, and the investigated structure can be considered as a set of in-parallel *p*-*n*-junctions.

Under the action of illumination of the PS surface in photogalvanic mode, generated electron-hole pairs were separated by a potential barrier, and holes were accumulated in PS nanocrystals forming positive potential on a porous layer.

Typical spectral dependences of the photo-emf of the studied PS/*n*-Si structures at the adsorption of iodine molecules are shown in Fig. 2.

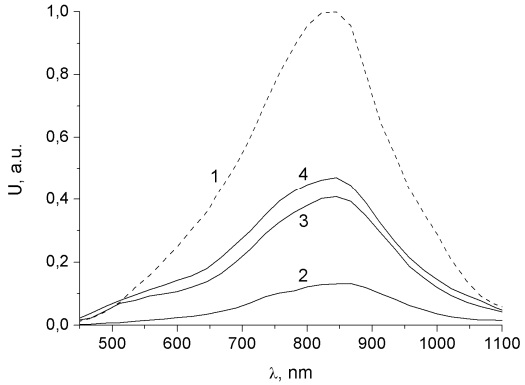

Fig. 2 – Spectral dependence of the photo-emf of a silicon photodiode (1) and PS/*n*-Si structures (2, 3, 4): 2 – at the adsorption of I_2 from 1% iodine solution in ethanol; 3 – 5%; 4 – 10%

Spectra of the photo-emf were characterized by a wide maximum in the wavelength range of 750-950 nm. Along with this, an insignificant increase in the photosensitivity in the short-wave spectral range was observed. Increase in the concentration of iodine molecules in the solution, from which adsorption occurred, and so, a number of molecules adsorbed by the surface of PS nanocrystals led to the increase in the photo-emf value

only and did not change a general view of the spectral characteristic of the obtained photodetectors.

At the transition to the short circuit mode, behavior of the spectral dependence of the photocurrent corresponded to the photo-emf spectra (Fig. 3).

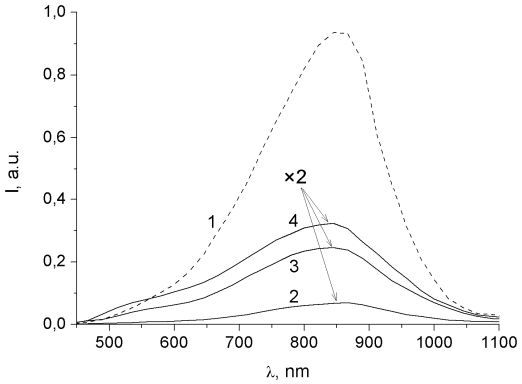

Fig. 3 – Spectral dependence of the photocurrent of silicon photodiode (1) and PS/*n*-Si structures (2, 3, 4): 2 – at the adsorption of I_2 from 1% iodine solution in ethanol; 3 – 5%; 4 – 10%

Analysis of the spectral characteristics of the obtained photodetectors based on PS has revealed their similarity to the spectra of the photoresponse of industrial silicon photodiode. Conformity of the spectral photosensitivity of photodiode PS/*n*-Si structures modified by iodine molecules and industrial silicon photodiode as well as a positive sign of photo-emf on the surface of PS, can be an additional argument in favor of the fact that photocarriers are separated on the boundary of porous layer with silicon substrate.

Temperature dependences of the photo-emf and photocurrent of the investigated structures measured in the photogalvanic mode are represented in Fig. 4. We have observed the increase in the photocurrent value with temperature up to 270 K, extreme when approaching room temperatures, and decrease in the photosignal at further heating to 325 K. Measurements have shown that the photoresponse value considerably depended on the conditions of pre-cooling: in the temperature range of 125-250 K photo-emf value of the structures, lightened during the temperature decrease, significantly differed from those typical for the case of cooling in dark. This fact can be connected with capture of non-equilibrium charge carriers by traps which are typical for the PS-based structures. In particular, different by the nature and activation energy capture levels were revealed in the investigations of thermal stimulated conduction and depolarization of PS [14, 15]. The photosignal value depended on the carrier confinement time on the capture levels which increased with the temperature decrease.

Thus, the observable non-monotonous behavior of the obtained temperature dependences can be defined by a number of reasons, in particular, by the change with temperature in the position of the Fermi level, presence of capture levels of non-equilibrium charge carriers both on the surface of silicon nanocrystals and at the boundary of porous layer and substrate, etc. [16, 17].

In order to obtain additional information about the photoelectron processes in modified PS/*n*-Si structures, their energy characteristics were investigated. Nature of the dependence of the photo-emf on the irradiation intensity was similar to the photosignal of silicon photodiode; however, depletion from linearity of the energy dependence of the photocurrent was observed (Fig. 5). Such sublinear dependence of the photocurrent on the illumination intensity also can be connected with the carrier trapping by traps.

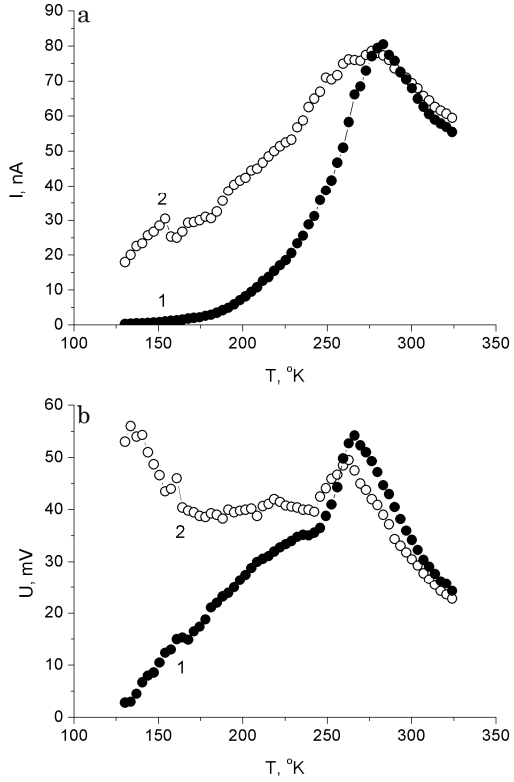

Fig. 4 – Temperature dependence of the photocurrent (a) and photo-emf (b) modified by I_2 molecules from 10% ethanol solution of the PS/*n*-Si structure under the action of irradiation of He-Ne laser: 1 – pre-cooling in dark; 2 – pre-cooling at light

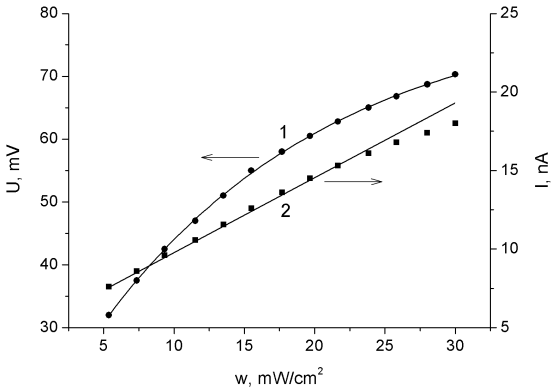

Fig. 5 – Dependence of the photo-emf (1) and photocurrent (2) modified by I_2 molecules from 10% ethanol solution of the PS/*n*-Si structure on the light intensity

We should also note that iodine desorption by PS (in the case of the experimental samples without protective coating) was accompanied by the decrease in the photovoltaic effect. On the other hand, zapon film not only prevents iodine desorption but also increases the effectiveness of photodiode structures because of better passivation of the surface of silicon nanocrystals, which

decreases the rate of surface recombination of charge carriers.

4. CONCLUSIONS

Influence of the adsorption of acceptor molecules of iodine on the electrical and photoelectrical properties of the PS/*n*-Si structures has been investigated. Change in the CVC behavior of modified structures from symmetrical to straightening indicates the appearance of photosensitive potential barriers conditioned by the inversion of the conduction type of meso-PS nanocrystals under the action of adsorption of iodine molecules. The obtained data implies the possibility of the control of the electron parameters of silicon nanostructures by the adsorption of chemically active molecules. Based on the investigation of the temperature dependences of the photoresponse of the PS/*n*-Si structures, we have revealed the existence in such structures of capture levels of non-equilibrium charge carriers which considerably influence the electron processes in PS nanostructures.

The studied samples were characterized by high sensitivity in the visible and near infrared spectral regions. Thus, adsorption-modified PS/*n*-Si structures are promising for monitoring of electromagnetic irradiation in a wide spectral range: from 450 nm to 1100 nm. The obtained experimental results can be useful in the production of photovoltaic devices of new generation.

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