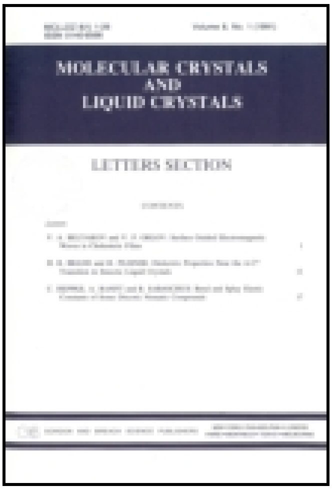

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Photosensitive Structures of Conjugated Polymer - Porous Silicon

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*The photosensitive hybrid structures poly-3,4-ethylenedioxythiophene (PEDOT)–porous silicon (PS)–*n-*Si are fabricated. Current-voltage characteristics of the obtained structures are investigated. It is shown that PS surface modification by PEDOT conjugated polymer gives rise to the appearance of a pronounced rectifying effect on the current-voltage characteristics. Spectral characteristics of photoresponse in the 450–1100 nm wavelength range, its temperature dependence in the 125–325 K range, and energy characteristics of the hybrid photovoltaic structures are studied. We propose possible mechanisms of the photoelectric processes in the hybrid structures PEDOT–PS–*n-*Si.*

Keywords Porous silicon; poly(3, 4-ethylenedioxythiophene); CVC; photoresponse; spectral characteristics

Introduction

The rapid development of nanoelectronics is associated with the search for new materials with predictable properties. Composite media, which are a collection of related to each other nanoscale particles, have practical perspectives of their application in various areas such as photoelectronics, sensors, optoelectronics, spintronics and others [1–3]. These media include also hybrid semiconductor structures based on of conjugated polymers and porous silicon (PS). An interaction between nanoparticles in the hybrid structures can lead to significant differences in their properties compared to those of the individual components - strengthening some of these properties or forming new ones [4–6]. By now various types of hybrid structures based on porous silicon or other semiconductor and conjugated polymers such as polyaniline [5, 6], poly (3-hexylthiophene) (P3HT) and poly (methoxy ethylexyloxyphenylenevinylene) (MEH PPV) etc [7] were studied. Among the family of conducting conjugated polymers, the poly-3,4-ethylenedioxythiophene (PEDOT) has attracted much attention due to its sufficiently high electrical conductivity, interesting electrooptical and electrochemical properties [8]. The use of PEDOT as an electron-blocking layer and as a collector of holes in photovoltaic structures was reported, but usually PEDOT doped by poly(styrenesulfonate) (PSS)–PEDOT:PSS is used as a hole injecting layer [9]. While studying the possibility of forming ohmic or Schottky rectifying contacts to metal-semiconductor heterojunctions with PEDOT:PSS, the unusual behaviour of current-voltage characteristics (CVC) with the region of negative differential resistance was found in the cases when

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heterojunctions were formed on gold, platinum or carbon. This non-linearity is assumed to be partly caused by the existence of a thin barrier layer on PEDOT:PSS film surface through which carriers could tunnel [10].

However, the heterostructures based on porous silicon are little-studied for the use of injecting PEDOT layers formed by electrochemical polymerization of 3,4-ethylenedioxythiophene on porous silicon surface. The purpose of the present work was to fabricate the hybrid nanostructures PEDOT–PS–*n*-Si with electrodeposited polymer layer and to study their electrical properties.

Experiment

In the experimental studies we used freshly prepared PS samples. The porous silicon layers were fabricated by means of electrochemical etching performed in galvanostatic mode on single-crystalline (100) silicon substrates with a thickness of 400 μm. The substrates have *n*-type of conductivity with an electrical resistivity of 4.5 Ohm·cm. We used the ethanol solution of hydrofluoric acid (the volume ratio of the components $HF:C_2H_5OH = 1:1$) as an electrolyte. For obtaining a homogeneous layer, we previously deposited a silver film with a thickness of about 1 μm on the back surface of the substrate by the thermovacuum method. This film also served as an electrical contact for further measurements. The anodic current density was equal to 20 mA/cm^2 and the etching time was 10 min. To ensure availability of holes in the surface layer of n-Si, which were necessary for occurrence of anodic reactions and formation of the PS, we irradiated the working surface of the plate with a white light during the whole process of electrochemical etching. Under these technological conditions the layers of PS with a porosity of about 60–70 % were formed [11, 12]. According to scanning electron microscope (SEM) studies of the porous layer, its thickness was about 15 μm. The structures were divided into samples with an area of about 1 cm^2.

Thin film PEDOT coatings on PS surfaces were produced by electrochemical polymerization of 0.1 M solution of 3,4-ethylendioxythiophene in water-ethanol solvent (1:1), with 0.5 M H_2SO_4 used as an electrolyte. The PEDOT film was formed at a current density of 0.1 mA/cm^2 for 10 min. During the electrochemical polymerization, the monomer penetrates into the pores of silicon and a conducting polymer is synthesized right on the surface of the electrode and inside the pores [5, 13]. The formation of PEDOT films was recorded using a scanning electron microscopy SELMI (the spatial resolution is equal to 5 nm, the energy resolution in the mode of X-ray microanalysis is equal to 143 eV) (Fig. 1a). The X-ray surface microanalysis (EDS) of the hybrid structures found the traces of silicon and carbon, oxygen and sulfur, which are the components of the PEDOT polymer (Fig. 1b). Then the contact with a diameter of $\sim$3 mm was deposited on the surface of the polymer film using colloidal carbon.

Investigations of electrical parameters of the obtained structures were carried out with standard techniques during the electric current flow through the structure in the direction perpendicular to its surface [14]. CVC were measured by changing the voltage from -3 V to 1.5 V with an increment of 50 mV. Photoelectrical phenomena were studied after the PEDOT – PS – *n*-Si hybrid structure illumination from the surface of the polymer film in the direction perpendicular to its surface. The light of a He-Ne laser was used for this purpose, with the wavelength $\lambda = 0.63$ μm and a radiation power of 2 mW. The spectral dependences of the photovoltage and photocurrent were measured with standard optical equipment based on a diffraction grating monochromator and a filament lamp (2800 K). The photoresponse spectra were normalized to black-body radiation reference spectrum with a temperature of 2800 K and then corrected for the spectral sensitivity of the setup.

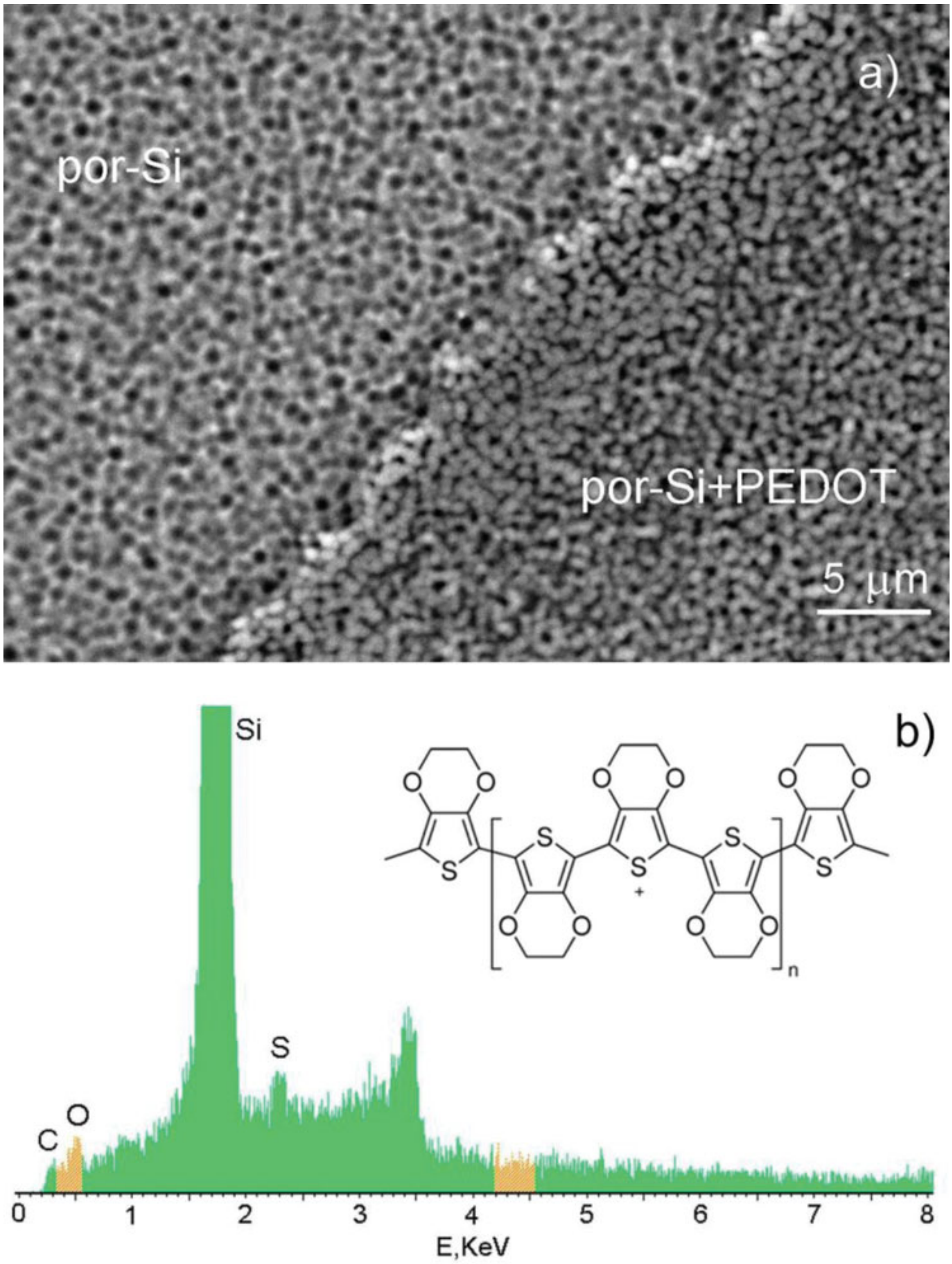

Figure 1. SEM images (a) and X-ray microanalysis (b) of surface PEDOT – PS – *n*-Si structure.

The spectral dependence of photoresponse of an industrial silicon photodiode was also measured for a comparison.

To measure the temperature dependences of photocurrent and photovoltage, the fabricated PEDOT – PS – *n*-Si structure was placed in a cryostat evacuated to a residual pressure of about 10^{-3} mm Hg. The measurements were carried out under the conditions of linear

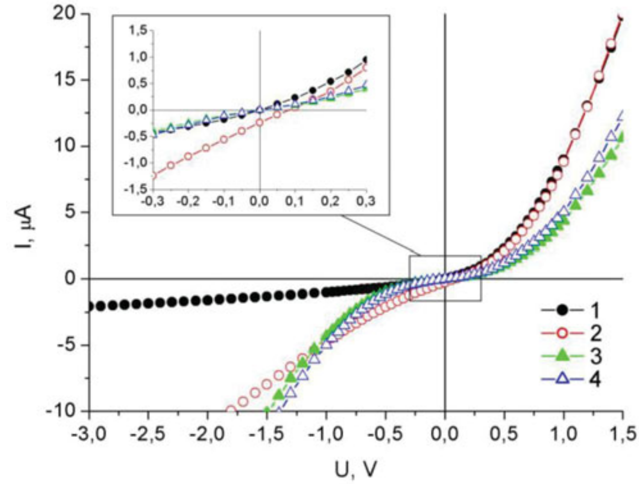

Figure 2. CVC of the PEDOT – PS – *n*-Si (1,2) and PS–*n*-Si (3,4) structures obtained in the dark (curves 1and 3) and under irradiation by the He-Ne laser (λ=0,63 μm) with the intensity of 60 mW/cm^2 (curves 2 and 4).

heating of the sample from 120 K to 320 K at a rate of 0.1 K/s during irradiation He-Ne laser with an intensity of 60 mW/cm^2. The study of the energy performance of this structure was carried out using LED FYL-3014 UWC, intensity of which was directly proportional to the current in the range of current values from 4 to 20 mA.

Results and Discussion

The reference sample of PS–*n*-Si (without polymer film) shows symmetrical nonlinear CVC indicating the existence in this structure of several potential barriers (Fig. 2, curve 3). The nonlinear CVC can be caused by contact phenomena, electric barriers in the porous layer and at the interface of PS - silicon substrate. Modification of the PS surface with conjugated polymer PEDOT led to a change in the nature of the observed CVC. It was observed the rectifier CVC of the hybrid structure of PEDOT – PS – *n*-Si, with dirent branch of the CVC being corresponded to the positive potential on the polymer film (see Fig. 2, curve 1). The rectification factor of the CVC for this structure was about 10 and 15 at a voltage of ±1.0 V and ±1.5 V, correspondingly.

Under the illumination of the PS surface by He-Ne laser with an intensity of 60 mW/cm^2, the CVC of PEDOT–PS–*n*-Si hybrid structure changes similarly to those observed in a photodiode structure (see Fig. 2, curve 2). On the other hand, illumination of the PS-n-Si structure does not cause significant changes in their CVC. Only a slight increase in current at the expense the photoconductivity (see Fig. 2, curve 4) was observed.

Rectifying CVC may be caused by the appearance of a new electric barrier PEDOT–PS interface as well as by the dominance of one of the existing potential barriers due to modification of electrical parameters of the porous layer under the influence of polymer. A significant change in the concentration of free charge carriers and even the inversion of the conductivity type was observed for mesoporous silicon after the adsorption of molecules with donor or acceptor properties [15–17]. Due to inversion of the conductivity type of silicon nanocrystals, photosensitive electric barriers at the interface between the PS and

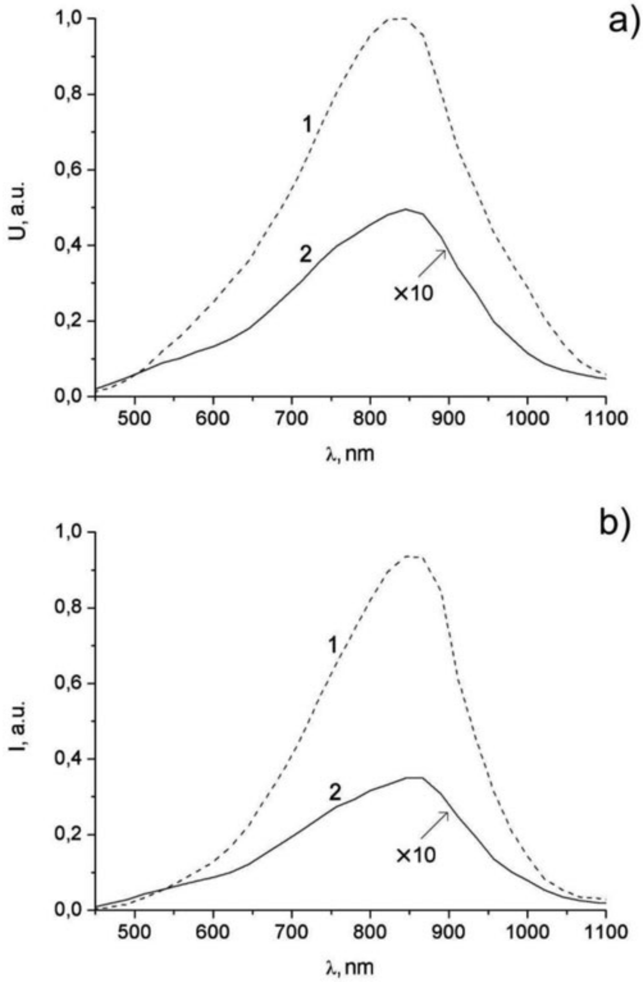

Figure 3. Spectral dependence of photovoltage (a) and photocurrent (b) for industrial silicon photodiode (1) and PEDOT – PS – *n*-Si structure (2).

silicon substrate are formed [17]. Since the PEDOT can be a catalyst in the oxidation-reduction reaction [18], and efficiently localizes the free electrons due to electrostatic interactions [19], we assume that inversion of n- type conductivity of silicon nanocrystals takes place with the appearance of a potential barrier at the border of PS - silicon substrate. However, establishing the nature of the photosensitive barrier needs further research.

Under illumination of the surface of PEDOT–PS–*n*-Si structure in the open circuit regime, the photo-generated electron-hole pairs are separated by a potential barrier. During this process the electrons are accumulated at the silicon substrate, thus creating a negative potential on the substrate with respect to that on the polymer film.

The photovoltage spectra of PEDOT–PS–*n*-Si hybrid structure measured in the open-circuit regime are similar to the photovoltaic spectral response of the industrial silicon photodiode. They are characterized by a broad band with maximum in the region of 750–950 nm (Fig. 3a).

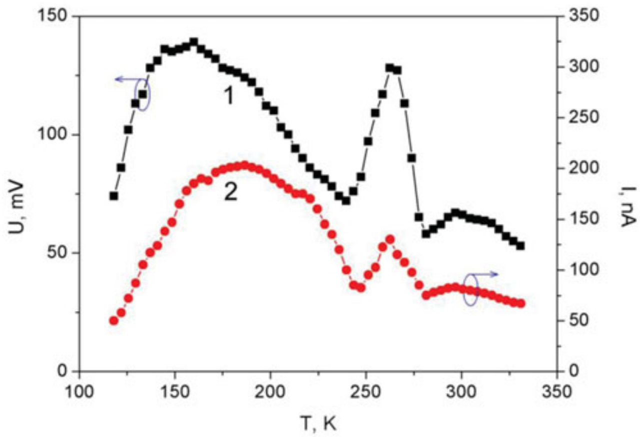

Figure 4. Temperature dependence of photovoltage (1) and photocurrent (2) PEDOT – PS – *n*-Si structure under irradiation by the He-Ne laser (λ=0,63 μm) with the intensity of 60 mW/cm^2.

Under short-circuit conditions, the character of spectral dependence of photocurrent was similar to the photovoltage spectra (Fig. 3b). The similarity of the spectral dependence of the photoresponse from the PEDOT – PS – *n*-Si structure with that from silicon photodiode suggests that the observed photovoltage response relates to the separation of photocarriers at the silicon – PS interface. This, along with the positive sign of the photovoltage on the polymer film, can be an argument in favour of the proposed qualitative model for modification of electrical parameters of PS under the influence of PEDOT.

Temperature dependences of photocurrent and photovoltage of the hybrid structure measured in the photovoltaic mode are shown in Fig. 4. Maximum photoresponse values are observed in 150–190 and 260–270 K temperature range, and are decreasing under further heating up to 330 K. The observed nonmonotonic character of the temperature dependence can be caused by a number of reasons, including changes in the temperature position of the Fermi level, the presence of nonequilibrium carrier capture processes in both PS and at the interface between the porous layer with silicon substrate and polymer [20, 21]. The differences in the nature and activation energy of the trap levels were discovered while studying thermally stimulated depolarization of PS [11]. The value of photosignal depends on the retention time of carriers at the trap levels which increases with decreasing the temperature.

For gaining more information about the photoelectronic processes in the hybrid structure of PEDOT–PS–*n*-Si, we studied its energy characteristics. The character of the photovoltage dependence on the illumination intensity was similar to the photosignal from silicon photodiode, but with a deviation from linearity in the photocurrent energy dependence (Fig. 5). This sublinear dependence of the photocurrent on the light intensity can be associated with the capture of nonequilibrium carries at trap levels, too.

It should be noted that PEDOT does not only modify the PS layer, but it also improves the efficiency of the photodiode structures due to better surface passivation of silicon nanocrystals, which reduces the rate of surface recombination of charge carriers.

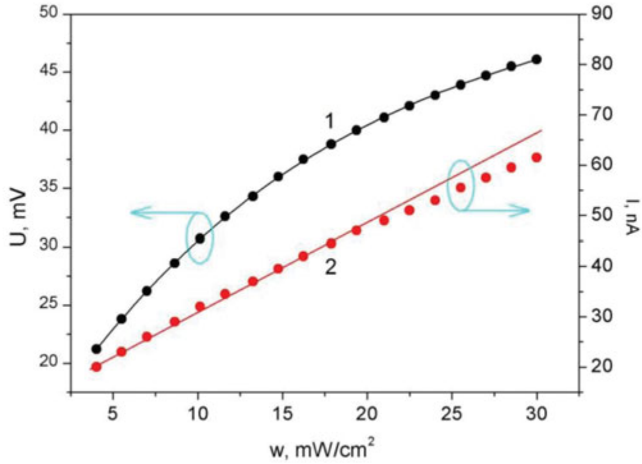

Figure 5. Dependences of photovoltage (1) and photocurrent (2) of PEDOT – PS – *n*-Si structure on the light intensity.

Conclusions

The rectifying nature of CVC of PEDOT–PS–*n*-Si hybrid structures indicates the presence of photosensitive potential barriers caused by the polymer. The studied samples are characterized by high sensitivity in the visible and near infrared spectral regions. Based on studying the temperature dependences of the photoresponse the existence of the trap levels for nonequilibrium carriers in the hybrid structures is revealed which significantly influence their electronic processes.

The small size of the PS nanocrystals, large surface area and smaller reflection coefficient compared to bulk silicon [22], cause significant sensitivity of electrical properties of the fabricated hybrid composites to the electromagnetic radiation in a wide spectral range. The experimental results obtained can be used for the development of photodetectors of visible radiation and other electronic devices based on hybrid structures of conjugated polymers–porous silicon.

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