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Photovoltaic properties of a heterostructure on the basis of porous silicon and polyaniline

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An electric junction between porous silicon (n-type conductivity) and conductive polyaniline (p-type conductivity) has been made by electrochemical polymerization of aniline on the porous silicon surface. This heterostructure has been found to exhibit rectifying I–V characteristics. Under illumination, a considerable increase of the current is observed with a reverse bias. The structure photosensitivity is defined mainly by two barriers, namely, by the polymer/porous silicon interphase and the porous silicon/crystalline silicon barrier.

Электрический контакт между пористым кремнием с n-типа проводимостью и проводящим полианилином с проводимостью p-типа изготовлен путем электрохимической полимеризации анилина на поверхности пористого кремния. Найдено, что такая гетероструктура демонстрирует выпрямляющие I–V характеристики. При освещении наблюдалось значительное повышение тока при обратном смещении. Фоточувствительность структуры преимущественно определяется двумя барьерами: интерфазой полимер-пористый кремний и пористый кремний-монокристаллический кремний.

Since the visible luminescence of porous silicon (PS) was discovered, the field of development of light-emitting devices on the basis of that material is under continuous attention [1, 2]. Moreover, the porous silicon application in development of solar converters and gas sensors has been exemplified [3]. The devices on the basis of the PS/conductive polymer structures show some advantages over other heterostructures, the main drawback of the latter consists in high voltage required for the effective device operation. An enhancement in current characteristics of polyaniline/PS heterostructures as compared to the PS/gold ones (of the Schottky diode type) is observed within a wide voltage range [3]. This is explained by a better electric contact of the polymer with PS due to a high level of pore filling. The devices containing a conductive polymer exhibit some additional advantages in view of the low operation voltage preventing the device against early degradation. Those advantages include the polymer transparency in a certain spectral range, resulting in that the polymer layer does not influence the electroluminescence radiation.

In earlier works [3, 4], the conductive polymer is considered to be only an injector of holes into the PS. At the same time, no attention is given to specific properties of porous polymers, such as the ability of free carrier generation under illumination [5, 6] that may be helpful in operation of light emitting devices. The purpose of this work is to study the charge transfer processes in the Au/polyaniline (PAN)/porous silicon (PS)-Al heterostructure excited by illumination.

To prepare porous silicon, were used the (100) oriented silicon single-crystalline plates with the n-type conductivity and specific resistance of 6.5 Ω·cm. The plate back side was coated with sputtered aluminum layer and then the plate was annealed at 725 K to provide an ohmic contact. The plates were anodized in 40 % HF solution in ethanol. During the electrochemical anodi-

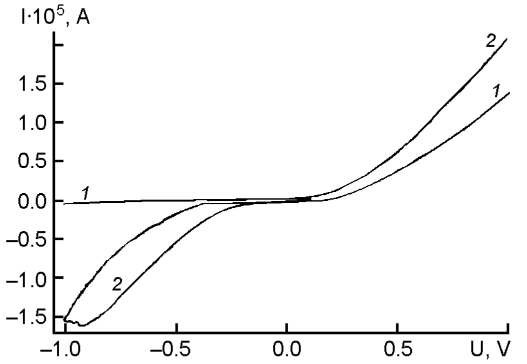

Fig. 1. Current-voltage characteristics of the polyaniline/porous silicon heterostructure in darkness (*1*) and under illumination (*2*).

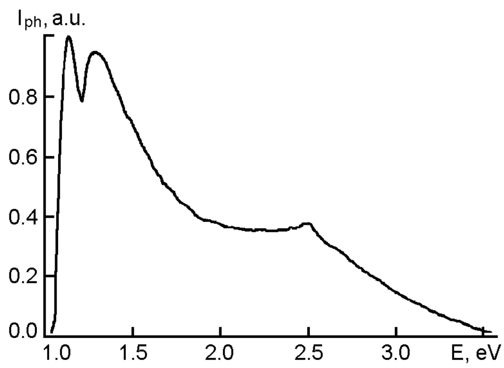

Fig. 2. Photosensitivity spectrum of the polyaniline/porous silicon heterostructure.

zation, the plate was illuminated with a 150 W tungsten incandescent lamp. The sample was etched for 5 min at the current density $i = 20$ mA/cm^2. The porous silicon layer thickness did not exceed 5 μm. The polyaniline films on the porous silicon were formed by electrolysis of 0.1M solution of purified aniline monomer in 0.5 M H_2SO_4 at the current density 0.1 mA/cm^2 for 10 min. The film was washed with de-ionized water and dried in dynamic vacuum at 343 K for 4 h. A semi-transparent gold layer was deposited onto the polymer film by magnetron sputtering.

The current-voltage characteristics (IV) of the heterostructures were obtained using an AUTOLAB unit. The measurements were carried out at the voltage variation from 1 to −1 V. The forward bias was obtained at negative potential on the Al electrode and positive on the Au one, to provide the back bias, the electrodes were connected in the reverse manner. A DDC-30 deuterium lamp was used as the light source to obtain the light IVC. The heterostructure photoelectric properties were studied by means of impedance measurements under sinusoidal oscillations with −1 V amplitude at frequency being varied from 105 to 1 Hz using the AUTOLAB unit.

The Au/PAN/PS/Al heterostructure under study has been found to demonstrate the rectifying IV (Fig. 1). The light and dark IV are essentially identical within the −0.24 to +0.24 V range. At higher voltages applied, a considerable increase of current is observed at both positive and negative biases and the light and dark IV become different from each other.

The difference between the both IV is especially clear at a back bias (Fig. 1). In those conditions, the negative potential is applied to the polyaniline film, and the polymer being in the conductive emeraldine form may undergo reduction. From the forward current values, the series resistance is determined to be of the order of several hundreds Ohm, thus being in a good correlation with the impedance spectroscopy data. Under illumination, the IVCs are typical as for a photodiode. At the back bias, the photocurrent increases very slowly. A hysteresis loop is observed in the IV corresponding branch under illumination. This fact confirms the presence of slow hole traps in the band gap of PS [7].

Fig. 2 presents the photosensitivity spectrum of the Au/PAN/PS/Al heterostructure at room temperature in the 1 to 3.5 eV spectral range. The spectrum includes three photosensitivity maxima related to the photoabsorption of single-crystalline silicon (the low-energy photosensitivity edge limited by the band gap width [1, 2]), a higher energy peak inherent in the photosensitivity of PS, as well as a low intensity peak near 2.5 eV that can be ascribed to polyaniline [8].

The photocurrent increase duration under illumination is rather long (50 to 60 s), while as the illumination is switched off, the current drop takes place after few seconds. This behavior agrees with that of the photocurrent observed for the emeraldine form of polyaniline [6]. But the time to attain the stationary photocurrent is much longer (about 60 s). This long-time character of the photocurrent increase and drop in the heterostructure can be explained by the effect of adhesion levels in the polyaniline layer on the photoconductance. Taking into account that the photoconductance is believed to be associated mainly with porous silicon [7], the light absorption in PS can be supposed to result in generation of electron-hole pairs, a large amount of the latter is

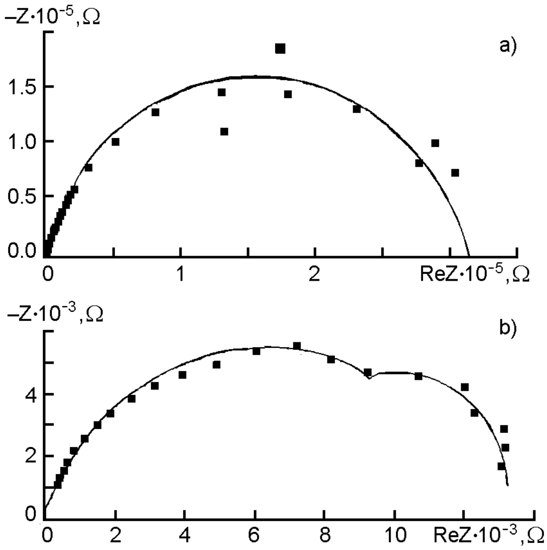

Fig. 3. Impedance dependences in darkness (a) and under illumination (b) at −1 V voltage.

trapped by the adhesion levels in the polyaniline layer.

The measurements using the impedance spectroscopy (IS) method were carried out under application of sinusoidal oscillation of −1 V amplitude at frequency being varied from 10^5 to 1 Hz, in darkness and at the sample illumination. Under illumination, the Nyquist diagram exhibits two semicircles while in darkness, the system shows a higher impedance and the second semicircle is absent (Fig. 3).

The data presented shon the existence of two barriers, the first one is in the polymer/PS interphase, the second is the PS/single crystal Si one. Without illumination, the resistance of the polymer/PS barrier is higher than that of the PS/single crystal Si one. Under illumination, the resistance of the potential barrier between PAN and PS is reduced considerably (from 370 kΩ to 14 kΩ), that can be related to increase of the PAN layer specific resistance due to increased fraction of reduced PAN fragments [6].

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Фотовольтаїчні властивості гетероструктури на основі поруватого кремнію і поліаніліну

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Електричний контакт між поруватим кремнієм з *n*-типу провідністю і електропровідним полімером — поліаніліном з провідністю *p*-типу створено шляхом електрохімічної полімеризації аніліну на поверхні поруватого кремнію. Знайдено, що така гетероструктура демонструє випрямляючі I–V характеристики. При освітленні спостерігалося значне підвищення струму при зворотному зміщенні. Фоточутливість структури переважно визначається двома бар'єрами: інтерфазою полімер-поруватий кремній та поруватий кремній-монокристалічний кремній.