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CREATION OF BILATERAL STRUCTURES OF MACROPOROUS SILICON WITH NANOCOATINGS FOR SOLAR CELLS

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We have proposed a new technological solution for the creation of solar energy elements using bilateral structures of macroporous silicon to increase the overall efficiency of converting light energy into electricity. Recently, the research on R&D in solar cell technology has focused mainly on crystalline silicon technologies and photovoltaic systems, including organic ones. The main physical phenomenon that determines the prospects of two-dimensional structures of macroporous silicon with nanocoatings as solar cells is the increase in absorption of electromagnetic radiation and photoconductivity as a result of interaction of optical modes with the developed surface of cylindrical macropores with a barrier on the nanocoating-surface boundary. We fabricated two-sided macroporous silicon structures with nanocoatings for solar cells, including silicon technology, organic nanoformations, and photovoltaic system formation. Silicon is a promising material for the manufacture of structures with a cylindrical geometry of air macropores due to the anisotropy of the cheap process of photoelectrochemical etching. The presence of periodically located cylindrical pores separated by silicon columns provides a large effective surface of the samples and enhanced optical and photophysical characteristics of silicon structures. Polymer composites with nanocoatings with CdS nanocrystals and multilayer carbon nanotubes in polyethyleneimine generate charges of opposite sign on both surfaces of the structures under illumination. The formation of bilateral structures of macroporous silicon with nanocoatings increases the overall energy conversion efficiency in solar cells by up to 60 %. In addition, one can use our proposed solar cells in the upper atmosphere.

Keywords: macroporous silicon, nanocoatings, bilateral structures, solar cell technology

INTRODUCTION

Energy provides essential human needs such as heating and cooling, electricity to our homes, factories, and businesses. Solar cell technologies meet these needs better than existing technologies due to renewable and efficiency of solar energetic and environmental impact. The solar cell industry demonstrates growth across the world. For example, the average annual growth rate is 68 % in USA. Growth in solar industry led to falling prices by more than 70 % since 2010. In 2016, solar industry installed 39 % of all new electric generating capacity. Increasing competitiveness of solar industry against other technologies has allowed it to increase its share of total electrical generation: from 0.1 % in 2010 to 1.4 % today (in USA). In 2020 the solar industry should surpass 3 % of total generation and is expected to hit 5 % by 2022.

Recently the R&D investigations in area of solar cell technologies are concentrated mainly on the crystalline silicon technologies and photovoltaic systems including organic one. Now new solar-related technologies are close to becoming commercial reality.

One of the promising materials for the development of 2D photonic structures is macroporous silicon obtained using photoanodic etching. It is connected with formation of structures with necessary geometry and high ratio between the cylindrical macropore depth and diameter [1, 2]. Presence of periodically located cylindrical pores divided by silicon columns provides large effective surface of samples and enhanced optical and photophysical characteristics of macroporous silicon structures [3–5]. For wavelengths below the optical period of structures, the reduction of light absorption is observed owing to the guided and radiation optical modes formed by macroporous

silicon as a short waveguide [6]. Thus, we proposed bilateral structures of macroporous silicon with nanocoatings to increase the total efficiency of energy conversion in solar cells. The development of solar cells is based on oxidized bilateral macroporous silicon with optimal geometry of macropores and CdS nanocrystals [7] in a polyethyleneimine on one surface and multilayer carbon nanotubes [8] in a polyethyleneimine on the opposite surface.

The aim of the work is to develop highly efficient technologies for creating bilateral macroporous silicon structures with various nanocoatings for generation under illumination of charges of the opposite signs and obtaining high efficiency of a solar cell on the base of bilateral macroporous silicon structures with nanocoatings. It provides the solution of the following main tasks:

- manufacturing of bilateral macroporous silicon structures on silicon substrates by photoelectrochemical etching;
- formation of nanocoating SiO_2 on the surface of macropores using the method of dry oxidation of macroporous silicon structures;
- fabrication of a nanocoating with CdS nanocrystals on one surface of oxidized macroporous silicon structures and nanocoating on the basis of multiwalled carbon nanotubes in a

polymer on another surface of macroporous silicon structure;

- measurement of photoelectric characteristics of bilateral macroporous silicon structures with nanocoatings;
- fabrication of a laboratory sample and determination of the efficiency of a solar cell on the basis of bilateral macroporous silicon structures with nanocoatings.

PROCEDURE

The samples to be studied were made of silicon wafers with thickness $H = 520 \mu\text{m}$, resistivity of $4.5 \Omega \cdot \text{cm}$, characterized by the (100) orientation and n -type of conductivity (the electron concentration $n_0 = 10^{15} \text{cm}^{-3}$). We used the technique of electrochemical etching at the backside illumination of a silicon substrate (thickness $H = 520 \mu\text{m}$) [9, 10]. Macropores were etched in the form of a square lattice of parallel air cylinders with diameter $D_p = 2 \pm 0.2 \mu\text{m}$, period $4 \mu\text{m}$, depth $h_p = 50\text{--}100 \mu\text{m}$, and concentration $N_p = 6.25 \cdot 10^6 \text{cm}^{-2}$ (Fig. 1 *a*). The initial specimens are complex micropore-macropore silicon structures consisting of 100 nm micropore layers on macropore walls. Addition anisotropy etching in 10 % solution of KOH permits to remove microporous layers from the macropore surface.

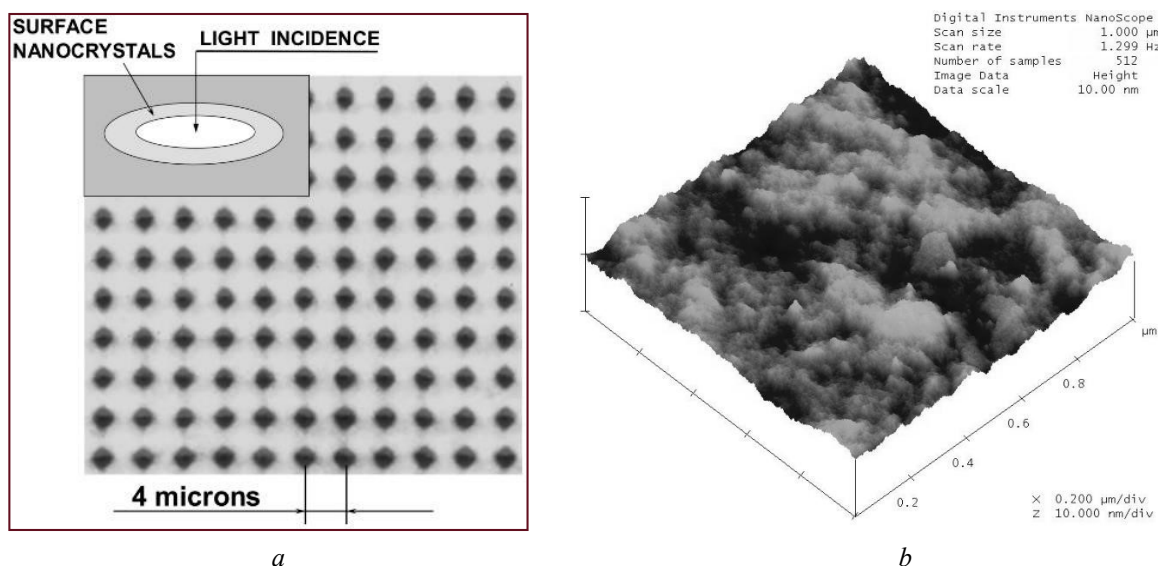


Fig. 1. *a* – macroporous silicon structures with macropore diameter $D_p = 2 \mu\text{m}$ and period $4 \mu\text{m}$; insertion: normal incidence of IR radiation on a sample (along the pores); *b* – atomic force microscopy of CdS nanocrystals

SiO₂ nanocoatings were formed in the diffusion stove after treatment of macroporous silicon substrates in the nitrogen atmosphere [10]. The oxide layers (thickness of 5–50 nm) were formed on macroporous silicon samples in dry oxygen during 40–60 min at the temperature of 1050 °C. Silicon oxide layers of 100 and 200 nm thickness were made for 50 min at 1100 °C in wet oxygen atmosphere using steam from deionized water. The oxide thickness was measured using ellipsometry.

The method of synthesis in aqueous and ethanol solutions of polyethyleneimine of ultrasmall cadmium sulphide nanoparticles was worked out under condition of saturation of the Cd cations with amino groups [11]. The average sizes of CdS nanocrystals (1.8–2 nm) were determined based on atomic force microscopy

(Fig. 1 b). X-ray diffraction spectra of CdS nanocrystals in polyethyleneimine confirmed the crystalline structure of nanoparticles [12]. CdS nanoparticles were deposited on the surface of macropores from the colloidal solutions in polyethyleneimine at the following ratio: nanocrystals – 10±2 %; polyethyleneimine – 18±2 %; water – the rest.

Carbon high purity multiwall nanotubes (CNTs) of 2 μm length and 20 nm diameter (Fig. 2) were obtained by catalytic pyrolysis of unsaturated hydrocarbons [12]. Nanoparticle morphology was investigated by the atomic force microscopy (AFM, NanoScope IIIa Dimension 3000TM, Advance Surface Microscopy Inc.). The composite nanocoating were made of carbon multiwall nanotubes with the colloidal solutions in polyethyleneimine.

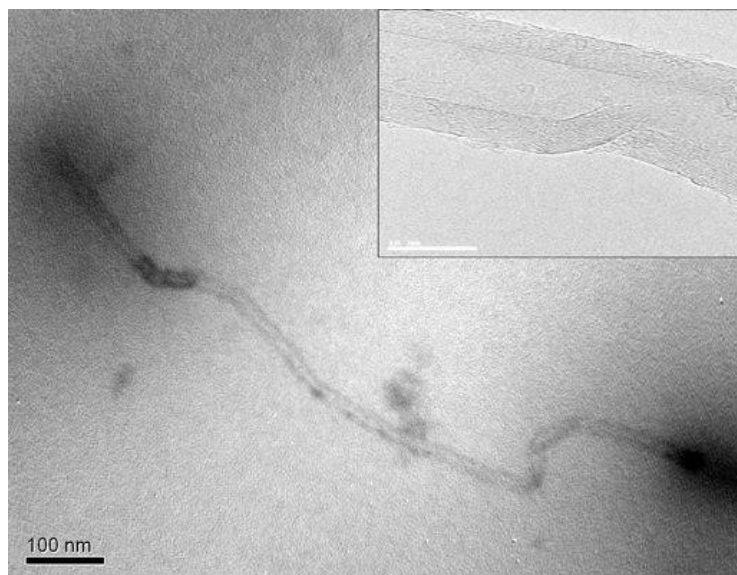


Fig. 2. Morphology of multiwall nanotubes according to the data of the atomic force microscopy

Fig. 3 shows bilateral structure of macroporous silicon with different nanocoatings: SiO₂ nanocoating on the macropore surface and nanocoating “polyethyleneimine-CdS nanocrystals” on one side and nanocoating “polyethyleneimine-multiwall carbon nanotubes” on the opposite surface of bilateral macroporous silicon structures.

Chemical states on the surface of macroporous silicon structures with nanocoatings were identified by IR absorption spectra using a PerkinElmer Spectrum BXII IR Fourier spectrometer in the spectral range of 300–8000 cm⁻¹. The optical absorption spectra

were measured at normal incidence of IR radiation on the sample, in air at room temperature.

RESULTS

The main physical phenomenon that determines the promise of two-dimensional macroporous silicon structures with nanocoatings as solar power elements is the enhancement of absorption of electromagnetic radiation and photoconductivity due to the interaction of optical modes with the developed surface of cylindrical macropores with the barrier at the “nanocoating-surface macropore” boundary [13, 14].

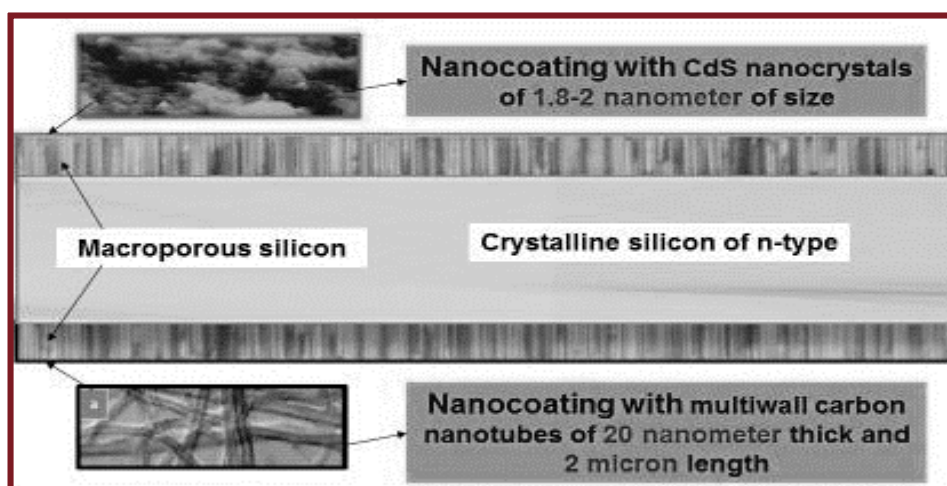


Fig. 3. Bilateral structures of macroporous silicon with nanocoatings for solar cells

2D macroporous silicon structures show Franz-Keldysh oscillations due to the intrinsic electric field on macropores surface with 1.7 nm depth [15]. One should take into account recharging of the local surface centers at energies below that of the indirect band-to-band transition in view of the potential barrier on a macropore surface. The experimental IR absorption spectra of macroporous silicon agree well with the corresponding spectral dependences of the electro-optical energy and the imaginary part of permittivity in the weak electric field approximation, thus confirming realization of impurity Franz-Keldysh effect [16]. In addition, we investigated the IR light absorption oscillations in 2D macroporous silicon with surface nanocrystals and SiO₂ layers, taking into account the electro-optical effects at strong electric fields. Thus, the resonance electron scattering on surface bonds and realization of the Wannier-Stark effect were confirmed [13, 17]. In this case, the Wannier-Stark effect is due to the large-time electron scattering as compared with the period of its oscillations in the strong electric field of illuminated “silicon-nanocoating” boundary.

IR spectra were measured on oxidized macroporous silicon structures (oxide thickness of 5–20 nm) with preliminary surface cleaning and the layer of CdS nanocrystals with thickness of 10–30 nm. Fig. 4 shows the infrared absorption spectra of oxidized macroporous silicon structures without (1, 2) and with (1', 2') a nanolayer of CdS nanoparticles 30 nm thick; the

oxide thickness: 1, 1' – 10 nm, 2, 2' – 20 nm. IR absorption of oxidized macroporous silicon structures with a layer of CdS nanoparticles increases in comparison with IR absorption of oxidized macroporous silicon structures without a layer of CdS nanoparticles (1, 2).

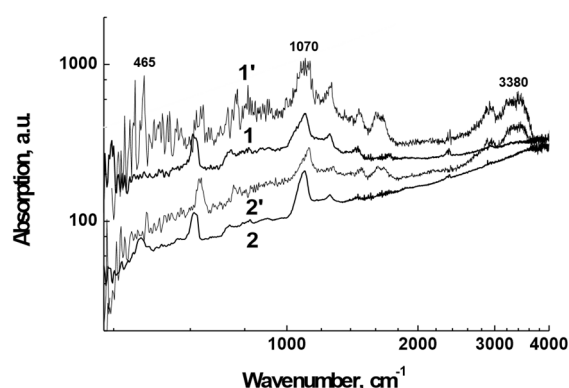


Fig. 4. The infrared absorption spectra of oxidized macroporous silicon structures without (1, 2) and with (1', 2') a nanolayer of CdS nanoparticles 30 nm thick; the oxide thickness: 1, 1' – 10 nm, 2, 2' – 20 nm

The obtained dependences of oscillation amplitudes ΔA on absorption A (Fig. 5) correspond to scattering of electrons by ionized impurities with $E^{3/2}$. The electron scattering by ionized impurities increases the flow of electrons from the silicon matrix towards the CdS nanocrystal layer in comparison with the resonance scattering with E . Thus, the deposition of a nanolayer of CdS increases IR absorption in comparison with IR absorption of oxidized

macroporous silicon structures without a layer of CdS nanoparticles and save mechanism of the electron scattering on ionized surface states.

The dependences of the spectral position of oscillation maxima (Fig. 5) in macroporous silicon with CdS nanoparticles are linear. The corresponding electric field strength ($F = \Delta E/a$) varies from $4.5 \cdot 10^4$ to $6.8 \cdot 10^4$ V/cm (Table).

After formation of nanocoatings “polyethyleneimine-multiwall carbon nanotubes” (Fig. 6) intensive peaks of sp^3 -hybrid orbitals (D), sp^2 -hybrid orbitals (G), 2D and CH_2 bonds were measured in the IR and Raman spectra of multiwall carbon nanotubes [18]. It increased IR absorbance of nanocoating “polyethyleneimine-multiwall carbon nanotubes” on macroporous silicon structure.

Fig. 7 shows IR absorption spectra of macroporous silicon structure without nanocoatings (1), bilateral macroporous silicon structure without nanocoatings (2), bilateral

macroporous silicon structure with nanocoatings CdS nanocrystals and multiwall carbon nanotubes in a polyethyleneimine, illuminated from nc-CdS side (3) and from CNTs side (4).

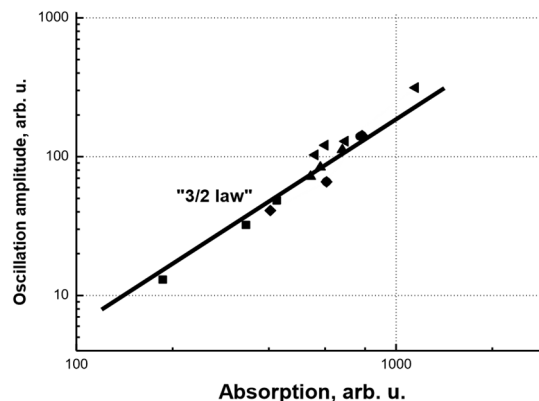


Fig. 5. Dependences of oscillation amplitudes (ΔA) on absorption (A) for macroporous silicon samples with CdS nanocrystals and with the silicon oxide thicknesses 5 nm (■), 10 nm (◆) and 20 nm (▲) for surface Si–O bonds

Table. The electric field intensity for oxidized macroporous silicon structures with CdS nanoparticles

d_{SiO_2}, nm	d_{CdS}, nm		
	10	20	30
	$F_S \cdot 10^{-4}, V/cm$	$F_S \cdot 10^{-4}, V/cm$	$F_S \cdot 10^{-4}, V/cm$
10	4.5	5.8	6.8
20	4.9	5.7	6.4

d_{SiO_2}, nm	d_{CdS}, nm		
	10	20	30
	$F_S \cdot 10^{-4}, V/cm$	$F_S \cdot 10^{-4}, V/cm$	$F_S \cdot 10^{-4}, V/cm$
10	4.5	5.8	6.8
20	4.9	5.7	6.4

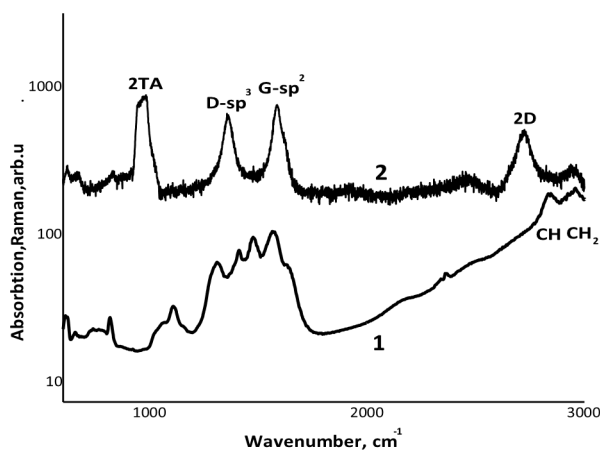


Fig. 6. IR absorption (1) and Raman (2) spectra of multiwall carbon nanotubes

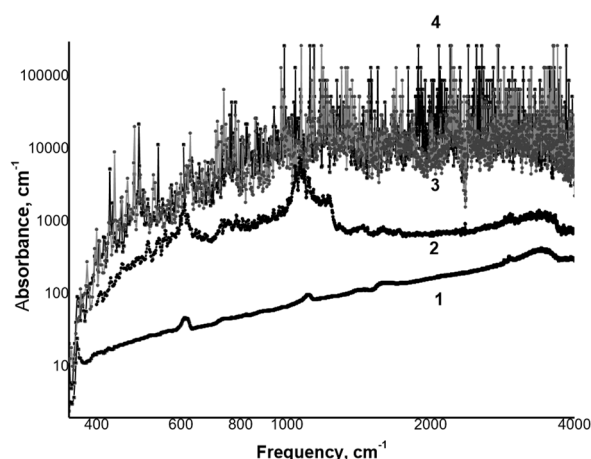


Fig. 7. IR absorption spectra of macroporous silicon structure (1), bilateral macroporous silicon structure without nanocoatings (2); bilateral macroporous silicon structure with nanocoatings nc-CdS and CNTs in PEI, illuminated from nc-CdS (3) and from CNTs (4)

For bilateral macroporous silicon structure with nanocoatings nc-CdS and CNTs in polyethyleneimine the light absorption increases 10 times (Fig. 7) in comparison with bilateral macroporous silicon structure without nanocoatings. In addition, polymer composites of nanocoatings with CdS nanocrystals and multiwall carbon nanotubes in a polyethyleneimine generate under illumination charges of the opposite sign on both surfaces of structures. As a result, overall efficiency of conversion of light energy into electric current increased by 60 %.

CONCLUSIONS

We developed bilateral structures of macroporous silicon with nanocoatings for solar cells including silicon technology, organic nanocoatings and photovoltaic system formation. Silicon is a promising material for the fabrication

of macroporous structures with cylindrical geometry of air macropores due to anisotropy and cheap process of photo-electrochemical etching. Polymer composites of nanocoatings with CdS nanocrystals and multiwall carbon nanotubes in a polyethyleneimine generate under illumination charges of the opposite sign on both surfaces of structures. Formation of bilateral structures of macroporous silicon with organic nanocoatings increases the total efficiency of energy conversion in solar cells up to 60 %. New technological solution for the creation of solar power elements by using bilateral macroporous silicon structures increased the overall efficiency of conversion of light energy into electric current, volt-watt sensitivity of structures. In addition, it is possible to use our solar cells in the field and in the upper atmosphere.

Створення двосторонніх структур макропористого кремнію з нанопокриттями для сонячних елементів

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Ми запропонували нове технологічне рішення для створення сонячних енергетичних елементів за допомогою двосторонніх структур макропористого кремнію для підвищення загальної ефективності перетворення енергії світла в електричний струм. Останнім часом дослідження R&D в області технологій сонячних елементів зосереджені в основному на кристалічних кремнієвих технологіях і фотоелектричних системах, включаючи органічні. Основним фізичним явищем, що визначає перспективність двовимірних структур макропористого кремнію з нанопокриттями як сонячних елементів, є підвищення поглинання електромагнітного випромінювання і фотопровідності в результаті взаємодії оптичних мод з розвиненою поверхнею циліндричних макропор з бар'єром на межі «нанопокриття – поверхня макропор». Ми виготовили двосторонні структури макропористого кремнію з нанопокриттями для сонячних елементів, включаючи кремнієву технологію, органічні наноутворення та формування фотоелектричної системи. Кремній є перспективним матеріалом для виготовлення структур з циліндричною геометрією повітряних макропор завдяки анізотропії дешевого процесу фотоелектрохімічного травлення. Наявність періодично розташованих циліндричних пор, розділених кремнієвими колонами, забезпечує велику ефективну поверхню зразків і посилені оптичні та фотофізичні характеристики кремнієвих структур. Полімерні композити з нанопокриттями з нанокристаллами CdS і багатощаровими вуглецевими нанотрубками в поліетиленіміні генерують при освітленні заряди протилежного знаку на обох поверхнях структур. Формування двосторонніх структур макропористого кремнію з нанопокриттями підвищує загальну ефективність перетворення енергії в сонячних елементах до 60 %. Крім того, можна використовувати запропоновані нами сонячні елементи у верхніх шарах атмосфери.

Ключові слова: макропористий кремній, нанопокриття, білатеральні структури, технологія сонячних комірок

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