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Optical Properties of Monocrystalline Silicon Nanowires

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The paper presents the results of a study of the optical reflection and transmission spectra of a silicon single crystal p-Si (100) with silicon nanowires grown on both sides and porous silicon p-Si (100) on a single crystal substrate in the spectral range 0.2 ÷ 1.7 µm. The layers of nanowires had a thickness of 5.5 µm, 20 µm, 50 µm and a porosity of 60 %. The porous silicon layers had a thickness of 5 µm, 50 µm and a porosity of 45 %, 55 % and 65 %. The change in the energy band structure in single-crystal silicon nanowires and in a single-crystal matrix of porous silicon is shown.

Keywords: porous silicon p-Si (100), silicon nanowires, reflection spectra, transmission spectra, absorption spectra, quantum size effect.

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Introduction

A promising material for modern micro- and nanoelectronics is monocrystalline silicon nanowires and porous silicon. Porous silicon has a fairly efficient photoluminescence in the visible region of the spectrum at room temperature. On low-resistance silicon substrates, mesoporous layers of porous silicon are almost always created, which do not luminesce in the visible region of the spectrum [1].

Films of porous silicon and silicon nanowires have found application in solar energy, as broadband antireflection coatings in solar cells, and are also used for the manufacture of light-emitting diodes and chemical sensors [1]. The properties of a material that consists of grains of micro or nanometer size depend on its specific surface area. An effective method of increasing the specific surface of a sample is to reduce the size of its grains, or to introduce small voids into the bulk material [2]. The optical and electrical parameters of the films of porous silicon and silicon nanowires, namely, the absorption coefficient α, the refractive index n, characteristic of crystalline films, were determined from optical studies similarly to [3], and the parameters of the films and the electronic properties of the semiconductor surface were determined using phenomenological approach, as in [4]

Monocrystalline silicon nanowires and porous silicon have found applications in photodetectors and solar cells. A layer of porous silicon or monocrystalline silicon nanowires is created on one or both sides on a monocrystalline silicon wafer, from which a solar cell or detector will then be made. A layer of porous silicon or monocrystalline silicon nanowires improves light absorption due to multiple reflection and scattering of light (electromagnetic) waves in pores or between nanowires. The surface of porous silicon is covered with a silicon dioxide film. The thickness of the silicon dioxide film is increased to improve surface passivation and reduce the effective lifetime of minority charge carriers [5]. The relationship between the morphology of the porous layer, absorption, light transmission, and the effective lifetime of minority carriers in porous silicon, which is used in solar cells, is modelled using an analytical model [6, 7]. The kinetics of photoconductivity in porous silicon is calculated using a diffusion model of photoconductivity relaxation. The relaxation time of photoconductivity in porous silicon was found from the solution of the non-stationary diffusion equation of minority charge carriers and the boundary conditions written for the porous layer and single-crystal substrate [7, 8]. The depth of pores, diameter of pores, distance between pores, porosity affect absorption, light transmission, effective lifetime of minority charge carriers and the kinetics of photoconductivity in one-sided [7, 8] and two-sided porous silicon [6].

The aim of this work is to study the optical reflectance and transmission spectra in the spectral range 200 - 1800 nm of single-crystal silicon nanowires and porous silicon of various heights and porosity to obtain data on the energy band structure.

I. Experimental technique

On the surface of a monocrystalline silicon wafer (100) - oriented p + - type silicon, pores were prepared by electrochemical etching in a solution of concentrated hydrofluoric acid (49 % HF in water) and pure ethanol. The monocrystalline silicon wafer had a thickness of 510 ± 20 µm and a resistivity of 0.01 Ωcm. The magnitude of the current density that passed through the monocrystalline silicon wafer and the etching time of the sample determined the thickness of the porous layer and its porosity. The prepared samples of porous silicon had a porous layer thickness of 5 µm and 50 µm and a porosity of 45 %; 55 %; 65 %.

Monocrystalline silicon nanowires (NWs) were grown on the surface of a monocrystalline silicon wafer (100) - oriented p+ - type silicon using metal-assisted wet chemical etching (MAWCE). The monocrystalline silicon wafer had a thickness of 510 ± 20 µm and a resistivity of 0.01 Ωcm. Monocrystalline silicon nanowiress were grown using two solutions in two stages. The time of chemical etching, which varied from 10 to 60 min, determined the length (height) of monocrystalline silicon nanowires. The prepared samples with layers of monocrystalline silicon nanowires had a porosity of 60 % (the volume fraction of nanowires is 40 %). The length of monocrystalline silicon nanowires l_{NW} filaments was 5.5 µm; 20 µm; 50 µm.

Optical studies (reflection and transmission) were carried out on a Shimadzu UV-3600 double-beam spectrophotometer in the range 200 - 1800 nm. The resolution of the device was no more than 0.01 nm. The studies were carried out at room temperature.

II. Results and discussion

The energy of a quantum mechanical particle (electron or hole) is described using the formula:

$$E(\mathbf{k}) = E_0(\mathbf{k}) + \Delta E(\mathbf{k}), \qquad (1)$$

where **k** is the wave vector, E_0 (**k**) is the energy of the fundamental optical transition of the material under study; $\Delta E(\mathbf{k})$ is a quantum size addition to the hole energy (dimensional quantization energy). It should be taken into account that the effective mass of the hole is negative. The energy of the ground state, in comparison with the state of the crystal, without limitation increases or decreases by the value [9]:

$$\Delta E = \frac{\hbar^2 \pi^2}{2m^* L^2}, \qquad (2)$$

where m^* is the effective mass of a free particle whose motion is limited by infinitely high non-penetrating barriers located at a distance L.

Fig. 1, 2 show the optical reflection and transmission spectra of porous silicon with a pore size of 5 µm (l_{por} Si layer) with different porosities of 45 %, 55 %, 65 %. Two energy peaks E_1 = 3.35 eV ($E_1(\Lambda_1^C - \Lambda_3^V)$ [9]) and E_2 = 4.465 ($E_2(\Lambda_1^C - \Lambda_5^V)$ [10]) are observed in the high-

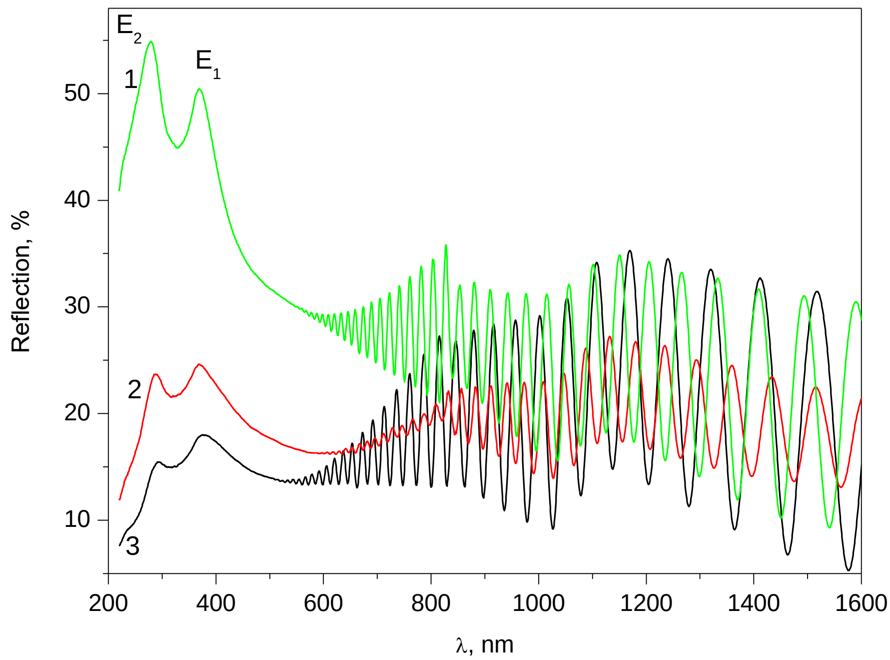

Fig. 1. Reflection spectra of porous silicon with a pore size of 5 µm (l_{por} Si layer): curve 1 - porosity 45 %; curve 2 - porosity 55 %; curve 3 - porosity 65 %.

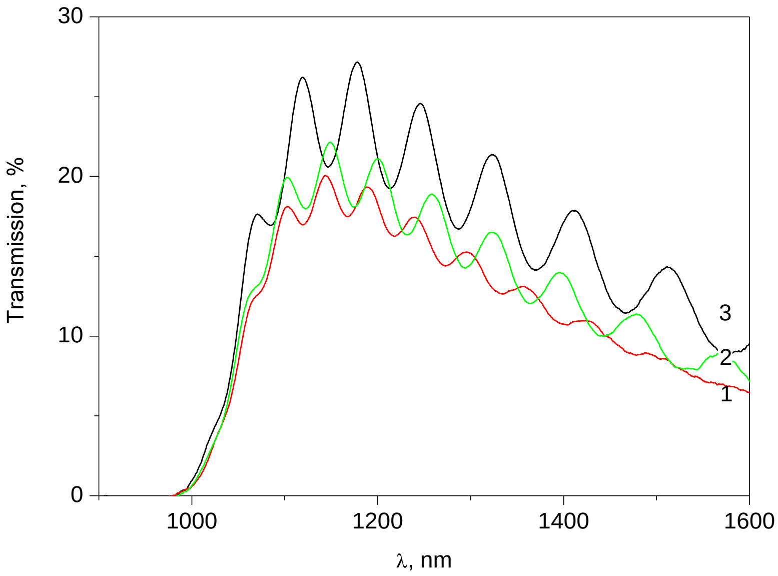

Fig. 2. Transmission spectra of porous silicon with a pore size of 5 μm (l_{por} Si layer): curve 1 - porosity 45 %; curve 2 - porosity 55 %; curve 3 - porosity 65 %.

energy region of the reflection spectrum of porous silicon p-Si (100) (see Fig. 1, curves 1-3). These energy peaks are also observed in monocrystalline silicon in this region of the spectrum. The interference pattern, which is observed in the low-energy region of the reflection spectrum of porous silicon p-Si (100), is determined by both oxides SiO_x i SiO_2 (Fig. 1) and a layer of porous silicon p-Si (100). With a decrease in the porosity of porous silicon samples, the intensity of the high-energy peaks E_1 and E_2 increases. The oxide coating of the real silicon surface is an amorphous film whose thickness ranges from 0.5 nm to 7 nm [11, 12]. The thickness of the SiO_x transition layer between the silicon single crystal and silicon dioxide is 0.5-0.7 nm [13].

Since the reflection coefficient $R = R(\lambda)$ is related to the transmission coefficient $T = T(\lambda)$ and absorption $D = D(\lambda)$ by the relation $R(\lambda) + T(\lambda) + D(\lambda) = 1$, then in this work we also plotted absorption spectra $D(\lambda) = 1 - [R(\lambda) + T(\lambda)]$ (Fig. 3). The absorption spectra of porous silicon with a pore size of 5 μm (lpor Si layer) and porosity of 45 %, 55 %, 65 % completely correlate with the reflection spectra (Fig. 1) and transmission spectra (Fig. 2).

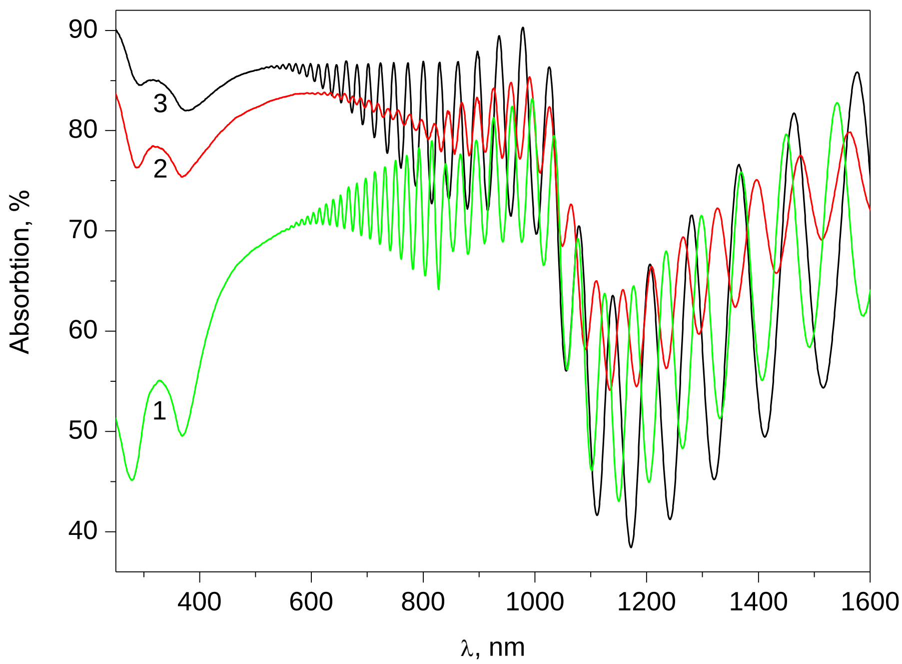

Fig. 3. Absorption spectra of porous silicon with a pore size of 5 μm (l_{por} Si layer): curve 1 - porosity 45 %; curve 2 - porosity 55 %; curve 3 - porosity 65 %.

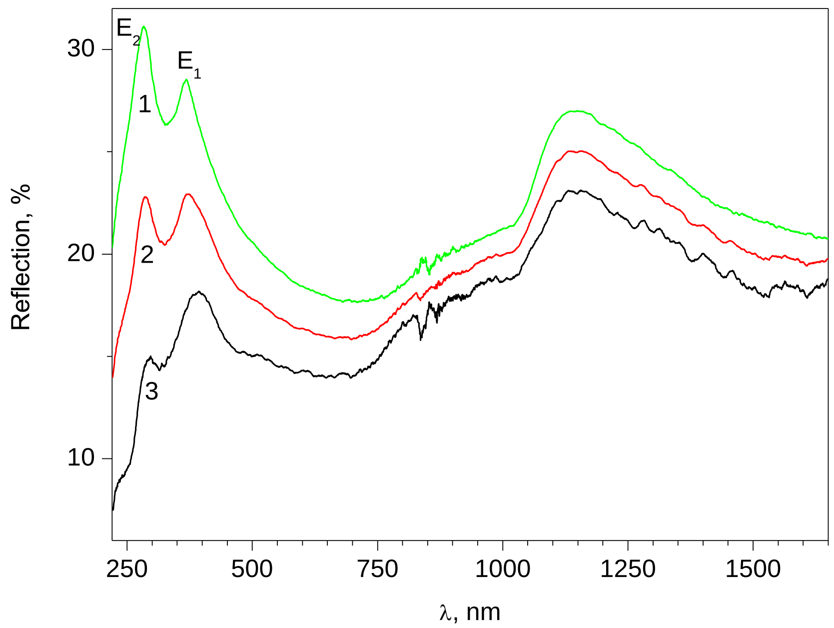

Fig. 4. Reflection spectra of porous silicon with a pore size of 50 μm (l_{por} Si layer): curve 1 – 45 % porosity; curve 2 - porosity 55 %; curve 3 - porosity 65 %.

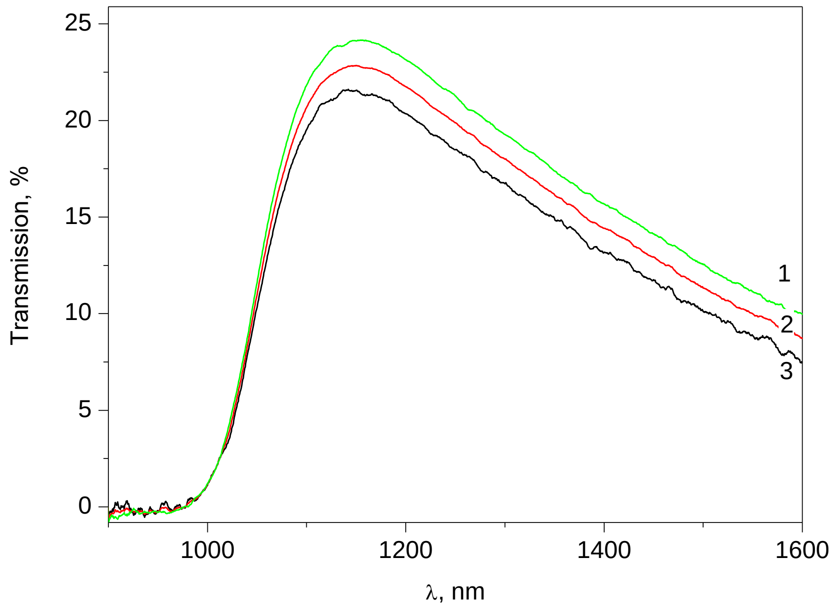

Fig. 5. Transmission spectra of porous silicon with a pore size of 50 μm (l_{por} Si layer): curve 1 – 45 % porosity; curve 2 - porosity 55 %; curve 3 - porosity 65 %.

Fig. 4 shows the optical reflectance spectra of porous silicon with a pore size of 50 μm (l_{por} Si layer) with different porosities of 45 %, 55 %, and 65 %. As can be seen from Fig. 4, peaks E_1 and E_2 (curve 1, porosity 45 %) correspond to energies of 3.396 eV and 4.375 eV, respectively (these are the peaks of single-crystal silicon p-Si (100)). With a porosity of 55 % (Fig. 4, curve 2), the peaks E_1 and E_2 correspond to energies of 3.396 eV and 4.469 eV, respectively; at a porosity of 65 % (Fig. 4, curve 3), the peaks E_1 and E_2 correspond to energies of 3.396 eV and 4.367 eV, respectively.

Figure 5 shows the optical transmission spectra of porous silicon with a pore size of 50 μm (l_{por} Si layer) with porosities of 45 %, 55 %, and 65 %. As can be seen from Figures 4 and 5, the reflectance and transmission spectra at porosities of 45 %, 55 % and 65 % (curves 1-3) are similar to the spectra of monocrystalline silicon. As you know, the main parameter of a porous material is the porosity index. It determines how much of the volume of the material is occupied by the pores. When this volume is small, the properties of such a material are close to those of monocrystalline silicon, which is also observed in our case.

Fig. 6 shows the absorption spectra at a pore size of 50 μm (l_{por} Si layer) and a porosity of 45 %; 55 %; 65 %. As can be seen from Fig. 6, the absorption spectra of porous silicon at a pore size of 50 μm (l_{por} Si layer) and porosity of 45 %, 55 %, 65 % completely correlate with

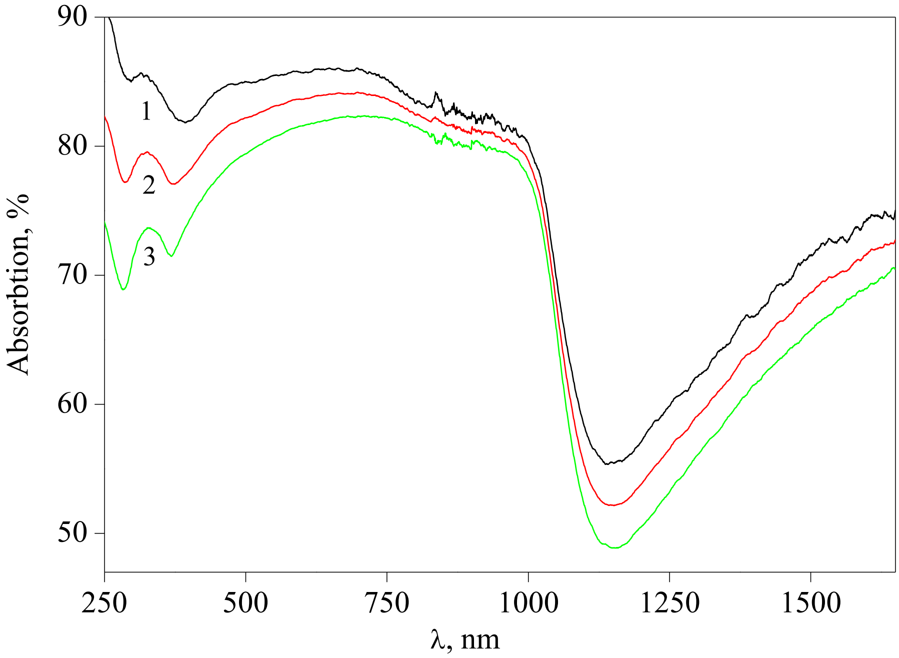

Fig. 6. Absorption spectra of porous silicon with a pore size of 50 µm (l_{por} Si layer): curve 1 – 45 % porosity; curve 2 - porosity 55 %; curve 3 - porosity 65 %.

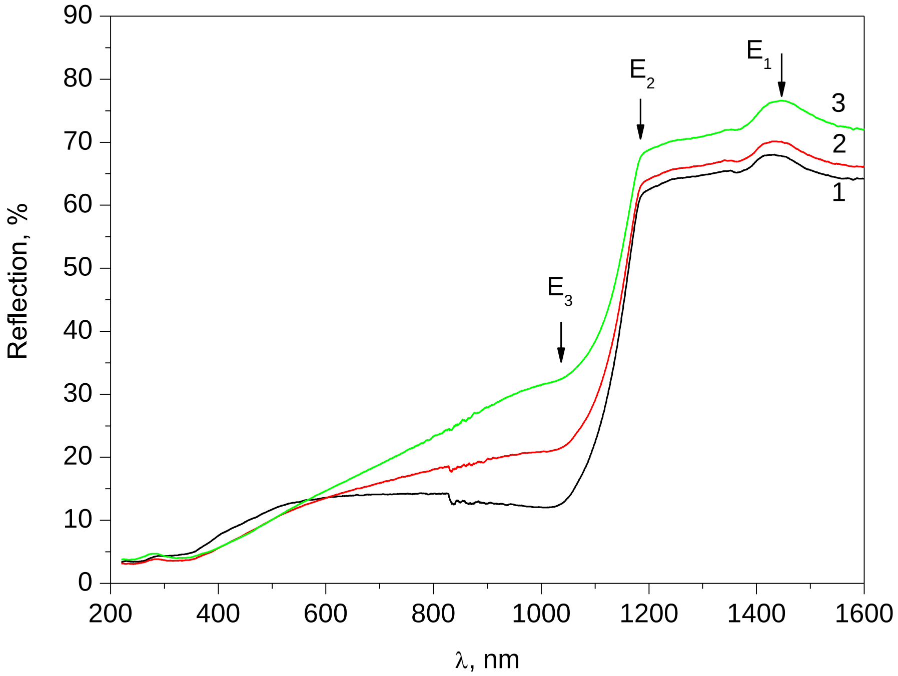

Fig. 7. Reflection spectra of silicon nanowires: curve 1 - l_{NW} = 5.5 µm; curve 2 - l_{NW} = 20 µm; curve 3 - l_{NW} = 50 µm. The porosity of the samples is 60 %.

the reflection spectra (Fig. 4) and transmission spectra (Fig. 5). In the low-energy region of the spectrum, absorption decreases; when approaching the fundamental optical transition energy E_0 of the material under study, absorption increases sharply and reaches its maximum value.

Fig. 7 shows the optical reflection spectra of silicon nanowires in the wavelength range λ = 0.2 - 1.8 µm with a nanowire length of 5.5 µm, 20 µm, 50 µm. The porosity of the samples is 60 %. Optical reflectance spectra are identical on both sides of the sample (silicon nanowires formed on both sides of p-Si (100)). Fig. 7 shows three energy positions E_1; E_2; E_3, which correspond to energies of 0.862 eV; 1.046 eV and 1.198 eV, respectively. With an increase in the length of silicon nanowires, the reflection coefficient R in the wavelength range of 0.2 - 1.8 µm increases.

Figure 8 shows the transmission spectra of silicon nanowires l_{NW} = 5.5 µm; 20 µm; 50 µm and porosity of samples – 60 %. As you can see from the figure, we have two energy peaks E_1; E_2, which correspond to energies of 0.854 eV and 1.048 eV, respectively. As the length of silicon nanowires increases, the transmittance of this material decreases.

In Fig. 9 shows the absorption spectra of silicon nanowires with a length of l_{NW} = 5.5 µm; 20 µm; 50 µm and porosity of samples – 60 %. As can be seen from Fig. 9, the absorption spectra of silicon nanowires completely correlate with the reflection spectra (Fig. 7) and transmission spectra (Fig. 8). In the low-energy region of the spectrum, the absorption is minimal; when approaching the energy of the fundamental optical transition of a given material, the absorption E_0 sharply increases and reaches its maximum value.

Based on the Heisenberg uncertainty principle for energies E and time t ($\Delta E \cdot \Delta t \geq \hbar$), relaxation effects in light absorption by a crystal are described by the broadening parameter $\Delta E = \hbar/\tau$ (the broadening of the electronic transition E_0 is related to the lifetime of free charge carriers through their interaction with lattice vibrations, impurities, defects, including surface defects), where τ is the energy relaxation time of photogenerated charge carriers.

According to the experimental data, according to the optical reflection and transmission spectra (Fig. 1-2;

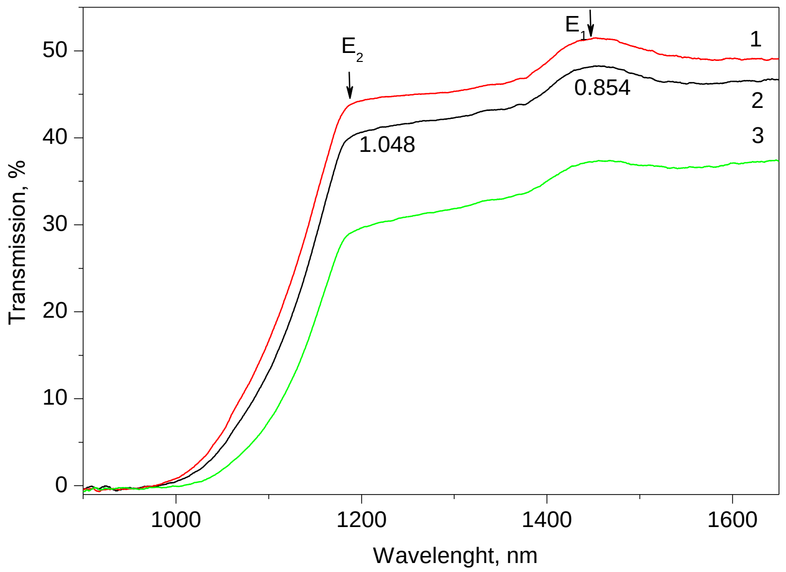

Fig. 8. Transmission spectra of silicon nanowires: curve 1 - l_{NW} = 5.5 µm; curve 2 - l_{NW} = 20 µm; curve 3 - l_{NW} = 50 µm. The porosity of the samples is 60 %.

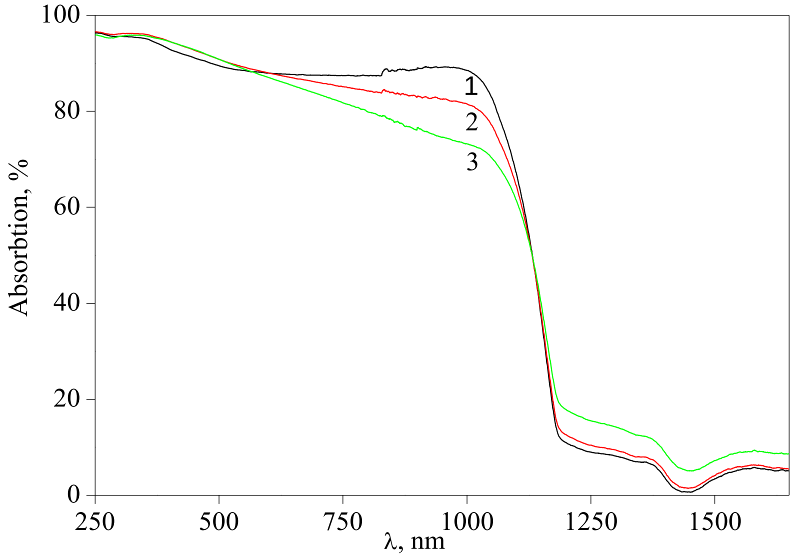

Fig. 9. Absorption spectra of silicon nanowires: curve 1 - l_{NW} = 5.5 µm; curve 2 - l_{NW} = 20 µm; curve 3 - l_{NW} = 50 µm. The porosity of the samples is 60 %.

Fig. 4-5; Fig. 7-8) for porous silicon with a pore size of 5 µm (l_{por} Si layer) for porous silicon with a pore size of 50 µm ; for silicon nanowires with lengths l_{NW} = 5.5 µm; l_{NW} = 20 µm; l_{por} = 50 µm the energy broadening of the optical spectra of these materials is 0.167 eV; 0.162 eV; 0.184 eV, respectively. Energy relaxation time of photogenerated charge carriers τ for porous silicon with a pore size of 5 µm (l_{por} Si layer), for porous silicon with a pore size of 50 µm; for silicon nanowires with lengths l_{NW} = 5.5 µm; l_{NW} = 20 µm; l_{NW} = 50 µm is equal to 3.941 10^{-15} s; 4.063 10^{15} s and 3.577 10^{-15} s, respectively.

Conclusions

According to experimental data and calculations, the decrease in the band gap of porous silicon p-Si (100) and single-crystal silicon filaments, as compared to the single crystal of p-Si (100), is explained by the quantum-size effect that occurs in the objects under study. It is shown that the energy spectra of the studied structures depend on their specific surface area.

The absorption spectra of silicon nanowires are constructed and analyzed. The energy broadening ΔE of the optical spectra and the energy relaxation time of photogenerated charge carriers τ of the materials under study are estimated.

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Оптичні властивості монокристалічних кремнієвих нанониток

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В роботі представлені результати дослідження оптичних спектрів відбивання та пропускання монокристалу кремнію p-Si (100) з кремнієвими нанонитками вирощеними з обох сторін та пористого кремнію p-Si (100) на монокристалічній підкладці в спектральному діапазоні 0,2 ÷ 1,7 мкм. Шари нанониток мали товщину 5,5 мкм, 20 мкм, 50 мкм та пористість 60 %. Шари пористого кремнію мали товщину 5 мкм, 50 мкм та пористість 45 %, 55 % та 65 %. Показано зміну енергетичної зонної структури в монокристалічних кремнієвих нанонитках та в монокристалічній матриці пористого кремнію.

Ключові слова: пористий кремній p-Si (100), кремнієві нанонитки, спектри відбивання, спектри пропускання, спектри поглинання, квантоворозмірний ефект.