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COHERENT OSCILLATIONS IN IR SPECTRA OF 2D MACROPOROUS SILICON STRUCTURES WITH SURFACE NANOCOATINGS

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One of the promising materials for the development of 2D photonic structures is macroporous silicon obtained using photoanodic etching. Presence of periodically located cylindrical pores divided by silicon columns provides large effective surface of samples and enhanced optical and photo-physical characteristics of macroporous silicon structures. In this paper, the near-IR light absorption oscillations of 2D macroporous silicon structures with microporous silicon layers, SiO₂ nanocoatings and CdTe, ZnO surface nanocrystals are studied taking into account the Wannier–Stark electro-optical effect. An analysis of the experimental absorption spectra was carried out within the model of the resonant electron scattering with infinite amplitude on impurity states in strong electric field, with difference between two resonant energies equaled to the step of Wannier–Stark ladder. The constant oscillation period specifies the realization of Wannier–Stark effect on the randomly distributed surface bonds on silicon-nanocoating interface. We compared the IR absorption oscillations in 2D macroporous silicon with surface nanocoatings, analyzed shifts and deviations of oscillation peaks. The coherence of the IR spectra oscillations increases with the decrease of surface state concentration and with the optimal area of contact of nanocrystals to the macropore surface. Thus, the shift of oscillations for ZnO nanoparticles with optimal size of nanocrystals (3.7–4.4 nm) leads to deviations of the oscillation peaks within 0.26–0.42 meV, the oscillation coherence reaches 0.25–0.4 %. The small broadening parameter of the Wannier–Stark ladder levels $\Gamma = 0.3 \pm 0.8 \text{ cm}^{-1}$ equals to that for surface phonon polaritons measured in thin films of II–VI semiconductors. Controllability and coherence of the investigated system are determined by forming of coherent Wannier levels in a narrow triangular potential well formed by an electric field at the silicon-nanocoating interface. In addition, we have proposed a high coherent optical quantum computer based on the quantum Wannier–Stark electro-optical effect on a silicon matrix with macropores and a layer of nanocrystals on the macropore surface.

Keywords: 2D macroporous silicon, surface nanocoatings, IR spectra, coherent oscillations

INTRODUCTION

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 photo-physical 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].

2D macroporous silicon structures show Franz-Keldysh oscillations due to the intrinsic electric field on macropores surface with 1.7 nm

depth [7]. 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 [8]. 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 [9, 10]. 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.

In this paper, the IR light absorption oscillations of 2D macroporous silicon structures with microporous silicon layers, SiO₂ nanocoatings and CdTe, ZnO surface nanocrystals are studied taking into account the electro-optical effect within the strong electric field approximation. The experimental absorption spectra were analyzed within the model of resonant electron scattering on impurity states in strong electric field with infinite amplitude and with a difference between two resonant energies equaled to steps of the Wannier–Stark ladder. We compared the IR light absorption oscillations in 2D macroporous silicon with surface nanocoatings, analyzed the shift and deviations of oscillation peaks, the broadening parameter Γ of the Wannier–Stark ladders and the influence of “quantum superiority” on coherence of Wannier levels. In addition, we have proposed a high coherent optical quantum computer based on a silicon matrix with macropores and a layer of

nanocrystals on the surface of macropores for the implementation of Wannier-Stark quantum electro-optical effect.

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 $H = 520 \mu\text{m}$) [3, 11]. 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 $h_p = 50 \div 100 \mu\text{m}$, 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.

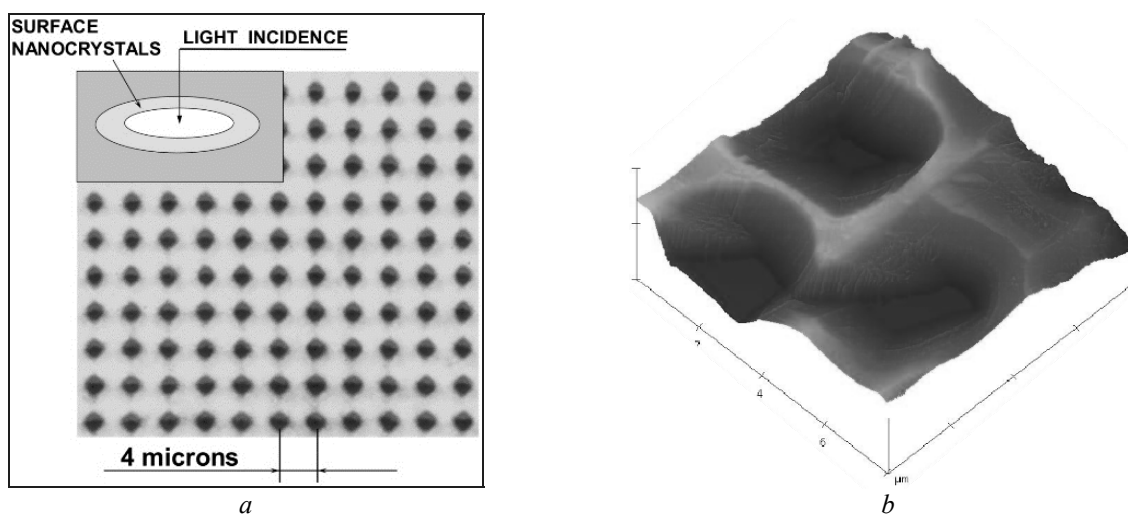


Fig. 1. *a* – macroporous silicon structures with macropore diameter $D_p = 2 \mu\text{m}$ and period $4 \mu\text{m}$; insertion: normal incidence of IR radiation on a sample (along the pores); *b* – fragment of macroporous silicon structure with CdTe nanocrystals

CdTe nanocrystals 20 nm in size were grown on the modified installation of metal dispersion using “a hot wall” [12, 13] molecular epitaxy on macroporous silicon substrates. The undoped CdTe sputtered at the substrate temperature of 475 K and the source temperature of 650 K served as element of evaporation. The thickness

of the deposited films (200 nm) was set by time of structure stay above the source of evaporation [14]. Methods of synthesis of ZnO nanoparticles in isopropanol and from solution of zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$ in ethanol have been developed in [15]. The sample obtained was washed with distilled water to remove external salts. The

average sizes of ZnO nanoparticles 4 ± 0.4 nm were determined based on absorption spectra and atomic force microscopy.

The method of synthesis in aqueous and ethanol solutions of polyethyleneimine of ultrasmall cadmium sulfide nanoparticles was worked out under condition of saturation of the Cd cations with amino groups [16]. The average sizes of CdS nanocrystals (1.8–2 nm) were determined based on atomic force microscopy. X-ray diffraction spectra of CdS nanocrystals in polyethyleneimine confirmed the crystalline structure of nanoparticles [17]. ZnO or 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.

SiO₂ nanocoatings were formed in the diffusion stove after treatment of macroporous silicon substrates in the nitrogen atmosphere [10]. The oxide layers (thickness of $5\div 50$ nm) were formed on macroporous silicon samples in dry oxygen during $40\div 60$ 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.

We performed optical investigations in the spectral range $300\div 7800$ cm⁻¹ using an IR Fourier spectrometer “Perkin Elmer” (Spectrum BXII). The optical absorption spectra were measured at normal incidence of IR radiation on a sample (along the cylindrical macropores, (Fig. 1 a, insertion) in the air at room temperature. The spectral measurement error was about 2 cm⁻¹.

EXPERIMENTAL

IR oscillations. For macroporous silicon structures with nanocoatings of surface nanocrystals and microporous silicon layers, the light absorption increases, and an oscillating structure occurs with amplitudes of the same order (Fig. 2 a, b). The absorption spectra of macroporous silicon structures with CdTe surface nanocrystals (Fig. 2 a, curve 1) and without nanocoatings (Fig. 2 a, curve 2) have similar shapes. The absorption spectra of macroporous silicon structures with ZnO surface nanocrystals (Fig. 2 b, curve 1) and with the

initial microporous layer (Fig. 2 b, curve 2) have similar shapes at photon energies over 200 meV.

The amplitude of oscillations is maximal at spectral ranges of surface levels (organic species, Si-H, C-H and O-H bonds [9–10]) in the absorption spectra of macroporous silicon structures with CdTe and ZnO surface nanocrystals.

Si-O-Si, Si-Si, Si-H₂, Si-O, SiCH₃, C=O bonds were observed only in absorption spectra of macroporous silicon structures without nanocoatings (Fig. 2 a, curve 2 and Fig. 2 b, curve 3) or with the microporous silicon layer (Fig. 2 b, curve 2). The form of oscillations (Fig. 2c, curves 1, 3) indicates its resonant character.

The spectral positions of oscillation maxima of macroporous silicon structures with microporous layers and surface nanocrystals vs. oscillation number (Fig. 3 a, curves 1–3) are straight lines. The oscillations of small amplitudes (Fig. 3 a, curve 4) were studied in macroporous silicon structures without nanocoatings [8]. The experimental 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 the impurity Franz–Keldysh effect. The oscillation period is almost constant (Fig. 3 b). The oscillation energies ΔE of macroporous silicon structures with microporous layers lie within 0.7–2 meV.

Comparison of IR spectra. Fig. 4 a shows the experimental dependences of the IR absorption of structures of macroporous silicon with SiO₂ layer of 50 nm thick (1) and microporous layer of 100 nm thick (2) in the spectral range 500–1500 cm⁻¹.

For macroporous silicon structures with SiO₂ and microporous silicon layers the light absorption increases, and an oscillating structure with giant amplitudes occurs (Fig. 4 a).

Fig. 4 b shows the experimental dependences of the IR absorption of macroporous silicon structures with surface nanocrystals CdTe (1), ZnO (2), CdS (3) in the spectral range 500–1500 cm⁻¹ too.

The small coherence of oscillations is evaluated for macroporous silicon with SiO₂ nanocoatings (Fig. 4 a, curve 1) and with microporous silicon layer (Fig. 4 a, curve 2) due

to high concentrations of surface states [10]. Better oscillation coherence was obtained for CdTe and ZnO nanocrystals (Fig. 4 *b*, curves 1 and 2). However, for structures of macroporous silicon with CdTe nanocrystals (Fig. 4 *b*, curve 1) of a size 20 nm, the coherence of the

oscillations is less than that for structures with ZnO nanocrystals with size 4 ± 0.4 nm (Fig. 4 *b*, curve 2 and Fig. 4 *c*). Structures of macroporous silicon with CdS nanocrystals of 1.8–2 nm in size (Fig. 4 *b*, curve 3) are also significantly inferior to those for ZnO nanocrystals.

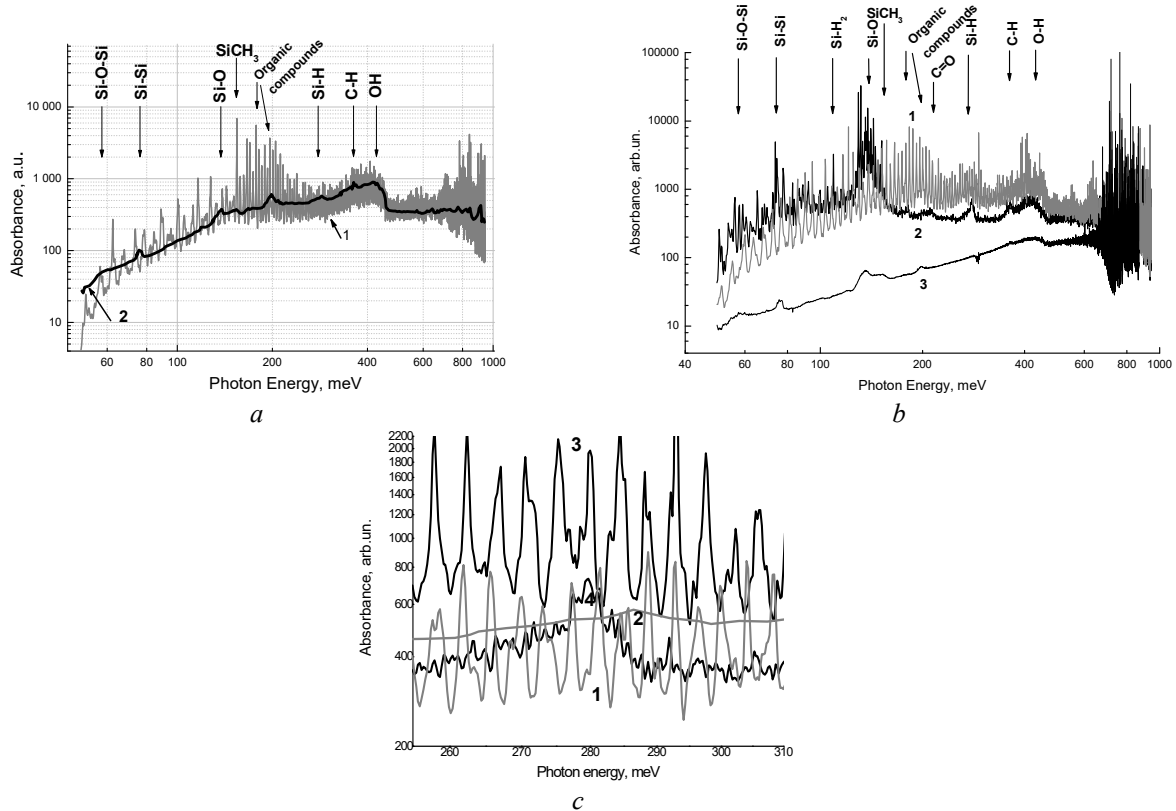


Fig. 2. *a* – absorption spectra of macroporous silicon structures with CdTe surface nanocrystals (1) and without coatings (2); *b* – absorption spectra of macroporous silicon structures with ZnO surface nanocrystals (1) and with (2) and without (3) microporous layers; *c* – fragments of absorption spectra of macroporous silicon structures with CdTe surface nanocrystals (1), without coatings (2), with ZnO surface nanocrystals (3) and with microporous layers (4) in the vicinity of Si-H bonds

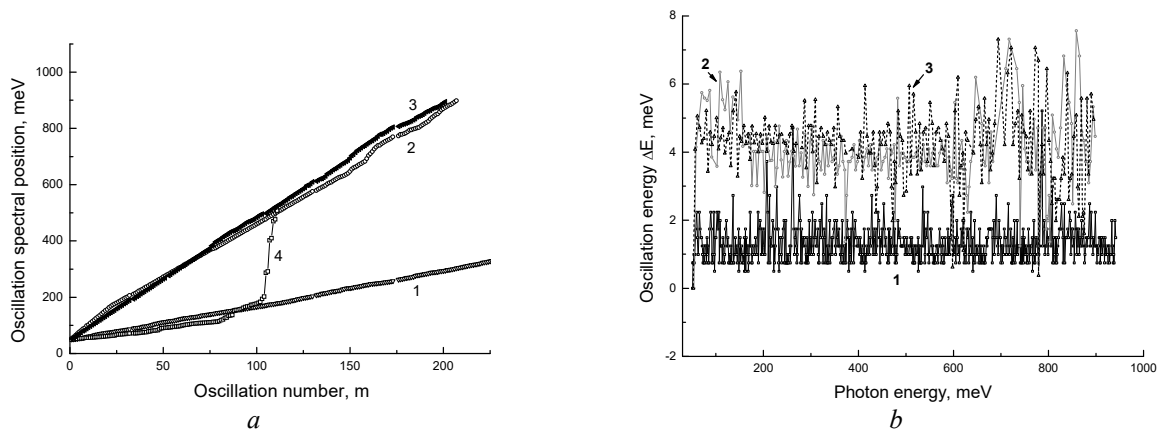


Fig. 3. *a* – the spectral position of oscillation maxima of macroporous silicon structures with microporous layers (1), CdTe (2), ZnO (3) surface nanocrystals and without coatings (4) as function of oscillation number; *b* – spectral dependences of the oscillation period of macroporous silicon structures with microporous layers (1), CdTe (2), ZnO (3) surface nanocrystals

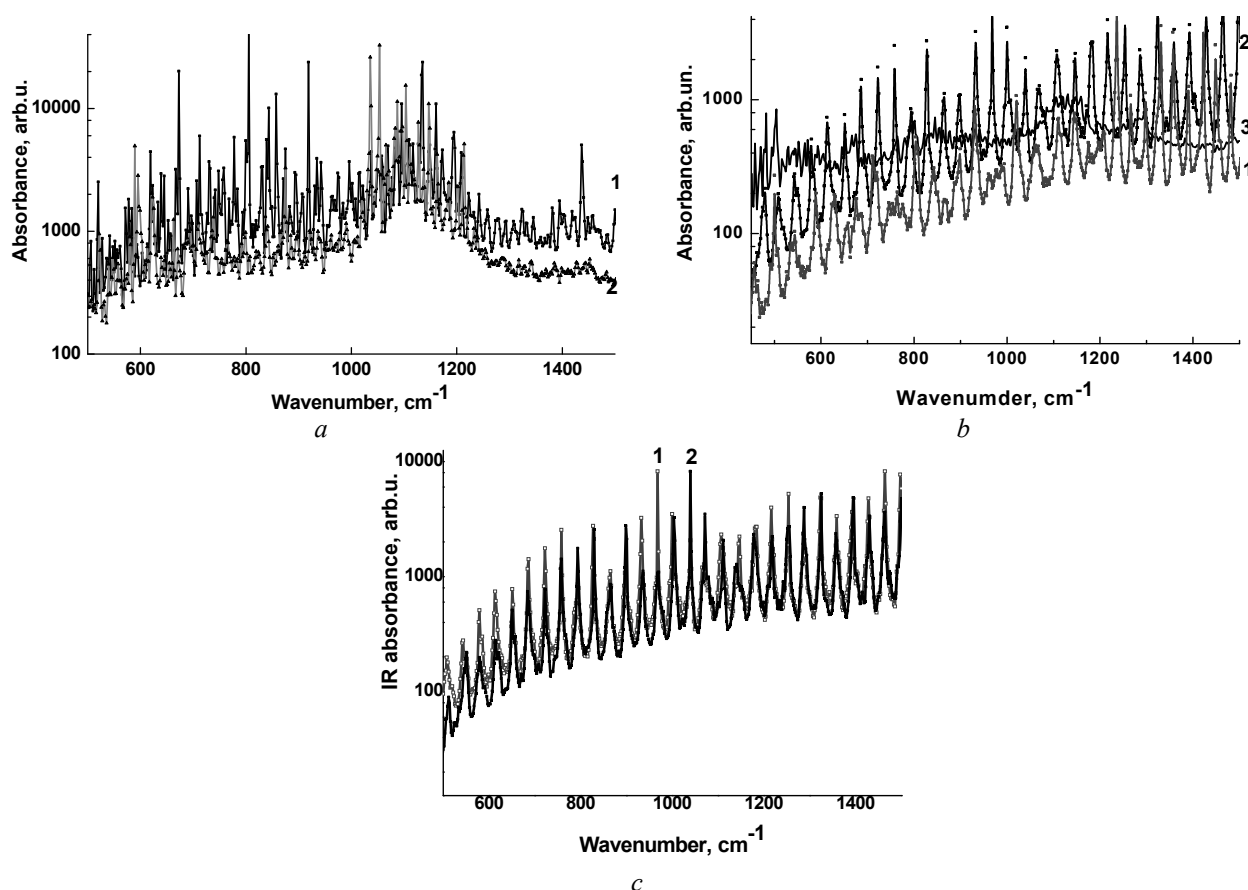


Fig. 4. *a* – experimental dependences of the IR absorption of structures of macroporous silicon with SiO₂ layer of 50 nm thick (1) and microporous layer of 100 nm thick (2) in the spectral range 500–1500 cm⁻¹; *b* – experimental dependences of the IR absorption of macroporous silicon structures with surface nanocrystals CdTe (1), ZnO (2), CdS (3) in the spectral range 500–1500 cm⁻¹; *c* – experimental dependences of the IR absorption of macroporous silicon structures with surface ZnO nanocrystals: 1 – in the spectral range 500–1500 cm⁻¹; 2 – the same spectrum of IR absorption, moved for 2 periods

Thus, the coherence of oscillations increases with the decrease of the concentration of surface states and with the optimal area of contact of nanocrystals to the surface of the macropores due to optimal size of nanocrystals (4 ± 0.4 nm). For ZnO nanoparticles, the distance between resonant oscillations is 4.4 ± 0.28 meV, and the shift of oscillations by 1 and 2 periods (Fig. 4 *c*) leads to deviations of the oscillation peaks within 0.26–0.42 meV, i.e. the oscillation coherence reaches 0.25–0.4 %.

DISCUSSION

We observed the oscillating structure in the absorption spectra of macroporous silicon structures with surface nanocrystals. The amplitude of oscillations is maximal at the spectral ranges of organic species, Si-H, C-H and O-H bonds. The results obtained indicate strong

effect of impurity states on the surface of macroporous silicon structures with nanocoatings. This may result from scattering of both electromagnetic radiation and electrons on the impurity states. The form of oscillations (Fig. 4 *c*) and constant oscillation period (Fig. 3 *b*) indicate the resonant character of scattering.

The oscillations of small amplitude in macroporous silicon structures without nanocoatings [8] correspond to the weak electric field approximation. The macroporous silicon structures with surface nanocrystals investigated in this paper have higher surface potential of nanocoatings with surface bonds. Therefore, the onset of oscillations with giant amplitude can be explained by the electro-optical processes in strong electric field. Moreover, the constant oscillation period (Fig. 3 *b*) may specify the

realization of the Wannier–Stark effect on randomly distributed surface bonds on nanocrystals [9].

A method of experimental observation of Wannier–Stark ladder was proposed in papers [18, 19]. It was shown that the scattering amplitude has resonant behavior in the case of electron scattering on impurities. If the electric field is directed along the x -axis of the crystal, then electron scattering occurs in the plane (y, z) , and the difference between two resonant energies is approximately equal to the step of Wannier–Stark ladder. In our case, an electric field of “silicon-nanocoating” heterojunctions on the macropore surface is directed perpendicularly to the surface too (Fig. 5), and surface states that scatter electrons are concentrated perpendicularly to the x -direction in the plane (y, z) that is the plane of resonant scattering.

Let us consider a semiconductor with the dispersion law $E(k) = E_0 - \Delta (\cos k_y a + \cos k_z a)$, where k is a quasi-momentum with components k_y, k_z , E_0 the energy corresponding to the midgap, Δ the energy equal to 1/6 of the band gap, a the lattice parameter. The wave function in the Wannier representation was written as in [19]:

$$\langle j | \psi_E \rangle = \langle j | \Phi_E \rangle + \frac{\langle j | \hat{G}_0(E) | 0 \rangle V_0 \langle 0 | \Phi_E \rangle}{1 - V_0 \langle 0 | \hat{G}_0(E) | 0 \rangle}. \quad (1)$$

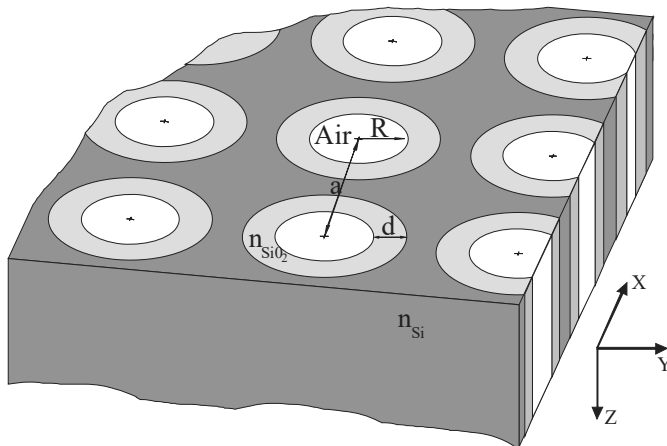


Fig. 5. A fragment of system considered

Here the first (second) term describes the incident wave (scattered waves); j numbers the lattice site, $\hat{G}_0(E)$ is the Green operator, V_0 is the impurity potential. The complex energies for which the denominator of the second term (1) becomes zero correspond to the resonances in electron scattering

$$1/V_0 = \langle 0 | \hat{G}_0(E) | 0 \rangle \quad (2)$$

at $E = \varepsilon - i\Gamma (\Gamma > 0)$. The difference of two neighbouring resonance energies is approximately equal to the value of the step in the Wannier–Stark ladder.

The Wannier–Stark steps can exist when the scattering time τ_s of the carriers is large enough to realize at least one cycle of complete Bloch oscillation of the field-accelerated carriers. In our case, the electric field is at the boundary of the “silicon matrix-nanocoating”, and the vector of the electric field is in the plane (100) of silicon (Fig. 5). After illumination, electrons are accelerated in the electric field of the enriched electric potential (Fig. 6), oscillate and scatter by surface states in the radial direction x relative to the macropore, in the plane (y, z) (Fig. 5), which is the plane of resonance scattering with infinity amplitude [19]. The resonant electron scattering results in the infinity growth of dielectric constants and corresponding changes in IR absorption at room temperature.

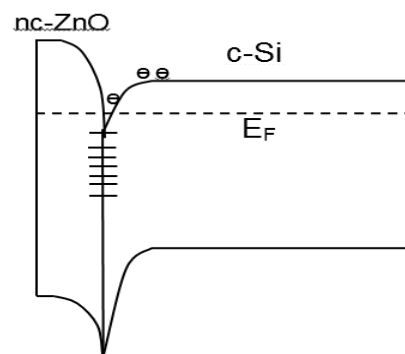


Fig. 6. Scheme of potential well and band bending on the surface of macropores between silicon c-Si matrix c-Si with Fermi level E_F and layer ZnO nanocrystals (circles–electrons, stokes–impurity states)

Table 1. Structure parameters and the electric field intensity

Nanocrystal material	Oscillation period, meV	Lattice parameter, a , Å	Band gap, eV	Nanocrystals size, d , nm	Electric field intensity $F=\Delta E/a$, V/cm	Electric field intensity $F=\Delta E/d$, V/cm
Si	1.4±0.6	5.43	1.1	2÷3	(1.5÷4)·10 ⁴	(3÷9)·10 ³
CdTe	3.9±0.5	6.48	1.6	20	(6÷8)·10 ⁴	(2÷3)·10 ³
ZnO	4.2±1.0	3.2	3.4	5÷6	(1÷1.3)·10 ⁵	(6÷8)·10 ³
		5.6			(6÷7.4)·10 ⁴	

The big scattering time is needed to make possible generation of well-separated oscillations [20]. If the scattering time is much bigger than the lifetime of the most stable state, then the oscillation has some minima (Fig. 7) that are due to crossings with the higher excited Wannier–Stark ladder [9]. The oscillation periods ΔE for macroporous silicon structures with surface nanocrystals and microporous layers depend mainly on the band gap of the nanocrystal material (see Fig. 2 *c* and Table 1). The electric field intensity F is equal to $10^4 \div 10^5$ V/cm for $F = \Delta E/a$, and $(3 \div 8) \cdot 10^3$ V/cm for $F = \Delta E/d$ (see Table 1). The latter value of electric field intensity is too small, the Bloch time is bigger than the relaxation time, and therefore neither Bloch oscillations nor Wannier–Stark ladders have been observed yet. This proves the validity of the model of electron oscillation in the atomic lattice.

The fact is that the levels of the Wannier–Stark ladder have a certain width Γ , while its detection requires that this width be less than the difference of energies of adjacent levels, $\Gamma < Fd$. The contributions to the width Γ come from the interband interaction, electron-phonon interaction, and interaction with impurity atoms. The interband interaction has been studied and demonstrated that it does not break the Wannier–Stark ladder [18]. The electron-phonon interaction was considered in [21]. According to [18], the phonon damping effect leads to an additional shift towards the phase behavior. Paper [20] deals with the influence of impurities on the Wannier–Stark ladder and calculation of the width of the Wannier–Stark ladder levels ΔE due to scattering from impurities. The Wannier–Stark ladder is not broken by impurities if the intervals between the transitions due to scattering from impurity atoms with lifetime τ are bigger than the period of electron oscillations in external field. In [20], the

following estimate of the probability W for an electron to leave the state per unit time due to scattering from an impurity atom at lattice site was obtained: $W < 2V_0 N_i / (Nh)$, where V_0 is the impurity potential, N_i the impurity concentration and $N \approx (a^2)^{-1}$ the density of states. As a result, the inequality $\tau/T_B > 1$ passes to $N_i < \Delta E / (4\pi a^2 V_0)$. Using the last inequality, we find a numerical estimate of impurity concentration. The surface state concentration in macroporous silicon structures varies from 10^{10} to 10^{11} cm⁻² [21] and $N_i^{\max} > 10^{12}$ cm⁻² for the considered spectral range. In this case, the Wannier–Stark ladder is preserved in the whole spectral range for macroporous silicon structures with microporous layers, CdTe, and ZnO surface nanocrystals (Fig. 7). The Bloch oscillation time is equal to $T_B \approx (4 \div 8) \cdot 10^{-12}$ s for macroporous silicon structures with surface nanocrystals, and $T_B \approx (1 \div 4) \cdot 10^{-11}$ s for macroporous silicon structures with microporous layers. The lifetime relation is $\tau/T_B > 1$ in the whole spectral region studied for macroporous silicon structures with CdTe and ZnO surface nanocrystals.

We obtained the surface impurity concentration in macroporous silicon structures by the method of the photoconductivity dependence on the distance between macropores [21] and the temperature dependences of the photocarrier lifetime in macroporous silicon. From the experimental temperature dependences of the photocarrier lifetime in 2D macroporous silicon structures the dimensionless surface potential y_0 is about 12 at room temperature what corresponds to the equilibrium surface band bending of about 0.31 eV and to the surface impurity concentration $N_i = 5 \cdot 10^{10}$ cm⁻² for the electron concentration $n_0 = 10^{15}$ cm⁻³ of investigated macroporous silicon samples. Relatively long electron scattering time in 2D macroporous silicon structures is due to the

small surface impurity concentration on macropore surface ($N_i \leq 5 \cdot 10^{10} \text{ cm}^{-2}$).

Wannier-Stark quantum electro-optical effect includes an effective mechanism for the implementation of strong, coherent interactions are the resonance oscillations in IR absorption spectra [9]. The basis for the development of this direction is the interaction of the quantum system of oscillating electrons with the quantum system of the Wannier levels. The Wannier-Stark steps can exist when the scattering time τ_s of the carriers is large enough to realize at least one cycle of complete Bloch oscillation of the field-accelerated carriers. In our case, the electric field

is at the boundary of the “silicon matrix-nanocoating”, and the vector of the electric field is in the plane (100) of silicon (Fig. 5). After illumination, electrons are accelerated in the electric field of the enriched electric potential (Fig. 6), oscillate and scatter by surface states in the radial direction x relative to the macropore, in the plane (y, z) (Fig. 5), which is the plane of resonance scattering with infinity amplitude [11]. The resonant electron scattering results in the infinity growth of dielectric constants and corresponding changes in IR absorption at room temperature.

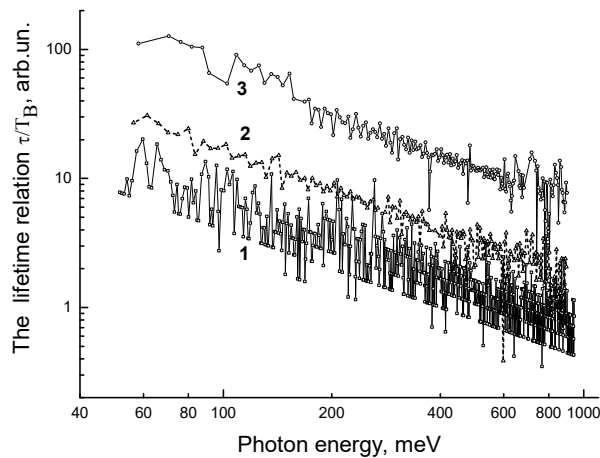


Fig. 7. Spectral dependence of the lifetime relation τ/Γ_B for macroporous silicon structures with microporous layers (1) and CdTe (2), ZnO (3) surface nanocrystals

Controllability and coherence of the system are determined by forming of coherent Wannier levels in a narrow triangular potential well formed by an electric field at the silicon-nanocoating boundary (Fig. 6). The presence/absence of resonance scattering of an oscillating electron in an electric field at the potential of an impurity surface state with quantum Wannier levels is controlled and measured at room temperature by the resonant maxima of the IR absorption. The resonant maxima are stored for 20 seconds after switching off the illumination. This is 200 times longer than of macroporous silicon structures without nanocoatings [20].

Electron-phonon interaction. We investigated the contribution of the electron-phonon interaction to the broadening parameter Γ of the Wannier–Stark ladders in oxidized macroporous silicon structures [21]. The effect of broadening on the amplitude of the

oscillations in IR absorption spectra (ΔA) is calculated in the form of convolution of the “nonbroadened” oscillation amplitude (ΔA_0) with Lorentz distribution:

$$\Delta A / \Delta A_0 = \frac{\Gamma}{\pi} \int \frac{d\omega'}{(\omega' - \omega)^2 + \Gamma^2} = \arctan(\Delta\omega / \Gamma) / \pi. \quad (3)$$

In (3) we used $\Delta\omega = \omega' - \omega$ as the energy of the Wannier–Stark step Fa .

For experimental data on IR absorption by macroporous silicon structures with oxide thicknesses 10–200 nm in the spectral region of Si–O surface states and $\Delta A_0 / \Delta A = 3 \div 20$ (Fig. 8), that confirmed low values $\Gamma / Fa \ll 1$, where $\Gamma = 0.3 \div 0.8 \text{ cm}^{-1}$ equals to that for surface phonon polaritons measured in thin films of II–VI semiconductors [22]. The obtained parameter Γ of the Wannier–Stark ladder is much less of the adjacent level energy due to the giant amplitude of oscillations after resonance

electron scattering on the surface states with the infinity amplitude of scattering.

Quantum superiority. To achieve a high degree of coherence of the quantum system at room temperature, it is necessary to achieve “quantum superiority” due to the hundreds of coupled acts of the electron scattering operating steadily and with a small number of errors, high accuracy and speed of measurements. The

oscillating motion of an electron together with its spin enhances the circulating flow of energy in the field of its wave. Resonant scattering rotates electrons on 90° and converts the superposition of the states of the microscopic system into the superposition of the states of the macroscopic system. The gain mechanism of a mixed state involves also the interaction of the quantum macropore system with other macropores.

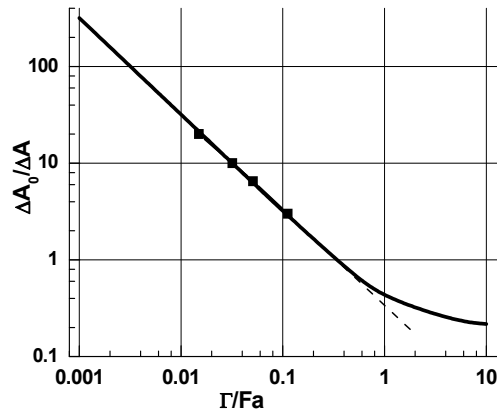


Fig. 8. The results of calculation (curve) of the $\Delta A_0/\Delta A$ dependence on Γ/Fa by Eq. (2). The symbols are experimental data on IR absorption by macroporous silicon structures with oxide thicknesses of 10–200 nm in the spectral region of Si-O-Si surface states

From other side, the potential of impurities in the electric field of the deep well (Fig. 6) between the macropore surface and the nanocoating is sufficient. Thus, the influence of “quantum superiority” on coherence is significant for the formation of Wannier levels. Moreover, oscillating motion of an electron together with its spin enhances the circulating flow of energy in the field of its wave. Resonant scattering rotates the electron flow on 90° and converts the superposition of the states of the microscopic system into the superposition of the states of the macroscopic system. This mechanism includes also the interaction of the macropore quantum system with other macropores, which causes quantum correlation and forms a superposition of the states of the macroscopic system. The effective formation of quantum states and the strengthening of quantum systems on the surface of periodically located macropores are resulted in the low value of the broadening parameter $\Gamma(10^{-3})$ of Wannier-Stark steps; and the oscillation coherence reaches 0.25–0.4 %.

The results obtained are perspective for the optical quantum computer development [23–26].

A quantum computer is a computing device that uses the phenomena of quantum mechanics (quantum superposition, quantum entanglement) to transmit and process data. A quantum computer operates not with bits with values of either 0 or 1, but with qubits having values of both 0 and 1 [23]. As a result, it is possible to process all possible states simultaneously and to obtain a huge advantage over other computers in a number of algorithms [24–26]. A logical qubit in our case is the presence/absence of the resonance scattering of oscillated electron on Wannier levels in the electric field at the boundary of the “silicon matrix-nanocoating”. Cubit is electron with quantum state of $|0\rangle$ and $|1\rangle$ in the plane of the infinite resonance scattering controlled by IR illumination and the resonant maximum of IR absorption. The number of oscillations in one IR spectrum is more than 100, thus, we have the multi-cubit system.

The interaction of qubits in arrays of individually controlled, cold neutral Ba atoms [24] is the propagation of internal atomic coherence to and from the direction of motion of the centers of mass of all ions. In such a system,

the total measurement time is 35 s, which is much less decoherence due to spontaneous emission (45 s), so the decoherence time is 6 s with an error of 5 %. A two-qubit quantum computer based on diamond crystal with impurities [26] includes two logical qubits of the spin electron and the nitrogen nucleus with coherence 10–17 % at room temperature. For our case, the broadening parameter 10^{-3} of the width of the Wannier-Stark step and the coherence of the oscillations 0.25–0.4 % at room temperature are much less than of the coherence of cold atoms (5 % [24, 25]) and diamond crystal with the nitrogen nuclei (10–17 %) at room temperature [26].

The presence/absence of resonance scattering of an oscillating electron in an electric field at the potential of an impurity surface state with quantum Wannier levels is controlled at room temperature by the resonant maximum of the IR absorption, which is 200 times longer than that of macroporous silicon structures without nanocoatings [20]. Thus, we proposed the high coherent optical quantum computer based on a macroporous silicon structure with the surface layer of nanocrystals for the implementation of the quantum electro-optical effect of Wannier-Stark [27].

CONCLUSIONS

CdTe nanocrystals 20 nm in size were deposited on macroporous silicon substrates by the “hot wall” molecular epitaxy. Methods of synthesis of ZnO nanoparticles (3.7–4.4 nm in size) in isopropanol and from solution of $\text{Zn}(\text{CH}_3\text{COO})_2$ in ethanol have been developed. Ultrasmall CdS nanoparticles (1.8–2 nm in size) were worked at the full saturation the Cd-cations with amino groups in aqueous and ethanol solutions of polyethyleneimine. SiO_2 nanocoatings (thickness of 5–280 nm) were obtained in the diffusion stove after treatment of macroporous silicon substrates in the nitrogen atmosphere.

We observed well-separated oscillations in absorption spectra of macroporous silicon structures with surface nanocrystals. The amplitude of oscillations is maximal in the spectral ranges of organic species, Si-H, C-H and O-H bonds. The results obtained indicate strong influence of impurity states on the surface of macroporous silicon structures with nanocoatings. It results from resonant electron

scattering on the impurity states in an electric field of “silicon-nanocoating” heterojunction on macropore surface. The constant oscillation period specifies the realization of Wannier–Stark effect on the randomly distributed surface bonds on nanocrystals. The amplitude of scattering has resonant behavior in the case of electron scattering on impurity, and the difference between two resonant energies is equal to the step of Wannier–Stark ladder. The oscillation periods ΔE of macroporous silicon structures with surface nanocrystals and microporous layers depend mainly on the band gap of the nanocrystal material. The electric field intensity F is $10^4\div 10^5$ V/cm for $F = \Delta E/a$, thus indicating validity of the model of electron oscillations in the atomic lattice.

Wannier–Stark ladders are not broken by impurities, if the intervals between the transitions due to scattering from impurity atoms with lifetime τ are bigger than the period of electron oscillations in external field, T_B . The lifetime relation is $\tau/T_B > 1$ in all spectral regions considered for macroporous silicon structures with CdTe, and ZnO surface nanocrystals, taking into account that the surface impurity concentration for macroporous silicon structures is less than $N_i \approx 5 \cdot 10^{10} \text{ cm}^{-2}$. The oscillations have some minima that are due to crossings with higher excited Wannier–Stark ladder for the big scattering lifetime.

Resonant electron scattering with infinity amplitude gives rise to the resonances of the permittivity at room temperature and corresponding change in the absorption. The influence of the permittivity resonances on the optical modes in two-dimensional macroporous silicon structures is a subject for further researches.

We compared the MIR light absorption oscillations in 2D macroporous silicon with CdTe, ZnO, CdS surface nanocrystals, microporous and SiO_2 layers, taking into account the electro-optical effects at strong electric fields. The coherence of the IR spectra oscillations increases with the decrease in the concentration of surface states and with the optimal area of contact of nanocrystals to the surface of the macropores. Thus, the shift of oscillations for ZnO nanoparticles with optimal size of nanocrystals (3.7–4.4 nm) leads to deviations of the oscillation peaks within

0.26–0.42 meV, i.e. the oscillation coherence reaches 0.25–0.4 %.

The small broadening parameter of the Wannier–Stark ladder levels $\Gamma = 0.3 \pm 0.8 \text{ cm}^{-1}$ equals to that for surface phonon polaritons measured in thin films of II–VI semiconductors. Controllability and coherence of the system are determined by forming of coherent Wannier levels in a narrow triangular potential well formed by an electric field at the silicon-nanocoating boundary. Thus, the influence of “quantum superiority” on coherence is significant for the formation of Wannier levels. In addition, oscillating motion of an electron together with its spin enhances the circulating flow of energy in the field of its wave. Resonant scattering rotates electrons on 90° and converts

the superposition of the states of the microscopic system into the superposition of the states of the macroscopic system. The gain mechanism also involves the interaction of the quantum macropore system with other macropores, involving them in a mixed state. As a result, the broadening parameter 10^{-3} of the width of the Wannier-Stark step, the coherence of the oscillations 0.25–0.4 % at room temperature are much less than that of cold atoms (5 %) and diamond crystal with the nitrogen nuclei (10–17 %) at room temperature. Thus, we proposed the high coherent optical quantum computer based on a macroporous silicon structure with the surface layer of nanocrystals for the implementation of the quantum electro-optical effect of Wannier-Stark.

Когерентні осциляції в ІЧ-спектрах 2D структур макропористого кремнію з поверхневими нанопокриттями

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Одним з перспективних матеріалів для розробки двовимірних фотонних структур є макропористий кремній, отриманий за допомогою фотоанодного травлення. Наявність періодично розташованих циліндричних пор, розділених кремнієвими колоннами, забезпечує велику ефективну поверхню структур, покращує оптичні та фотофізичні характеристики макропористого кремнію. У даній роботі досліджені осциляції ІЧ-поглинання двовимірними структурами макропористого кремнію з мікропористими шарами кремнію, SiO_2 нанопокриттями та CdTe , ZnO поверхневими нанокристаллами з врахуванням електро-оптичного ефекту Ваньє-Штарка. Аналіз експериментальних спектрів поглинання здійснено в рамках моделі резонансного розсіювання електронів з нескінченною амплітудою на поверхневих станах у сильному електричному полі, з різницею між двома резонансними енергіями, що дорівнює сходинок Ваньє-Штарка. Постійність періоду осциляцій вказує на реалізацію ефекту Ваньє-Штарка на довільно розподілених поверхневих станах на межі поділу «кремній-нанопокриття». Проведено порівняння ІЧ поглинання світла в 2D структурах макропористого кремнію з поверхневими нанопокриттями, проаналізовані зрушення і відхилення вершин коливань. Когерентність осциляцій ІЧ-спектрів підвищується в результаті зменшення концентрації поверхневих станів та оптимальної площі контакту нанокристалів до поверхні макропор. Таким чином, зсув осциляцій для наночастинок ZnO з оптимальним розміром нанокристалів (3.7–4.4 нм) призводить до відхилень коливань у межах 0.26–0.42 меВ, тобто узгодженість коливань досягає 0.25–0.4 %. Малий параметр уширення сходинок Ваньє-Штарка $\Gamma = 0.3 \pm 0.8 \text{ cm}^{-1}$ дорівнює цьому параметру для поверхневих тонких плівок напівпровідників II–VI. Контрольованість і когерентність дослідженої системи визначається формуванням когерентних рівнів Ваньє у вузькій трикутній потенціальній ямі, сформованій в електричному полі на межі поділу «кремній-нанопокриття». В результаті було запропоновано висококогерентний оптичний квантовий комп'ютер на основі реалізації квантового електро-оптичного ефекту Ваньє-Штарка на кремнієвій матриці з макропорами і шаром нанокристалів на поверхні макропор.

Ключові слова: 2D структури макропористого кремнію, поверхневі нанопокриття, ІЧ спектри, когерентні осциляції

Когерентные осцилляции в ИК-спектрах 2D структур макропористого кремния с поверхностными нанопокрывтиями

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Одним из перспективных материалов для разработки 2D фотонных структур является макропористый кремний, изготовленный с помощью фотоанодного травления. Наличие периодически расположенных цилиндрических пор, разделенных кремниевыми колоннами, обеспечивает большую эффективную поверхность образцов и улучшенные оптические и фотофизические характеристики макропористых кремниевых структур. В данной работе исследованы осцилляции ИК-поглощения двумерными структурами макропористого кремния с нанопокрывтиями микропористого кремния и SiO_2 , с CdTe , ZnO нанокристаллами с учетом электро-оптического эффекта Ванье-Штарка. Анализ экспериментальных спектров ИК поглощения был проведен в рамках модели резонансного рассеяния электронов с бесконечной амплитудой на поверхностных состояниях в сильном электрическом поле, с разностью между двумя резонансными энергиями, равной ступеньке лестницы Ванье-Штарка. На реализацию эффекта Ванье-Штарка указывает постоянность периода осцилляций на поверхностных состояниях в области границы «кремний-нанопокрывтие». Проведено сравнение осцилляций ИК поглощения света в 2D макропористом кремнии с поверхностными нанопокрывтиями, проанализированы сдвиг и отклонения пиков колебаний. Когерентность осцилляций ИК-спектров повышается в результате уменьшения концентрации поверхностных состояний и оптимальной площади контакта нанокристаллов к поверхности макропор. Таким образом, сдвиг осцилляций для наночастиц ZnO с оптимальным размером нанокристаллов (3.7–4.4 нм) приводит к отклонениям колебаний в пределах 0.26–0.42 мэВ, то есть согласованность колебаний достигает 0.25–0.4 %. Малый параметр уширения ступенек Ванье-Штарка $\Gamma = 0.3 \pm 0.8 \text{ см}^{-1}$ равен этому параметру для поверхностных тонких пленок полупроводников II-VI. Контролируемость и когерентность исследованной системы определяется формированием когерентных уровней Ванье в электрическом поле узкой треугольной потенциальной ямы на границе «кремний-нанопокрывтие». В результате был предложен высококогерентный оптический квантовый компьютер на основе реализации квантового электро-оптического эффекта Ванье-Штарка на кремниевой матрице с макропорами и слоем нанокристаллов на поверхности макропор.

Ключевые слова: 2D структуры макропористого кремния, поверхностные нанопокрывтия, ИК спектры, когерентные осцилляции

REFERENCES

1. Birner A., Wehrspohn R.B., Gösele U.M., Busch K. Silicon-Based Photonic Crystals. *Adv. Mater.* 2001. **13**(6): 377.
2. Karachevtseva L.A. Two-dimensional photonic crystals as perspective materials of modern nanoelectronics. *Semiconductor Physics, Quantum Electronics and Optoelectronics*. 2004. **7**(4): 430.
3. Karachevtseva L.A., Glushko A.E., Ivanov V.I., Lytvynenko O.O., Onishchenko V.F., Parshin K.A., Stronska O.J. Out-of-plane optical transmittance of 2D photonic macroporous silicon structures. *Semiconductor Physics, Quantum Electronics and Optoelectronics*. 2007. **10**(2): 51.
4. Glushko A., Karachevtseva L. Photonic band structure of oxidized macroporous silicon. *Opto-Electron. Rev.* 2006. **14**(3): 201.
5. Glushko A., Karachevtseva L. PBG properties of three-component 2D photonic crystals. *Photonics Nanostruct. Fundam. Appl.* 2006. **4**(3): 141.
6. Karachevtseva L., Karas N., Onishchenko V., Sizov F. Surface polaritons in 2D macroporous silicon structures. *Int. J. Nanotechnol.* 2006. **3**(1): 76.
7. Holinye R.Yu., Matveeva L.A., Venger E.F., Karachevtseva L.A., Lytvynenko O.A. Electroreflectance study of macroporous silicon surfaces. *Appl. Surf. Sci.* 2001. **172**(3–4): 214.
8. Karachevtseva L.A., Ivanov V.I., Lytvynenko O.O., Parshin K.A., Stronska O.J. The impurity Franz-Keldysh effect in 2D photonic macroporous silicon structures. *Appl. Surf. Sci.* 2008. **255**(5): 3328.

9. Karachevtseva L., Kuchmii S., Lytvynenko O., Sizov F., Stronska O., Stroyuk A. Oscillations of light absorption in 2D macroporous silicon structures with surface nanocoatings. *Appl. Surf. Sci.* 2011. **257**(8): 3331.
10. Karachevtseva L., Goltviansky Yu., Sapelnikova O., Lytvynenko O., Stronska O., Bo Wang, Kartel M. Wannier–Stark electro-optical effect, quasi-guided and photonic modes in 2D macroporous silicon structures with SiO₂ coatings. *Appl. Surf. Sci.* 2016. **388**(1): 120.
11. Karachevtseva L.A., Litvinenko O.A., Stronskaya E.I. Influence of Electrochemical Parameters on the Etching of Macropores in Silicon. *Theor. Exp. Chem.* 2003. **39**(6): 385.
12. Lopez-Otero A. Hot wall epitaxy. *Thin Solid Films.* 1978. **49**(1): 3.
13. Huber W., Lopez-Otero A. The electrical properties of CdTe films grown by hot wall epitaxy. *Thin Solid Films.* 1979. **58**(1): 21.
14. Bilevych Ye., Soshnikov A., Darchuk L., Apatskaya M., Tsybrii Z., Vuychik M., Boka A., Sizov F., Boelling O., Sulkiö-Cleff B. Influence of substrate materials on the properties of CdTe thin films grown by hot-wall epitaxy. *J. Crystal Growth.* 2005. **275**(1–2): e1177.
15. Stroyuk A.L., Shvalagin V.V., Kuchmii S.Ya. Photochemical synthesis and optical properties of binary and ternary metal–semiconductor composites based on zinc oxide nanoparticles. *J. Photochem. Photobiol. A.* 2005. **173**(2): 185.
16. Mao J., Yao J.-N., Wang L.-N., Liu W.-S. Easily prepared high-quantum-yield CdS quantum dots in water using hyperbranched polyethylenimine as modifier. *J. Colloid Interface Sci.* 2008. **319**(1): 353.
17. Karachevtseva L., Kuchmii S., Stroyuk A., Sapelnikova O., Lytvynenko O., Stronska O., Bo Wang, Kartel M. Light-emitting structures of CdS nanocrystals in oxidized macroporous silicon. *Appl. Surf. Sci.* 2016. **388**(1): 288.
18. Berezhkovskii A.M., Ovchinnikov A.A. Scattering of electrons on an impurity in a crystal in a constant electric field. *Theor. Math. Phys.* 1979. **39**: 466.
19. Berezhkovskii A.M., Ovchinnikov A.A. Influence of impurities on the Wannier-Stark ladder in semiconductor in a strong electric field. *Phys. Status Solidi B.* 1982. **110**(2): 455.
20. Karachevtseva L.A., Onyshchenko V.F., Sachenko A.V. Kinetics of photoconductivity in macroporous silicon structures. *Ukr. J. Phys.* 2008. **53**(9): 874.
21. Karachevtseva L., Goltviansky Yu., Kolesnyk O., Lytvynenko O., Stronska O. Wannier-Stark effect and electron-phonon interaction in macroporous silicon structures with SiO₂ nanocoatings. *Opto-Electron. Rev.* 2014. **22**(4): 201.
22. Vinogradov E.A., Zhizhin G.N., Yakovlev V.A. Resonance between dipole oscillations of atoms and interference modes in crystalline films. *Sov. Phys. JETP.* 1979. **50**: 486.
23. Shor P.W. Scheme for reducing decoherence in quantum computer memory. *Phys. Rev.* 1995. **A52**: 2493.
24. Sleator T., Weinfurter H. Realizable Universal Quantum Logic Gates. *Phys. Rev. Lett.* 1995. **74**(20): 4087.
25. Bernien H., Schwartz S., Keesling A., Levine H., Omran A. Probing many-body dynamics on a 51-atom quantum simulator. *Nature.* 2017. **551**: 579.
26. Van der Sar T., Wang Z.H., Blok M.S., Bernien H., Taminiu T.H., Toyli D.M., Lidar D.A., Awschalom D.D., Hanson R., Dobrovitski V.V. Decoherence protected quantum gates for a hybrid solid-state spin register. *Nature.* 2012. **484**: 82.
27. Patent UA 136455. Karachevtseva L. Method for Manufacturing of Optical Quantum Computer, Utility Model. 2019.

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