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# **EXCITON-POLARITONS IN 2D MACROPOROUS SILICON STRUCTURES WITH NANO-COATINGS**

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In this paper, we investigated high-resolution IR absorption and reflection spectra in one-sided periodical 2D macroporous silicon structures with nano-coatings of  $SiO_2$  and CdS, ZnO nanoparticles, as well as two-sided structures of macroporous silicon without nano-coatings. After changing the resolution of spectra measurements from 2 to 1 cm<sup>-1</sup>, the oscillation period of Wannier-Stark electro-optical effect decreases by 3 times, and absorption increases by 60–100 times; and for two-sided structures the oscillation period decreases by 1.5 times and absorption increases by 25–30 %. In addition, giant absorption oscillations with positive and negative amplitudes of  $10^7$  arb. un. were evaluated in spectral regions of Si–Si–bonds and  $P_b$  centers. Similar oscillations in the reflection spectra have much less amplitudes up to  $4.10^4$  arb. un. In the spectral area of the transverse phonon  $\omega_{TO}$  (Si–Si–bonds) absorption spectra of 2D macroporous silicon structures consistent fully with data for phonon polaritons in microresonators as a result of resonance interaction of dipole-active vibrations with the frequency of  $\omega_{TO}$  in thin films with the surface modes of microresonator. In addition, microresonators interact both with each other in one-sided macroporous silicon structures and in the system of two-sided macroporous silicon. The giant absorption oscillations testify the strong interaction of surface polaritons with photons. The coherence of oscillations and large-scale spatial correlation are a result of exciton-polariton condensation on macropores as microresonators. In 2D macroporous silicon structures with nano-coatings band bending on the surface of the macropores are significant. Therefore, the generated photoelectrons link with holes, forming electron-hole pairs named as exciton-polaritons according to phenomenon of Bose-Einstein condensation.

Keywords: one-sided and two-sided macroporous silicon structures, nano-coatings of nanocrystals, excitonpolaritons, Bose-Einstein condensation

### **INTRODUCTION**

One of the promising materials for the development of 2D photonic structures is macroporous silicon prepared by 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 was observed owing to the guided and radiation optical modes formed by macroporous silicon as a short waveguide [6]. In the electroreflectance spectra of macroporous silicon structures in the area of the direct band-to-band transition, the Franz-Keldvsh oscillations were measured as a result of the local electric field on the surface of macropores [7]. In the wavelengths, compared with the optical period of the macroporous silicon

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structures for the normal fall of light, the measured IR absorption is by two orders of magnitude higher than the absorption of the silicon single crystal; the formation of steps was also found [8]. The change in optical absorption by the 3/2 law correlates with the frequency dependence of the dielectric permeability between the surface levels and the forbidden zones in the crystal under the influence of an electric field, which is characteristic of the impurity effect of Franz-Keldysh. In 2D structures of macroporous silicon with layers of microporous silicon and surface nanocrystals, oscillations of IR absorption with the maximum amplitude in the region of absorption by surface states were detected [9]. The dependence of the oscillation maxima on its number is linear with a constant period. The analysis of IR absorption oscillations was performed within the model of resonant scattering of electrons on surface states in a strong electric field with a difference between two resonant energies equal to the Wannier-Stark step  $\Delta E = Fa$  (*F* is the electric field strength, and

*a* is silicon lattice constant) [10]. IR light absorption oscillations in 2D macroporous silicon with surface nano-coatings were compared in [11], the shift and deviations of oscillation peaks, the broadening parameter  $\Gamma$  of the Wannier– Stark ladders and the influence of "quantum superiority" on coherence of Wannier levels were analysed. In addition, we proposed the 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 the Wannier-Stark quantum electro-optical effect [12].

In this work, high-resolution optical absorption spectra of 2D macroporous silicon structures with nano-coatings and two-sided structures of macroporous silicon without nanocoatings are investigated. The mechanisms of interaction of surface polaritons with photons and formation of exciton-polaritons are revealed. A comparative analysis of the results on electrooptical effects in macroporous silicon and the phenomenon of condensation of excitonpolaritons on macroporesis performed.

### 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  $H = 520 \ \mu\text{m}$ ) [13]. 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  $N_p = 6.25 \cdot 10^6$  cm<sup>-2</sup> (Fig. 1 *a*). Addition anisotropy etching in 10 % solution of KOH permits one to remove microporous layers from the macropore surface.

SiO<sub>2</sub>nano-coatings were formed in the diffusion stove after treatment of macroporous silicon substrates in the nitrogen atmosphere [10]. The oxide layers (thickness of 10 and 20 nm) were obtained on macroporous silicon samples in dry oxygen during 40÷60 min at the temperature of 1050 °C. The oxide thickness was measured using ellipsometry.

The method of synthesis in aqueous and ethanol solutions of polyethyleneimine of ultrasmall cadmium sulfide nanoparticles (1.8-2 nm) was worked out under condition of saturation of the Cd cations with amino groups [14, 15]. Methods of synthesis of ZnO nanoparticles in isopropanol and from solution of zinc compound  $Zn(CH_3COO)_2$  in ethanol have been developed in [14]. The average sizes of ZnO nanoparticles 4±0.4 nm were determined based on absorption spectra and atomic force microscopy. CdS or ZnO nanoparticles were deposited on the surface of macropores from the colloidal solutions in polyethyleneimine at the following ratio: nanocrystals  $10\pm 2$  %; polyethyleneimine  $18\pm 2$ ; water - the rest.

Two-sided structures of macroporous silicon with arbitrary macropore distribution were formed by photoelectrochemical etching of one side of silicon substrate and after that etching of other side of silicon substrate. Table 1 shows the parameters of the one-sided 2D macroporous silicon structures with nano-coatings and two-sided macroporous silicon structures without coatings.

No. of sample	Structure type	Macropore depth, µm	SiO2 layer thickness, nm	Thickness of polymer- nanocrystal layer	Diameter of nanocrystal,
					nm
1	One-sided	70±2	10	16 nm"PEI-ncCdS"	1.8–2
2	One-sided	70±2	20	16 nm"PEI-ncCdS"	1.8–2
3	One-sided	70±2	20	28 nm"PEI-ncCdS"	1.8–2
4	One-sided	70±2	20	28 nm"PEI-ncZnO"	3–4
5	Two-sided	150±5	Natural	No	_
		on both sides	oxide		
6	Two-sided	150±5	Natural	No	_
		on both sides	oxide		

Fable 1.	The parameters of the	one-sided 2D	macroporous	silicon	structures	with	nano-coating	s and	two-sided
	macroporous silicon st	ructures withou	t coatings (PE	I – polye	ethyleneim	ine)			

Optical absorption spectra were measured in the  $300\div7800 \text{ cm}^{-1}$  spectral range using an IR Fourier spectrometer "Perkin Elmer" (Spectrum BXII) with a resolution of 2 cm<sup>-1</sup>. High-resolution optical absorption spectra were measured in the  $200\div8500 \text{ cm}^{-1}$  spectral rangeon a triple Horiba Jobin-Yvon T64000 spectrometer with a resolution of 1 cm<sup>-1</sup>. The optical absorption spectra were obtained at normal incidence of IR radiation on a sample (along the cylindrical macropores, Fig. 1 a, insertion) in the air at room temperature.

### EXPERIMENTAL RESULTS

Comparative spectra of structure #1 (Table 1) are given in Fig. 1 *b* and Figs. 2–3 with a resolution of 2 cm<sup>-1</sup> (curves 1) and with a resolution of 1 cm<sup>-1</sup> (curves 2).



**Fig. 1.**  $a - \text{macroporous silicon structures with macropore diameter <math>D_p = 2 \ \mu\text{m}$  and period 4  $\mu\text{m}$ ; insertion: normal incidence of IR radiation on a sample (along the pores);  $b - \text{the optical absorption by 2D structures of macroporous silicon with nano-coatings for sample #1 from Table 1 measured with a resolution of 2 cm<sup>-1</sup> (curve 1) and with a resolution of 1 cm<sup>-1</sup> (curve 2)$ 

Oscillations of absorption were measured for both spectra from Fig. 1 b. Growth of resolution increases absorption by more than 60 times in the spectral region up to 5000 cm<sup>-1</sup>. In addition, giant oscillations of the positive and negative amplitudes of the absorption (almost 7 orders of magnitude exceed the amplitude of the oscillations for absorption according to Fig. 1 (curve 1) appear in the spectrum of curve 2 at Si-Si-bonds [13] and in the 5500-7500 cm<sup>-1</sup> spectral region of  $P_{b0}$  (0.75 meV) and  $P_{b1}$ (0.85 meV) absorption centers [17]. Fragments of the absorption spectra of the structure #1 from Fig. 1 *a* for the resolution of measurements  $2 \text{ cm}^{-1}$ (curve 1) and with a resolution of  $1 \text{ cm}^{-1}$  (curve 2) are showed in Fig. 2 a-c in three spectral ranges. As can be seen from Fig. 2 a-c, after changing measurement resolution from  $2 \text{ cm}^{-1}$  (curve 1) to the resolution 1 cm<sup>-1</sup> (curve 2), period of oscillations in optical absorption spectra decreases by 3 times: from  $10-12 \text{ cm}^{-1}$  (curves 1) to 3.5-4 cm<sup>-1</sup> (curves 2), and the optical absorption increases by 60-100 times.

Si-Si-bonds. Si-Si-bonds represent the transverse fluctuations of silicon atoms on the surface of the macropores, i.e., transverse phonons. Optical properties of crystals are determined by interaction of an external electromagnetic field with dipole-active states of the crystal volume and with defects of crystal structure. This interaction leads to the formation of a bound state of the oscillative movement of charged particles (dipole) with the electromagnetic field, named polaritons [18, 19]. Fig. 3 a-c show fragments of the absorption spectra of 2D macroporous silicon structures with nano-coatings (Table 1) in the region of Si-Si-bonds: a – spectrum includes one absorbance minimum for sample #1, two minima for sample #2 (Fig. 3 b) and three ones for sample #3 (Fig. 3 *c*).

Samples #1 and #2 differ in the thickness of the SiO<sub>2</sub> layer on the macropore surface (Table 1). At thickness 10 nm of the SiO<sub>2</sub> layer, the surface polaritons are formed (Fig. 3 *a*) at the frequency  $\omega_{s}$ , equal to the frequency of transverse phonon  $\omega_{\text{TO}}$ . When the SiO<sub>2</sub> thickness is 20 nm on the boundary "SiO<sub>2</sub>-macropore surface", the splitting of mode is formed (Fig. 3 *b*). For sample #3, the thickness of "PEI-ncCdS" layer increases to 28 nm (Table 1), thus additional modes and additional surface polaritons are formed [20] as a result of resonance interaction of dipole-active

oscillations with the frequency of  $\omega_{\rm TO}$  in a thin film with thickness *d* with surface polaritons. This resonance leads to the splitting of surface polariton and to the appearance of the slit at a frequency of  $\omega_{\rm O}$  in its spectrum with width proportional to  $(d/\lambda)^{1/2}$  [20].



**Fig. 2.** Fragments of the absorption spectra of the structure #1 from Fig. 1 for the resolution of measurements 2 cm<sup>-1</sup> (curve 1) and resolution 1 cm<sup>-1</sup> (curve 2): a – in the 590–630 cm<sup>-1</sup>spectral range; b – in the 3420–3460 cm<sup>-1</sup> spectral range; c – in the 6120–6140 cm<sup>-1</sup> spectral range



**Fig. 3.** Fragments of the absorption spectra of 2D macroporous silicon structures with nano-coatings from Table 1 in area of Si–Si–bonds: *a* – structure #1, *b* – structure #2, *c* – structure #3

**Reflection.** In the reflection spectra when changing the resolution of spectral measurements of 2D macroporous silicon structures with nanocoatings from 2 cm<sup>-1</sup> to resolution of 1 cm<sup>-1</sup>, oscillations with negative amplitude also appear at low light frequencies 200–500 cm<sup>-1</sup> (Fig. 4 *a*) and at frequencies of Si–Si–bonds 600–620 cm<sup>-1</sup> (Fig. 4 *b*).

Negative oscillations amplitudes up to  $-4 \cdot 10^6$  arb.un. were measured in reflection spectra at low oscillation frequencies 200–500 cm<sup>-1</sup> (Fig. 4 *a*) for all measured samples (samples #1–4, Table 1), and at frequencies of Si-Si-bonds for the

sample #2 only (Fig. 4 b) with a small negative amplitude of the oscillations up to -0.5 arb.un.

*Two-sided structures.* The giant negative oscillation amplitudes were measured at the resolution of 1 cm<sup>-1</sup> in spectra of two-sided macroporous silicon structures without nanocoatings (Fig. 5 *a*). The maximum negative oscillation amplitudes up to  $-1.5 \cdot 10^6$  arb.un. were measured in the spectral area of surface oscillations 550–650 cm<sup>-1</sup> on the border "silicon-silicon oxide" (Si–Si, Si–O bonds, Fig. 5 *b*) and up to  $-10^7$  arb. un. in the spectral area of P<sub>b</sub> centers 5500–7500 cm<sup>-1</sup> (Fig. 5 *c*). It is also evident from Fig. 5 that for two-sided structures of macroporous silicon without nano-coatings absorption (positive and negative) significantly increases in the area of rotational oscillations Si–O (465 cm<sup>-1</sup>), TO phonons (Si–Si–bonds at

 $600-620 \text{ cm}^{-1}$ ), TO phonons of surface natural SiO<sub>2</sub> layer (1056 cm<sup>-1</sup>), and also in the spectral region of absorption by P<sub>b</sub> centers (more than 5500 cm<sup>-1</sup>).



Fig. 4. The reflection spectra (with the resolution of 1 cm<sup>-1</sup>) measurements of 2D macroporous silicon structure with nano-coatings CdS (curve 1 – sample #2, curve 2 – sample #4 from Table 1): a – at low oscillation frequencies 200–500 cm<sup>-1</sup>; b – at frequencies of Si–Si–bonds



Fig. 5. Optical absorption of two-sided structures of macroporous silicon without nano-coatings (sample #5 from Table 1): a – for a resolution of measurements 2 cm<sup>-1</sup> (curve 1) and 1 cm<sup>-1</sup> (curve 2); b – for frequencies 550–650 cm<sup>-1</sup> of Si–Si–bonds and surface vibrations and c – in the field of P<sub>b</sub> centers 5500–7500 cm<sup>-1</sup>



Fig. 6. Fragments absorption spectra of two-sided (sample #5 from Table 1) for measurement resolution of 2 cm<sup>-1</sup> (curve 1) and resolution of 1 cm<sup>-1</sup> (curve 2): a – in the spectral range 590–630 cm<sup>-1</sup>; b – in the spectral range 3420–3460 cm<sup>-1</sup>; c – in the spectral range 6120–6140 cm<sup>-1</sup>

As can be seen from Fig. 6 a-c, when changing the resolution of measurements of optical absorption spectra from 2 cm<sup>-1</sup> (curve 1) at a resolution of 1 cm<sup>-1</sup> (curve 2), the oscillations period of two-sided macroporous silicon is reduced by 1.5 times: from 4–5 cm<sup>-1</sup> (curves 1) to 2.5–3.5 cm<sup>-1</sup> (curves 2); and the absorption is increased by 25–30 % (excluding the giant amplitudes of the oscillations).

### DISCUSSION OF RESULTS

Oscillations were measured in optical spectra from Figs. 1-6. For one-sided structures of macroporous silicon after changing the resolution of spectra measurements from 2  $cm^{-1}$  (curves 1) to  $1 \text{ cm}^{-1}$  (curves 2), the oscillation period decreases by 3 times: from  $10-12 \text{ cm}^{-1}$  (curves 1) to 3.5-4 cm<sup>-1</sup> (curves 2), and absorption increases by 60–100 times (Fig. 5 a-c). For two-sided macroporous silicon structures the oscillation period decreases by 1.5 times from 4-5 cm<sup>-1</sup> (curves 1) to 2, 5–3, 5 cm<sup>-1</sup> (curves 2); and absorption increased by 25-30 % (Fig. 6 *a*-*c*). In addition, giant oscillations with positive and negative amplitudes of 7-order value were measured in spectral regions of Si-Si-bonds [13] at 600–620 cm<sup>-1</sup> and of P<sub>b</sub> center absorption [17] at 5500–7500 cm<sup>-1</sup> (Fig. 7 *a*, *b*). Similar oscillations in the reflection spectra have much less amplitudes up to  $4 \cdot 10^4$  arb. un.

In the area of the transverse phonon  $\omega_{TO}$  (Si–Si–bonds), the absorption spectra of 2D macroporous silicon structures with nano-

coatings include from one to three negative absorption minima (Fig. 3 a-c) dependent on thickness and nature of nano-coatings (Table 1). Really, the samples #1 and #2 differ in the thickness of the SiO<sub>2</sub> layer on the macropore surface. For the thickness of the SiO<sub>2</sub> layer 10 nm (sample #1), the surface polariton is formed (Fig. 3 *a*) at the frequency  $\omega_{\rm S}$  - equaled to the frequency of transverse phonon  $\omega_{TO}$ , the mode splitting is formed (Fig. 3 b) when the SiO<sub>2</sub> layer thickness on the "SiO2-macropore surface" boundary is 20 nm (sample #2). Additional modes and additional surface polaritons are formed (Fig. 3 b) for sample #3 from Table 1 when the thickness of the "PEI-ncCdS" layer increases from 16 to 28 nm. The results obtained are fully consistent with data for phonon polaritons in microresonators [20] formed due to the resonance interaction of dipole-active oscillations with the frequency of  $\omega_{TO}$  in thin films with the surface modes of microresonator.

Oscillations with positive and with negative amplitudes also appear at low frequency of 200–500 cm<sup>-1</sup> and on Si–Si–bonds in the reflection spectra of 2D macroporous silicon structures with nano-coatings (Fig. 4). In addition, giant absorption oscillations were measured on the two-sided macroporous silicon structures without nano-coatings (Figs. 5–6) in the spectral area of rotational Si–O oscillations and Si–Si–bonds, TO phonon of the surface natural layer of SiO<sub>2</sub>, as well as in the spectral region P<sub>b</sub> centers (more than 5000 cm<sup>-1</sup>).



Fig. 7. Schemes of band bending on the surface of macropores between macroporous silicon c-Si matrix with Fermi level  $E_F$ , where:  $a - layers ncCdS+SiO_2$ ,  $b - layer SiO_2$  (circles – electrons and holes, lines – impurity states)

The giant oscillation measurements, both with positive and negative amplitude, testify the strong interaction of surface polaritons with photons. Indeed, in 2D the macroporous silicon structures with nano-coatings band bending on the surfaces of the macropores are significant for one-sided macroporous silicon structures (Fig. 7 a) and in the system of two-sided macroporous silicon (Fig. 7 b). In addition, macropores in 2D macroporous silicon structures are microresonators. In these conditions, the surface polaritons strongly interact with the photons [20, 21] due to the resonance interaction of dipole-active vibrations with surface modes in the microresonators (macropores). Therefore, the generated photoelectrons linked with the holes in the potential pits heavily, thus forming an excitonpolariton and its Bose condensation [21, 22].

The phenomenon of Bose condensation of exciton-polaritons, as well as composite bosons were found for the microresonators on the basis of quasi-2D semiconductor heterojunctions in 2006 [21, 22]. If the quantum well (or several quantum wells) is in the resonator of constant electromagnetic wave, and the energy of the 2D exciton coincides with the energy of the photon microcavity at K = 0, then the states of the exciton and photon interact with each other. As a result, quantum-mechanical mixing of photon and exciton is performed [21]. A narrow line grows in a threshold dipolar excitons corresponding to exciton condensate.

Table 2 shows the measured parameters of oscillations from Figs. 2–6 for samples of 2D macroporous silicon structures (oscillation period, half-width of oscillation minima, Rabi frequency).

Table 2. The parameters of oscillations of the samples of 2D macroporous silicon structures from Table 1

No of sample	Structure Type	Oscillation period (cm <sup>-1</sup> )		Half-width of oscillation	Rabi	
		Curve 1	Curve 2	minima (cm <sup>-1</sup> )	(cm <sup>-1</sup> )	
1	One-sided	10	3.3	0.4	1.0	
2	One-sided	10.7	4.4	0.6	1.0	
3	One-sided	9.1	3.3	0.5	1.0	
4	One-sided	10.5	4.3	0.45	1.0	
5	Two-sided	4.5	3	0.7	0.9-1.0	
6	Two-sided	4.5	4.2	1.0	1.0	

In accordance with the most important features and properties of the Bose-Einstein condensates [23], we measured narrow giant oscillations with positive and negative amplitudes and with half-width of oscillation minima  $0.4-1.0 \text{ cm}^{-1}$  (Table 2). It confirms the coherence of oscillations and large-scale spatial correlation. Thus, we measured the negative absorption amplitudes indicated the implementation of stimulated radiation, when filling of exciton polaritons is higher than the condensation threshold [22]. The coherence of oscillations and large-scale spatial correlation is also a result of condensation exciton-polaritons on macropores, as in the microresonators. In this case, microresonators interact both with each other (one-sided macroporous silicon structures) and in the system of two-sided macroporous silicon.

For our case (Table 2), the oscillation period reduced by 3 times for one-sided samples #1-4 and by 1.5 times for two-sided samples #5–6. The oscillation half-width both with positive and negative amplitude is very small and equal to 0.4-1 cm<sup>-1</sup>, the splitting of the Rabi equals to 0.9-1.0 cm<sup>-1</sup>. Our results allow comparing the phenomenon of exciton-polariton condensation on macropores with earlier results on electrooptical effects in macroporous silicon [9, 10]. In our case, at the increase of the resolution of optical spectra measurements IR absorption increases by 100 times, and the oscillations period decreases by 3 times. Oscillations associated with the realization of Wannier-Stark electrooptical effect with the period of Wannier-Stark steps Fa (F - the electrical field intensity on the "silicon")matrix-nano-coating" boundary, a - parameter of the silicon lattice). Reducing the width of steps is

determined by reducing the electric field intensity F. This result is associated with the change in the filling of silicon conductivity band by electrons. We directly measured the filling of silicon conductivity band by electrons in spectra of electro-optical reflection by the structures of macroporous silicon with nano-coatings [24].

The increase of the silicon conduction band filling by electrons leads to an increase in the total charge of electrons and stimulates the corresponding increase of holes charge in the valence band (Fig. 7). That reduces the electric field intensity at the boundary of "silicon matrixnano-coating" by 3 times for one-sided macroporous silicon structures and by 1.5 times for two-sided macroporous silicon structures. For the same amount of photons in these processes, one macropore in two-sided samples of macroporous silicon drops two times less photons. It reduces the filling of silicon conduction band by electrons and the electric field intensity at the "silicon matrix-nano-coating" border by only 1.5 times compared to those in one-sided structures.

In general, dipolar excitons occur only in spatial conditions, when excitons are in the lateral traps [23]. In this case, excitons are not "running away" because of dipole-dipole repulsion. The length of coherence in the plane of structure equals to 4 microns and is close to the perimeter of the ring trap, which far exceeds the thermal wavelength of de Broglie under the same microns). conditions (0.17)Thus, room temperature polaritonic nanolasers were demonstrated [25] by designing wide-gap semiconductor nanocavities to produce thermally stable excitons coupled with photons in nanocavity. In our case, the half-width of oscillation minima is 0.4-1 cm<sup>-1</sup>, which means high localization of the exciton-polariton on macropores, and decreases the condensation threshold at room temperature.

## CONCLUSIONS

Macroporous silicon structures with periodical macropore distribution were made by photoelectrochemical etching; SiO<sub>2</sub> nanocoatings were obtained in the diffusion stove after treatment of macroporous silicon substrates in the nitrogen atmosphere. CdS or ZnO nanoparticles were deposited on oxidized surface of macropores from the colloidal solutions in polyethyleneimine. Two-sided structures of macroporous silicon with arbitrary macropore distribution were formed by photoelectrochemical etching of one side of silicon substrate and after that etching of an other side of silicon substrate.

Optical absorption spectra were measured in the  $200 \div 8500$  cm<sup>-1</sup> spectral range with a resolution of 2 cm<sup>-1</sup> and with high-resolution of 1 cm<sup>-1</sup> at normal incidence of IR radiation on a sample in the air at room temperature. For onesided structures of macroporous silicon with nanocoatings after changing the resolution of spectra measurements from 2 to 1 cm<sup>-1</sup>, the oscillation period decreases by 3 times, and absorption increases by 60-100 times. For twosided macroporous silicon structures without nano-coatings, the oscillation period decreases by 1.5 times and absorption increases by 25-30 %. In addition, giant oscillations with positive and negative amplitudes of  $10^7$  arb. un. were evaluated in spectral regions of Si-Si-bonds and P<sub>b</sub> centers. Similar oscillations in the reflection spectra have much less amplitudes - up to  $4.10^4$  arb. un. Giant absorption oscillations were measured on the two-sided macroporous silicon structures without nano-coatings too at frequencies of rotational Si-O oscillations, Si-Si-bonds, TO-phonon of the surface natural layer of the SiO<sub>2</sub>, as well as P<sub>b</sub> centers.

In the spectral area of the transverse phonon  $\omega_{TO}$  (Si–Si–bonds), absorption spectra of 2D macroporous silicon structures with nanocoatings include from one to three negative absorption minima, dependent on thickness and nature of nano-coatings. It is fully consistent with the data for phonon polaritons in microresonators as the resonance interaction of dipole-active vibrations with the frequency of  $\omega_{\rm TO}$  in thin films with the microresonator surface modes. The giant oscillations with positive and negative amplitudes testify the strong interaction of surface polaritons with photons. Indeed, in 2D the macroporous silicon structures with nano-coatings band bendings on the surface of the macropores are significant. Therefore, the generated photoelectrons link with holes and form electronhole pairs named as exciton polaritons with narrowing of the polariton distributions; detection large-scale spatial correlation. of This phenomenon of exciton-polariton Bose-Einstein condensation was measured in 2006 on the microresonators of quasi-2D semiconductor heterojunctions. In accordance to the phenomenon of Bose-Einstein condensation, we measured narrow giant oscillations too with positive and negative amplitudes and with half-width of oscillation minima  $0.4-1.0 \text{ cm}^{-1}$ ; this confirms the coherence of oscillations and large-scale spatial correlation. Thus, we measured the negative absorption amplitudes indicating the implementation of stimulated radiation, when filling by exciton-polaritons is higher than the

condensation threshold. The coherence of oscillations and large-scale spatial correlation are also the result of exciton-polariton condensation in macropores, as in the microresonators. In this case, microresonators interact both with each other (one-sided macroporous silicon structures) and in the system of two-sided macroporous silicon.

### Екситон-поляритони в 2D структурах макропористого кремнію з нанопокриттями

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В роботі досліджені високороздільні спектри оптичного поглинання та відбивання в 2D односторонніх періодичних структурах макропористого кремнію з нанопокриттями SiO<sub>2</sub> та наночастинками CdS, ZnO та у двосторонніх структурах макропористого кремнію без нанопокриттів. Після зміни роздільної здатності вимірювань з 2 на 1 см<sup>-1</sup> період осциляцій електрооптичного ефекту Ваньє-Штарка зменшується у 3 рази, поглинання збільшується у 60–100 разів; для двосторонніх структур макропористого кремнію період осциляцій зменшується у 1.5 рази, поглинання збільшується на 25–30 %. На додаток, для односторонніх структур макропористого кремнію виміряні гігантські позитивні та негативні осциляції поглинання величиною 10<sup>7</sup> відн.од. та напівшириною 0.4–1.0 см<sup>-1</sup> в спектральній області поглинання Si–Si–зв'язками та  $P_b$  центрами. Подібні осииляції у спектрах відбивання мають набагато мениу амплітуду – до 4·10<sup>4</sup> відн. од. В спектральній області поперечного фонона ω<sub>TO</sub> (Si–Si–зв'язки) спектри поглинання повністю відповідають експериментальним даним по фононним поляритонам в тонких плівках в умовах резонансної взаємодії діпольно-активних коливань з частотою  $\omega_{TO}$  з поверхневими модами мікрорезонатора. У цьому випадку мікрорезонатори взаємодіють як між собою в односторонніх структурах, так і в системі двосторонніх структур макропористого кремнію. Гігантські осциляції свідчать про сильну взаємодію поверхневих поляритонів з фотонами. Когерентність осциляцій та великомасштабні макрокореляції є результатом конденсації екситонних поляритонів на макропорах як мікрорезонаторах. У 2D структурах макропористого кремнію з нано-покриттями вигини зон на поверхні макропор є значними. Тому, генеровані фотоелектрони зв'язуються з дірками в потенціальних ямах, утворюючи електрон-діркові пари, які називаються екситонними поляритонами відповідно до явища конденсації Бозе-Ейнштейна.

**Ключові слова**: односторонні та двосторонні структури макропористого кремнію, нанопокриття нанокристалів, екситонні поляритони, конденсація Бозе-Ейнштейна

### Экситон-поляритоны в 2D структурах макропористого кремния с нанопокрытиями

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В работе исследованы высокоразрешенные ИК спектры поглощения и отражения в 2D односторонних периодических структурах макропористого кремния с нанопокрытиями SiO<sub>2</sub> и наночастиц CdS, ZnO, а также в двухсторонних структурах макропористого кремния без нанопокрытий. После увеличения разрешающей способности оптических измерений с 2 на 1 см<sup>-1</sup> период осцилляций электро-оптического эффекта Ванье-Штарка уменьшается в 3 раза, поглощение увеличивается в 60–100 раз. Для двусторонних структур макропористого кремния период осцилляций уменьшается в 1.5 раза, а поглощение увеличивается на 25-30 %. В дополнение, для односторонних структур макропористого кремния измерены гигантские положительные и отрицательные осциляции поглощения величиной  $10^7$  отн. ед. и полушириной 0.4-1.0 см<sup>-1</sup> в спектральной области поглощения Si-Si-связями и Рь-центрами. Подобные осцилляции в спектрах отражения имеют гораздо меньшую амплитуду – до 4.104 отн. ед. В спектральной области поперечного фонона ω<sub>TO</sub> (Si–Si–связи) спектры поглошения полностью согласуются с экспериментальными данными по фононным поляритонам в тонких пленках в условиях резонансного взаимодействия дипольно-активных колебаний с частотой  $\omega_{TO}$  с поверхностными модами микрорезонатора. При этом микрорезонаторы взаимодействуют друг с другом как в односторонних структурах, так и в системе двусторонних структур макропористого кремния. Гигантские амплитуды осцилляций свидетельствуют о сильном взаимодействии поверхностных поляритонов с фотонами, формируя экситонные поляритоны. При этом когерентность осцилляций и крупномасштабная макрокорреляция являются результатом конденсации экситонных поляритонов в макропорах, как микрорезонаторах. В 2D структурах макропористого кремния с нанопокрытиями изгиб зон на поверхности макропор является значительным. Поэтому генерируемые фотоэлектроны связаны с дырками в потенциальных ямах, образуя электрон-дырочные пары, которые называются экситонными поляритонами в соответствии с явлением конденсации Бозе-Эйнштейна.

**Ключевые слова**: односторонние и двусторонние структуры макропористого кремния, нанопокрытия нанокристаллов, экситонные поляритоны, конденсация Бозе-Эйнштейна

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