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Wannier–Stark electro-optical effect and photonic modes in 2D macroporous silicon structures with SiO_2 nanocoatings

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Abstract. We have investigated the IR light absorption oscillations in 2D macroporous silicon structures with SiO_2 nanocoatings, taking into account the Wannier–Stark electro-optical effect caused by a strong electric field on the Si-SiO_2 boundary and an additional electric field of quasi-guided optical modes. The photonic modes and band gaps were also considered as peculiarities in absorbance spectra of macroporous silicon structures with a thick SiO_2 nanocoating. The photonic modes do not coincide with the quasi-guided modes in the silicon matrix.

Keywords: macroporous silicon, Wannier–Stark effect, photonic mode.

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1. Introduction

Macroporous silicon is a promising material for the development of 2D photonic structures with the required geometry and large effective surface [1, 2]. It determines optical and electro-optical characteristics of macroporous silicon structures [3-7]. In view of the potential barrier on a macropore surface, one should take into account recharging the local surface centers at energies below that of the indirect interband transition. The near-IR optical absorption in 2D photonic macroporous silicon structures was investigated in [6], with allowance made for the linear electro-optical effect. 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. In [7], we investigated the near-IR light absorption oscillations in 2D macroporous silicon structures with microporous silicon layers, CdTe and ZnO surface nanocrystals, taking into account the electro-optical effect within the strong electric field approximation. The model [8, 9] of the resonance electron scattering by impurity states in an electric field of the "silicon–nanocoating" heterojunction on a macropore surface and realization of the Wannier–Stark effect on randomly distributed surface bonds were confirmed. In this case, the Wannier–Stark effect is realized as a result of the large-time electron scattering as compared with the period of its oscillations in a strong electric field of the illuminated "silicon-nanocoating" interface.

In this paper, the near-IR light absorption oscillations of 2D macroporous silicon structures with SiO_2 nanocoatings were investigated taking into account the Wannier–Stark electro-optical effect caused by a strong electric field on the Si-SiO_2 interface and an additional electric field of quasi-guided modes. The photonic modes and band gaps were considered as peculiarities in absorbance spectra of macroporous silicon structures with a thick SiO_2 nanocoating.

2. Procedure

Macroporous silicon structures were made of silicon wafers characterized by the [100] orientation and *n*-type conductivity (the electron concentration $n_0 = 10^{15}\,\mathrm{cm}^{-3}$). We used the technique of electrochemical etching under illumination of the back side of silicon substrate [2]. The parallel cylindrical macropores were etched to form 2D periodic square-lattice structures (Fig. 1) with the period $a = 4$ μm, diameter $D_p = 2$ μm and macropore depth $h_p = 90…100$ μm.

The SiO_2 nanocoatings were treated in the diffusion stove in the nitrogen atmosphere. The oxide layers (thickness of 70 and 200 nm) were formed on macroporous silicon samples in dry oxygen for 40 and 60 min, respectively, at the temperatures 1050 °C and 1200 °C. The 800 nm oxide was formed for 50 min at the temperature 1100 °C in wet oxygen using a steam generator with deionized water. The oxide thickness was measured using ellipsometry.

We performed optical investigations within the 1.3 to 25 μm spectral range using a PerkinElmer Spectrum BXII IR Fourier spectrometer. The error of spectral measurements was about $2\,\mathrm{cm}^{-1}$. The optical absorption spectra were recorded at normal incidence of IR radiation on the sample (along the main axis of cylindrical macropores – Fig. 1, insertion). The experiments were carried out in air at room temperature.

3. Experimental results and discussion

3.1. Oscillations of light absorption

For macroporous silicon structures with SiO_2 nanocoatings, light absorption increases and an oscillating structure occurs (Fig. 2a, curves 1 and 2). We observed essential absorption growth in the spectral region of $Si-O$, $Si-H$, $O-H$ bonds and organic compounds. The amplitude of oscillations has its maximum in the spectral ranges of surface level absorption (Fig. 2b).

The dependence of oscillation maxima of macroporous silicon structures with SiO_2 nanocoating on oscillation number has the bends (Fig. 3a) at the energies of 250 meV (curve 1), 400 meV (curve 2) and 700 meV (curve 3). And the oscillation period fluctuates about a constant value at low spectral energies and becomes quadratic at photon energies depending on SiO_2 nanocoating thickness (Fig. 3b).

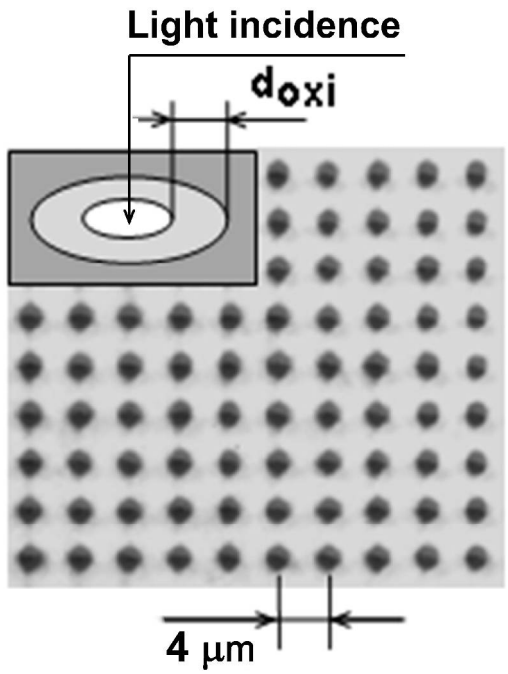

Fig. 1. 2D macroporous silicon square-lattice structure with the period $a = 4$ μm. Insertion: fragment of the cylindrical macropore with SiO_2 nanocoating and direction of light incidence on the sample (along the main axis of the cylindrical macropore).

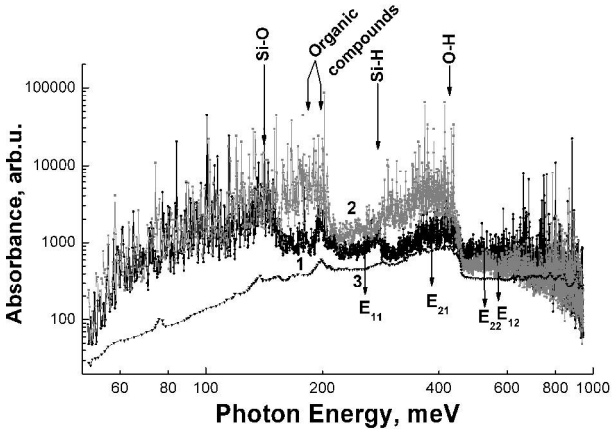

Fig. 2a. Absorption spectra of macroporous silicon structures with SiO_2 nanocoating: 70- (*1*) and 800-nm (*2*) thick and without coating (3).

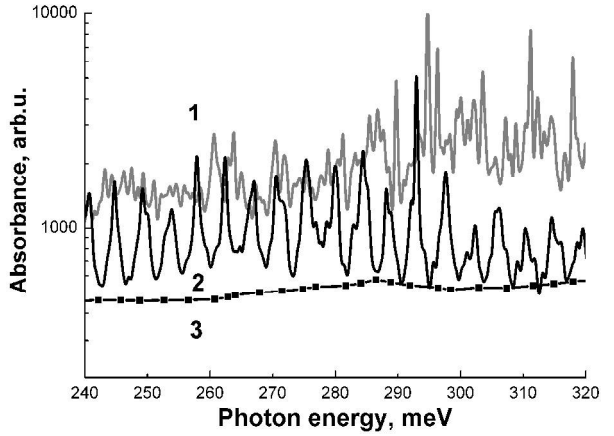

Fig. 2b. Fragment of absorption spectra of macroporous silicon structures with: SiO_2 nanocoating (*1*), ZnO nanocrystals (*2*) from [7] and without coating (3).

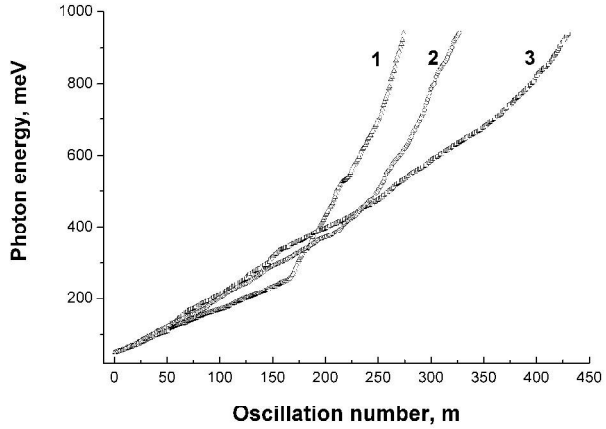

Fig. 3a. The spectral position of oscillation maxima in the macroporous silicon structures with SiO_2 nanocoatings of 70- (*1*), 200- (*2*) and 800-nm (*3*) thickness.

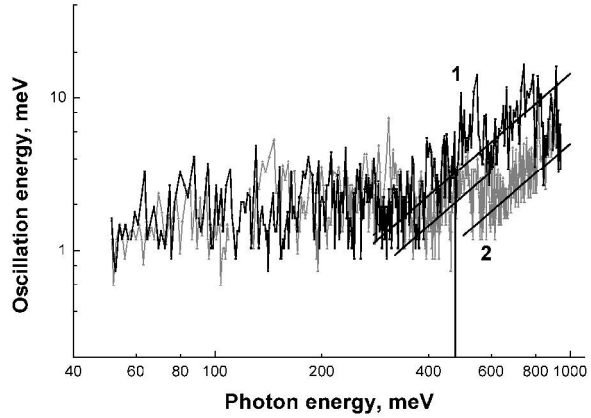

Fig. 3b. Spectral dependencies of the oscillation energy in the macroporous silicon structures with SiO_2 nanocoatings of: 200- (*1*) and 800-nm (*2*) thickness.

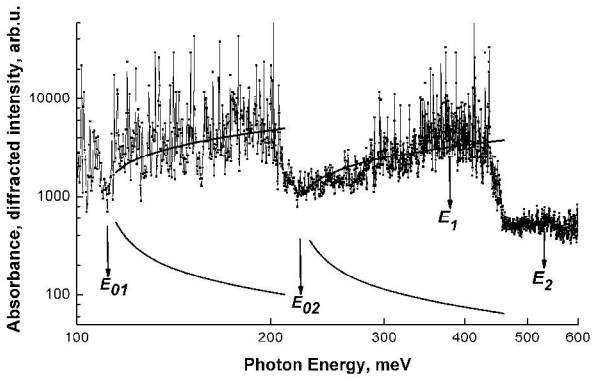

Fig. 4. Absorption spectra of macroporous silicon structures with the SiO_2 nanocoating of 800-nm thickness: E_1 and E_2 are the minimal energies of quasi-guided mode formation; E_{01} and E_{02} – critical points of peculiarities in absorption spectra of macroporous silicon structure. Below: spectral dependence of the diffracted beam intensity $D_i(\omega) \sim (h\omega - E_{0i})^{-1/2}$.

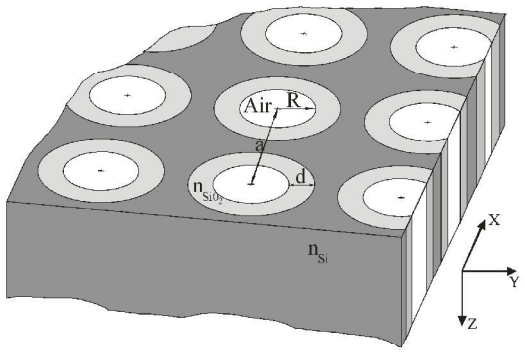

Fig. 5. Fragment of the system considered.

3.2. Peculiarities in absorption spectra of macroporous silicon structures with thick SiO_2 nanocoating

In addition, in Fig. 4 we observed the peculiarities at the photon energies 100 to 200 meV and 220 to 480 meV in absorption spectra of macroporous silicon structures with the SiO_2 nanocoating of the thickness 800 nm. The peculiarities are similar to those observed in reflectance spectra of macroporous silicon photonic crystals at near-normal (5°) light incidence [10]. The critical points E_{01} = 110 meV and E_{02} = 220 meV in absorbance may be related to singularities in a diffracted intensity $D_i(\omega) = C_i(h\omega - E_{0i})^{-1/2}$ due to photonic modes excitation as an "absorption" process that includes the intensity of a diffracted beam: $A = A_{0i} + (D_i)^{-1}$.

3.3. Wannier–Stark ladders

We observed the giant oscillations in absorption spectra of macroporous silicon structures with SiO_2 nanocoatings of 70…800-nm thickness. The oscillation amplitude is maximal in the spectral ranges of surface level absorption. The data obtained indicate a strong effect of impurity states on the surface of macroporous silicon structures with SiO_2 nanocoatings. This may result from scattering of both electromagnetic radiation and electrons by the impurity states. The form of oscillations (Fig. 2b) indicates a resonant character of scattering. Well-separated oscillations in the spectral ranges of surface bond absorption were observed in the absorption spectra of macroporous silicon structures with surface nanocrystals [7] and explained by realization of the Wannier–Stark effect on randomly distributed surface bonds.

A method of experimental observation of Wannier–Stark ladder was proposed in [8]. It was shown that the scattering amplitude has resonant behavior in the case of electron scattering by 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 Wannier–Stark ladder. In our case, an electric field of the "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 the quasi-momentum with the components k_y, k_z; E_0 – energy corresponding to the midgap, Δ – energy equal to 1/6 of the band gap, a – lattice parameter. The wave function in the Wannier representation was written as [8]:

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

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 – the impurity potential. The complex energies for which the denominator of the

second term becomes zero correspond to the resonances in the electron scattering

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

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

The fact is that the levels of the Wannier–Stark ladder have a certain width Γ, while its detection requires that this width should be less than the difference of the energies of adjacent levels, $\Gamma < Fd$ [9]. The Wannier–Stark ladder is not broken by impurities, if the intervals between the transitions caused by the scattering from impurity atoms with the lifetime τ are bigger than the period of electron oscillations in an external field, T_B ($\tau/T_B > 1$), where $T_B = 2\pi h/\Delta E$, τ is equal to $1/W$ (W is the probability for an electron to leave the state per unit time caused by the scattering from an impurity atom at the lattice site). In [9], the following estimate of the probability W for an electron to leave the state per unit time caused by the scattering from an impurity atom at the lattice site was obtained: $W < 2V_0N_i/(N_h)$, where V_0 is the impurity potential, N_i – impurity concentration and $N \approx (a^2)^{-1}$ – 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 latter inequality, we find a numerical estimate of the impurity concentration.

The surface state concentration in macroporous silicon structures changes from 10^{10} to 10^{11}cm^{-2} [11] and $N_i^{\max} > 10^{11}$cm^{-2} for the investigated spectral range. The spectral dependence of the lifetime ratio τ/T_B for macroporous silicon structures with SiO_2 nanocoatings of 200- (*1*) and 800-nm (*2*) thickness are presented in Fig. 6. The inequality $\tau/T_B > 1$ for the lifetime ratio is satisfied within the whole spectral region investigated for macroporous silicon structures with SiO_2 nanocoatings, taking into account that the surface impurity concentration for macroporous silicon structures N_i is less than 10^{11}cm^{-2}.

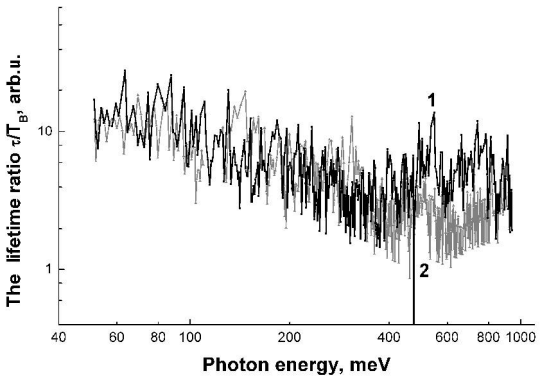

Fig. 6. Spectral dependence of the lifetime ratio τ/T_B for macroporous silicon structures with SiO_2 nanocoatings of 200- (*1*) and 800-nm (*2*) thickness.

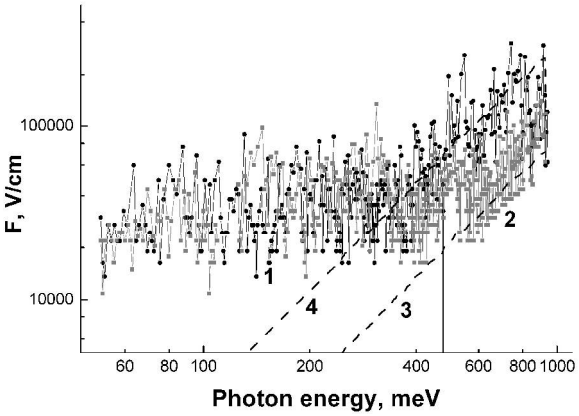

Fig. 7. Spectral dependences of the electric field F on the macroporous silicon surface for structures with SiO_2 nanocoatings of 200- (*1*) and 800-nm (*2*) thickness; spectral dependences of the electric field as a result of quasi-guided mode formation in the silicon matrix (3 and 4).

3.4. Quasi-guided modes

Usually, the basic sources of an external electric field at semiconductor surface are the charge of electron levels and built-in charge in semiconductor surface oxide [12]. The spectral dependences of the electric field F on the macroporous silicon surface for structures with SiO_2 nanocoatings of 200- and 800-nm thickness are presented in Fig. 7 (curves 1, 2). The oscillation period and electric field of macroporous silicon structures with SiO_2 nanocoatings fluctuate around a constant value at low spectral light energies and become quadratic at high spectral light energies (Fig. 7, curves 3, 4).

The electric field F becomes quadratic at light wavelengths equal to the geometrical sizes of silicon matrix and SiO_2 nanocoatings (Fig. 7, curves 3, 4 and Table). This dependence corresponds to quasi-guided mode formation [13] in the silicon matrix (minimal distance between macropores) with $2\rho_{Si\,i} = a - (D_p + d_{SiO_2})$ and in the silicon column with $2\rho_{Si\,i} = 1.4[a - (D_p + d_{SiO_2})]$. Comparison of the samples with quasi-guided mode characteristics in Table has confirmed that the mode parameter $Q_{Si} \sim k\rho_{Si\,i}$ [13] is determined by the beginning of the electric field quadratic growth in Fig. 7.

In general, at grazing angle of light incidence, the electric field of the reflected electromagnetic wave changes the local electric field in the near-surface region of the macropore walls with thickness $d \approx 0.1\lambda$ for the wavelength λ [14]. Let us assume that d is determined by an electric component of an electromagnetic wave with $\hbar\omega$ and by the change of a built-in electric field ΔF_s $\left(d = \hbar\omega/\left(e \cdot \Delta F_s\right)\right)$. Indeed, under our experimental conditions of the grazing angle of light incidence onto the macropore surface, the electric field on the macroporous silicon surface for structures with SiO_2 nanocoatings is about $F_s + \Delta F_s$ with

Table. The sample and quasi-guided mode characteristics

d_{SiO2}, nm	$D_p + d_{SiO2}$, μm	$a - (D_p + d_{SiO2})$, μm	Mode type	$2\rho_{Si}$, μm
70	2.07	2.4	Quasi-guided modes in the silicon matrix	$2[a - (D_p + d_{SiO2})] = 4.8$ (0.26 eV)
			Quasi-guided modes in the silicon matrix	$[a - (D_p + d_{SiO2})] = 2.2$ (0.56 eV)
200	2.2	2.27	Quasi-guided modes in the silicon matrix	$2[a - (D_p + d_{SiO2})] = 4.1$ (0.30 eV)
			Quasi-guided modes in the silicon column	$1.4[a - (D_p + d_{SiO2})] = 3.65$ (0.34 eV)
800	2.8	1.67	Quasi-guided modes in the silicon matrix	$2[a - (D_p + d_{SiO2})] = 3.25$ (0.38 eV)
			Quasi-guided modes in the silicon column	$1.4[a - (D_p + d_{SiO2})] = 2.34$ (0.53 eV)

$\Delta F_s \approx \hbar\omega/(0.1\lambda_1) \sim \hbar\omega^2$ according to the experiment (Fig. 7). The light wavelength is equal to $\lambda_1 = \lambda/n_i$ (n_i is the effective refractive index of pores with SiO_2 nanocoatings or the refractive index of SiO_2 nanocoatings).

3.5. Photonic modes

The peculiarities at the photon energies 100 to 200 meV and 220 to 480 meV in absorption spectra of macroporous silicon structures with the SiO_2 nanocoating of 800-nm thickness (Fig. 4) are similar to those observed in reflectance spectra of macroporous silicon photonic crystals at the near-normal (5°) light incidence [10]. These anomalies in absorbance of macroporous silicon structures are caused by the match of an external field with a Bloch state that behaves like a one-dimensional (1D) critical point with a density of states given by photon dispersion in the vertical direction along macropores only, whereas the in-plane momentum and the parallel vector k are conserved. Onset of a diffracted beam corresponds to a complex wave-vector component q that passes through zero and becomes real [15]. Out-of-plane dispersion of all the bands is quadratic in q around $q = 0$ [16] with a threshold at $E(\omega, q) = E_0$ and a diffracted intensity $D(\omega) \sim (\hbar\omega - E_0)^{-1/2}$, like for a 1D density of states. A structure in absorbance (Fig. 4) marks the onset of a photonic mode that is excited and remains propagating for higher frequencies [10].

The diffracted intensity $D_i(\omega)$ is removed from absorbance (Fig. 4) that has the form of the square root at $E(\omega, q) > E_0$, proving that the measured features in absorbance correspond to the 1D critical point [17], and the calculated diffracted intensities of allowed modes at normal incidence have the form of the inverse square root close to thresholds $E_{01} = 110$ meV and $E_{02} = 220$ meV. These bands do not appear in the absorption curves of macroporous silicon structures with SiO_2 layers of 70- and 200-nm thicknesses (Fig. 2b). They may have allowed bands, but very weak spectral strength.

The threshold energies E_{01} and E_{02} (Fig. 4) correspond to the normalized frequencies $\omega a/2\pi c = 0.36$ and 0.71. The results obtained are similar to calculations for the 2D square lattice composed of circular air-rods in dielectric material with the dielectric constant 2.1 and filling factor 0.25 [18]. There are two band gaps, one is between the first and second 1D eigenmodes (A modes), and the other is between the second and third A modes. The normalized frequency ranges of this band gaps are 0.36…0.39, 0.71…0.73 for E-polarization and 0.36…0.40, 0.73…0.74 for H-polarization. Our structure is three-component one, with the averaged refractive index 1.4, while the structure from [18] is two-component with the averaged refractive index 1.3. The pronounced structure that was observed in experimental reflectance spectra at near-normal (5°) light incidence on the macroporous silicon structure with the averaged refractive index 3 around the higher normalized frequency 0.47 [10] corresponded to the allowed band with symmetry Γ_5^-.

Quasi-guided mode formation in silicon matrix at the energies $E_1 = 0.38$ eV and $E_2 = 0.53$ eV (see Table) does not appear in the absorption spectra (Figs. 2a and 4) and does not coincide with the photonic modes as peculiarities in absorbance (and reflectance) spectra of macroporous silicon structures.

4. Conclusions

The near-IR light absorption oscillations in 2D macroporous silicon structures with SiO_2 nanocoatings of 70- to 800-nm thickness weare investigated taking into account the electro-optical effect within the strong electric field approximation. We observed the oscillating structure in the absorption spectra of macroporous silicon structures with SiO_2 nanocoatings. The

oscillation amplitude has its maximum in the spectral ranges of surface level absorption as a result of the resonance electron scattering by impurity states with the difference between these two resonance energies equal to the Wannier–Stark ladder.

The Wannier–Stark ladder is not destroyed by impurities, if the intervals between the transitions caused by the scattering from impurity atoms with lifetime τ are bigger than the period of electron oscillations in an external field, T_B. And the inequality $\tau / T_B > 1$ holds in the whole spectral regions considered for macroporous silicon structures with SiO_2 nanocoatings, taking into account that the surface impurity concentration N_i for macroporous silicon structures is less than 5×10^{11}cm^{-2}.

The oscillation period and electric field in macroporous silicon structures with SiO_2 nanocoatings fluctuate around a constant value at low photon energies and become quadratic in the photon energy, depending on the geometrical sizes of silicon matrix and SiO_2 nanocoatings. The relevant electric field growth corresponds to quasi-guided mode formation in silicon matrix (minimal distance between the macropores) and in the silicon column.

The peculiarities in absorption spectra of macroporous silicon structures with a thick SiO_2 nanocoating are similar to those observed in reflectance spectra of macroporous silicon photonic crystals [10] at near-normal light incidence. The match of an external field with a Bloch state behaves like a 1D critical point with a density of states given by photon dispersion in the vertical direction along macropores. The critical points in absorbance are related to photonic modes excitation as an "absorption" process that includes the intensity of a diffracted beam. The quasi-guided modes in silicon matrix influence the local electric field (electro-optical effect) and do not coincide with the photonic modes.

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