

Wannier-Stark effect and electron-phonon interaction in macroporous silicon structures with SiO₂ nanocoatings

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We investigated the contribution of electron-phonon interaction to the broadening parameter Γ of the Wannier-Stark ladder levels in oxidized macroporous silicon structures with different concentration of Si-O-Si states (TO and LO phonons). The obtained value of the Wannier-Stark ladder parameter Γ is much less than the adjacent level energy evaluated from giant oscillations of resonance electron scattering on the surface states. We determined the influence of broadening on the oscillation amplitude in IR absorption spectra as interaction of the surface multi-phonon polaritons with scattered electrons. This interaction transforms the resonance electron scattering in samples with low concentration of Si-O-Si states into ordinary scattering on ionized impurities for samples with high concentration of Si-O-Si states. The transformation takes place at the scattering lifetime coinciding with the period of electron oscillations in the surface electric field.

Keywords: Wannier-Stark effect, electron-phonon interaction, macroporous silicon structures, SiO₂ nanocoatings.

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]. This determines optical and electro-optical characteristics of macroporous silicon structures [3,4]. In view of the potential barrier on a macropore surface, one should take into account recharging of the local surface centres at energies below that of the indirect interband transition. The near-IR optical absorption in 2D photonic macroporous silicon structures was investigated in Ref. 5, with allowance made for the linear electro-optical effect. The experimental absorption spectra of macroporous silicon agree well with the corresponding spectral dependencies 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 Refs. 6 and 7 we investigated the near-IR light absorption oscillations in 2D macroporous silicon structures with surface II–VI nanocrystals and SiO₂ nanocoatings taking into account the electro-optical effect within the strong electric field approximation. The model of the resonance electron scattering on impurity states in an electric field of “silicon-nanocoating” heterojunction on macropore surface and realization of the Wannier-Stark effect on randomly distributed surface bonds were confirmed [8,9]. In this case the Wannier-Stark effect is realized. The fact is that the levels of the Wannier-Stark ladder have a certain width Γ , while its

detection requires this width to be less than the difference of energies of adjacent levels, $\Gamma < Fd$. The contributions to the broadening parameter Γ come from interband interaction, electron-phonon interaction, and interaction with impurity atoms. The Wannier-Stark ladder is not broken by impurities if the electron scattering time τ on surface states is bigger than the period T_b of electron oscillations in strong external field. The model [8,9] of the resonance electron scattering on surface states is realized in Ref. 6 and 7 due to a large-time electron scattering in the electric field of illuminated “silicon-nanocoating” boundary.

In this paper, the contribution of the electron-phonon interaction to the broadening parameter Γ of the levels of the Wannier-Stark ladders is investigated in oxidized macroporous silicon structures with different concentration of Si-O-Si states corresponding to the TO and LO phonons in SiO₂ nanocoatings.

2. Procedure

The samples to be studied were made of n-silicon wafers of [100] orientation (the electron concentration $n_0 = 10^{15} \text{ cm}^{-3}$) using the photoelectrochemical etching [3]. Macroporous silicon structures with macropore depth $h_p = 70\div 80 \text{ }\mu\text{m}$, diameter $D_p = 2\div 4 \text{ }\mu\text{m}$ and concentration $N_p = (1.2\div 1.9) \times 10^6 \text{ cm}^{-2}$ were etched (Fig. 1).

The SiO₂ nanocoatings were formed in a diffusion stove after treatment in the nitrogen atmosphere. The oxide layers (thickness of $5\div 50 \text{ nm}$) were formed on macroporous silicon samples in dry oxygen during $40\div 60 \text{ min.}$ at the temper-

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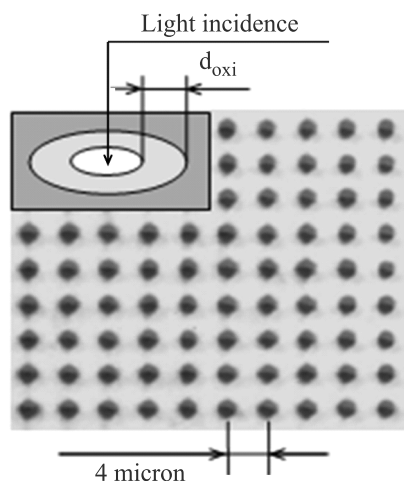


Fig. 1. A fragment of the macroporous silicon structure and direction of light incidence on the sample (along the main axis of cylindrical macropore).

ature of 1050°C. Silicon oxide layers of 100 and 200 nm thickness were formed 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 using a PerkinElmer Spectrum BXII IR Fourier spectrometer in the 300–8000 cm⁻¹ spectral range. The optical absorption spectra were recorded at normal incidence of IR radiation on the sample (along the main axis of cylindrical macropores – see Fig. 1). The experiments were carried out in air at room temperature.

To reduce the concentration of nonradiative recombination centres (mainly hydrogen), the structure surface cleaning was provided by its preliminary oxidation in atmosphere of dry oxygen at 900°C for 15 min. to an oxide thickness of 30 nm and further oxide etching off in 10% aqueous solution of HF.

3. Experimental

3.1. Macroporous silicon structures with and without surface cleaning

Figure 2 shows IR spectra of macroporous silicon before (curve 1) and after surface cleaning through oxidation and oxide etching off (curve 2). There are absorption peaks (Fig. 2, curve 1) associated with the one-phonon absorption in silicon (364 cm⁻¹), absorption of organic compounds (1416 cm⁻¹ and 1600 cm⁻¹); the peaks 2997 cm⁻¹ and 3405 cm⁻¹ are associated with the CH₃ vibrations and OH bonds due to water absorption [5]. At the same time, the IR spectrum of macroporous silicon after its oxidation and etching (Fig. 2, curve 2) includes an intense peak 609 cm⁻¹ associated with bulk Si-Si mode [4] and 1100 cm⁻¹ peak associated with Si-O bonds in O-Si-O compound [3–5]. Thus, preliminary treatment of the surface structures of macroporous silicon reduces absorption of organic compounds, CH₃ and OH bonds.

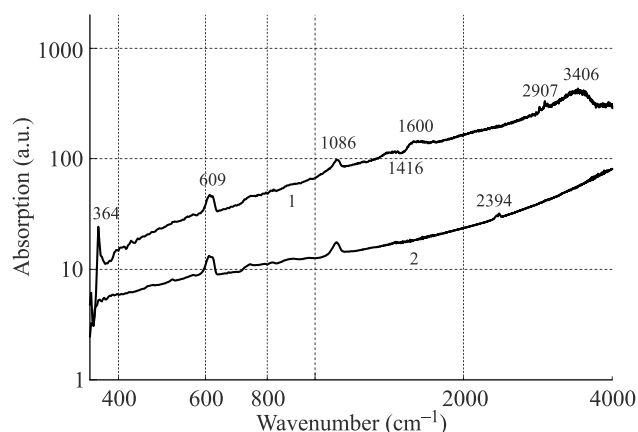


Fig. 2. IR absorption spectra of macroporous silicon before (curve 1) and after oxidation and oxide etching (curve 2).

The value of absorption of macroporous silicon without oxidation and etching is 2–10 times higher than that of macroporous silicon after these operations. In addition, the spectral absorption dependence obeys the “3/2 law” (Fig. 2, curve 1). The latter result suggests that the structure of macroporous silicon without oxidation and oxide etching demonstrates linear electro-optical Franz-Keldysh effect [5]. In this case, the energy barrier and the local electric field on the surface of macropores are due to a thin SiO_x layer in presence of hydrogen. Oxidation and oxide etching reduce the energy barrier and local electric field on the surface of macropores, thus leading to an almost linear spectral dependence of the absorption (Fig. 2, curve 2).

3.2. Macroporous silicon structures with SiO₂ nanocoatings

The IR absorption spectra of macroporous silicon structures with preliminary surface cleaning and next surface oxidation (thickness of 5–200 nm) are shown in Fig. 3. The IR absorption of the macroporous silicon with surface oxide thickness of 5 nm (curve 2) is 1.5 times bigger than the IR absorption of macroporous silicon sample without surface oxidation (curve 1). The nature and intensity of absorption peaks are almost identical for curves 1 and 2.

The IR spectrum of the sample of macroporous silicon with surface oxide thickness of 10 nm (curve 3) changes dramatically. We measured a peak 364 cm⁻¹ of one-phonon absorption and peak 465 cm⁻¹ associated with the Si-O-Si rotation [8]. There is a strong growth of the oxide peak Si-O-Si (1095 cm⁻¹) with further oxidation of macroporous silicon (curves 4–7). This indicates an increase of the concentration of bridge-like oxygen atoms in Si-O-Si (TO phonons) due to reduction of passivation of silicon and oxygen dangling bonds in absence of hydrogen [9]. In addition to the TO phonon peaks (1086–1095 cm⁻¹), LO phonon absorption peaks (1250–1256 cm⁻¹) are formed due to radiation incidence along the surface of cylindrical macropores (geometry of frustrated total Internal reflection [10]).

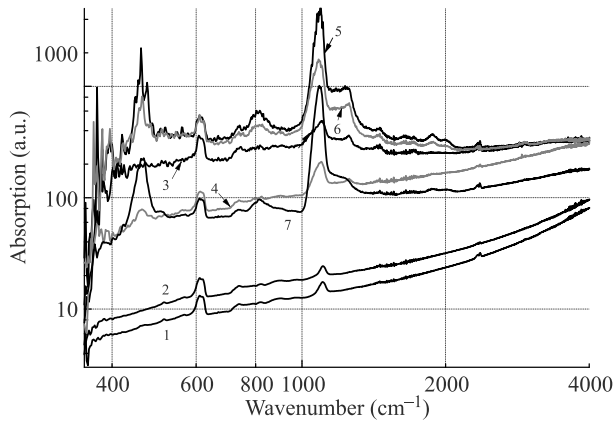


Fig. 3. IR spectra of macroporous silicon structures after surface cleaning and: without surface oxidation (curve 1), with the surface oxide thickness of 5 nm (curve 2), 10 nm (curve 3), 20 nm (curve 4), 50 nm (curve 5), 100 nm (curve 6) and 200 nm (curve 7).

The frequencies of TO and LO phonons decrease as the oxide thickness increases (Fig. 4, curves 1,2). The TO-LO phonon splitting decreases for oxide thickness of 5–50 nm and increases for oxide thickness over 50 nm (Fig. 4, curve 3). Reduction of the TO-LO phonon energy splitting corresponds to the stress relaxation in a silicon oxide layer [11]. The increase in the splitting of TO-LO phonons is associated with stoichiometry growth at the silicon-silicon oxide interface as the SiO₂ content in the SiO/SiO₂ mixture increases [12].

In addition, in spectral regions of TO and LO phonons new absorption peaks are formed at $\omega = 1467 \text{ cm}^{-1} = \omega_{\text{LO}} + (\omega_{\text{LO}} - \omega_{\text{TO}})$, $1646 \text{ cm}^{-1} = \omega_{\text{LO}} + 2(\omega_{\text{LO}} - \omega_{\text{TO}})$ and $1880 \text{ cm}^{-1} = \omega_{\text{LO}} + 3(\omega_{\text{LO}} - \omega_{\text{TO}})$ that are presented separately in Fig. 5. A series of light absorption bands at $\omega \geq \omega_{\text{LO}}$ can be explained by the formation of multi-phonon states as a result of the interaction of phonons of the SiO₂ film with waveguide modes in the silicon matrix [13]. It is known that the surface LO phonons are phonon polaritons [14], thus the waveguide modes increase the density of the polariton multi-phonon states [13]. As a result, absorption

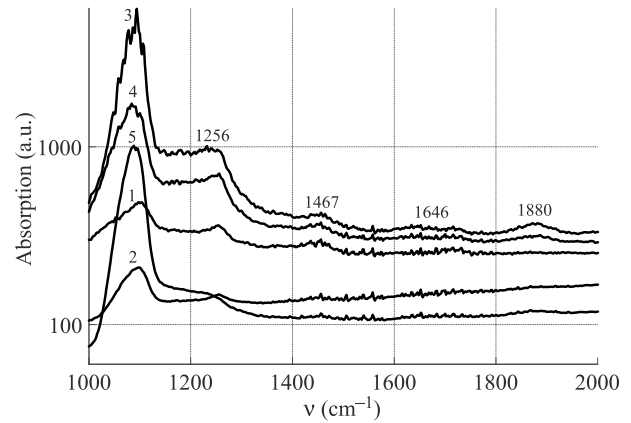


Fig. 5. IR absorption spectra of macroporous silicon with surface oxide thickness of 10 nm (curve 1), 20 nm (curve 2), 50 nm (curve 3), 100 nm (curve 4) and 200 nm (curve 5) in spectral region of TO and LO phonons.

increases as the frequency $(\omega_s^+)_N$ of the N -th mode of surface phonon-polariton coincides with the frequencies of the waveguide modes. In our case, guided and quasi-guided modes are formed on a silicon matrix with the parameters of modes equal to the distance between the macropores [5,7]. According to Fig. 5, the resonance frequency N -th mode of surface phonon polaritons is

$$(\omega_s^+)_N = \omega_{\text{TO}}[N(\epsilon_0/\epsilon_\infty)^{1/2} - (N-1)], \quad (1)$$

taking into account that the frequency of the longitudinal optical phonon is $\omega_{\text{LO}} = \omega_{\text{TO}}(\epsilon_0/\epsilon_\infty)^{1/2}$ for p-polarized surface mode [15]. It should be noted that impurities increase the density of the polariton states too [13].

3.3. Comparison of the IR spectra of macroporous silicon samples with SiO₂ nanocoatings

Figure 6 shows the IR spectra of macroporous silicon samples having surface oxide 50 and 200 nm thick, with (curves 1, 2) and without (curves 3, 4) surface cleaning.

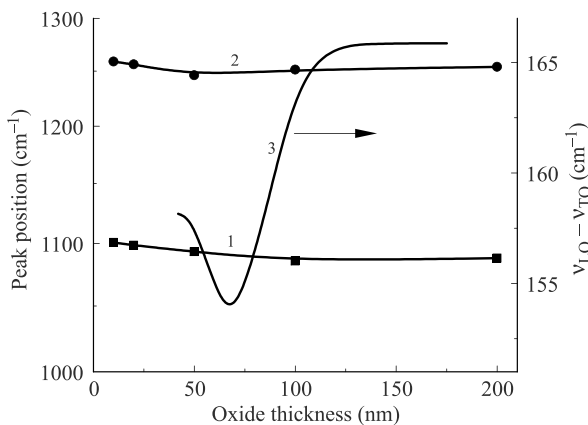


Fig. 4. Dependencies of the TO (1) and LO (2) phonons frequencies (left axis) and TO-LO phonon splitting (3, right axis) on the oxide thickness.

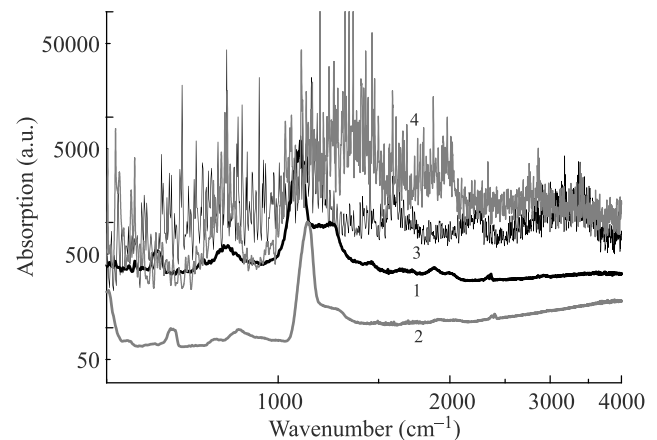


Fig. 6. IR absorption spectra of macroporous silicon having surface oxide 50 and 200 nm thick, with (curves 1, 2) and without (curves 3, 4) surface cleaning.

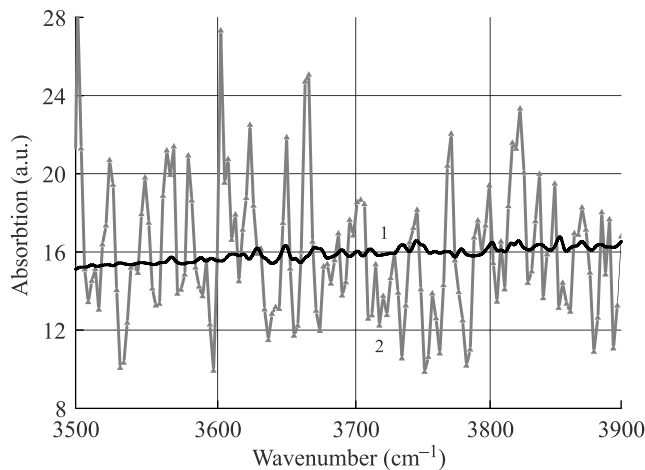


Fig. 7. Fragment of IR absorption spectra of macroporous silicon having surface oxide 200 nm thick, with (curve 1) and without (curve 2) surface cleaning.

Absorption of macroporous silicon samples without oxidation and oxide removal exceeds 4–20 times that of macroporous silicon samples with previous cleaning. The oscillations of IR absorption (Figs. 6 and 7) result from the electron resonance scattering in a strong electric field by impurity states on the surface of macropores, with the difference between two resonance energies $\Delta E = Fa = 8 \div 20 \text{ cm}^{-1}$ equal to the Wannier-Stark step [6]. The oscillations (Fig. 6) have small amplitudes of IR absorption and nearly the same period for samples with surface cleaning as compared with samples of macroporous silicon without previous surface cleaning (Fig. 7).

4. Discussion

The sharp decrease in the amplitude of oscillations in the electro-optical effects is determined by an increase of the broadening parameter Γ [16]. Calculations of the broadened electro-optical function for the Franz-Keldysh effect were performed in Refs. 16 and 17. It was found that influence of the broadening parameter Γ is evident not only in the oscillations' increase but in the growth of the oscillation width at $\Gamma/\hbar\Omega \geq 1$, as well ($\hbar\Omega$ is the electro-optical energy). The oscillation amplitude ΔA changes sharply at $1 \geq \Gamma/\hbar\Omega \geq 0.1$, with linear dependence $\Gamma(\Delta A)$. By analogy to this approach, we determined the effect of broadening on the amplitude of the oscillations in IR absorption spectra (ΔA) in the form of convolution of the “nonbroadened” oscillation amplitude (ΔA_0) with Lorentz distribution

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

where we used $\Delta\omega = \omega' - \omega$ as the energy of the Wannier-Stark step Fa . The results of calculation with Eq. (2) are shown in Fig. 8 from which it follows that the oscillation amplitude decreases linearly with Γ/Fa up to $\Gamma/Fa \approx 0.4$. The Γ/Fa values lie within $0.015 < \Gamma/Fa < 0.1$ for experi-

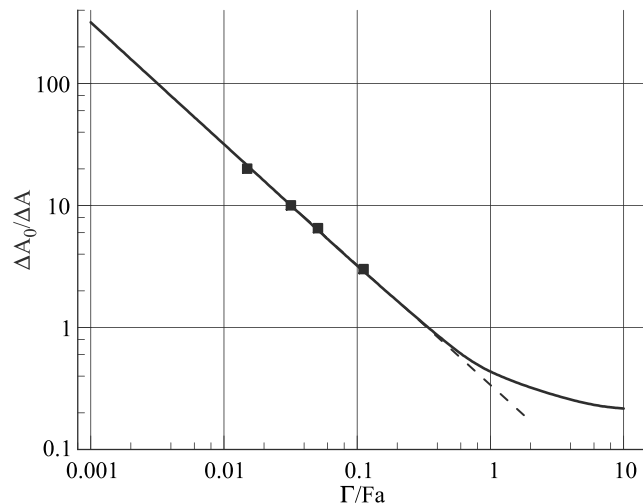


Fig. 8. Results of calculation (curve) of the $\Delta A_0/\Delta A$ dependence on Γ/Fa by Eq. (2). The symbols are experimental data on IR absorption by macroporous silicon structures with oxide thicknesses of $10 \div 200 \text{ nm}$ in the spectral region of Si-O-Si surface states.

mental data on IR absorption by macroporous silicon structures with oxide thicknesses $10 \div 200 \text{ nm}$ in the spectral region of surface states Si-O (Fig. 6) and $\Delta A_0/\Delta A = 3 \div 20$ (Fig. 8). The same period of oscillations (Fig. 7) confirmed low values $\Gamma/Fa \ll 1$, where $\Gamma = 0.3 \div 0.8 \text{ cm}^{-1}$. The obtained Γ values correspond to this parameter for surface phonon polaritons measured in thin films of II–VI semiconductors [15,18].

Let us analyse the dependencies of oscillation amplitudes ΔA on absorption A for local surface states of macroporous silicon structures (Fig. 9). The dependencies $\Delta A(A)$ for local surface states of macroporous silicon samples without surface cleaning and with surface oxide 7–200 nm thick (full symbols) which are linear. And the dependencies $\Delta A(A)$ obey the “3/2 law” for the samples after surface

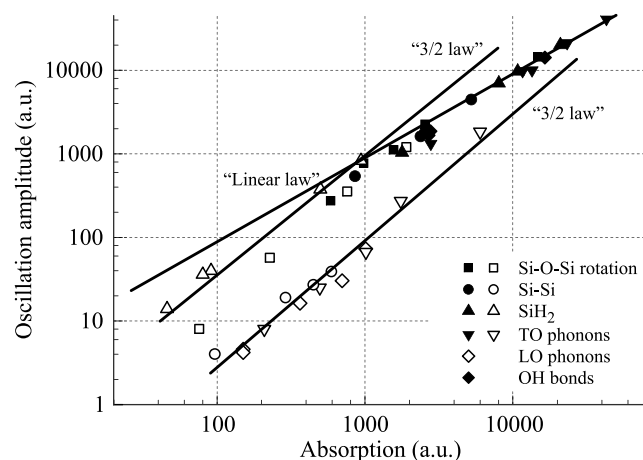


Fig. 9. Dependencies of oscillation amplitudes on absorption for local surface states of macroporous silicon samples with SiO₂ nanocoatings after preliminary surface cleaning (empty symbols) and without surface cleaning (full symbols).

cleaning and with surface oxide thicknesses of 10–200 nm (empty symbols).

The obtained dependencies of oscillation amplitudes ΔA on absorption A correspond to $\Gamma^{-1} \sim \tau \sim E$ or $E^{3/2}$ (where $\tau = \hbar/\Gamma$ is the electron scattering lifetime and E is the electron energy). Thus, the resonance scattering of oxidized macroporous silicon samples without preliminary surface cleaning with $\tau_r \sim E$ transforms into an ordinary electron scattering by ionized impurities with lifetime $\tau_l \sim E^{3/2}$ for the samples with surface cleaning. This transformation takes place at the commensurable values of τ_r and τ_l for scattering lifetime $\tau = \tau_r \tau_l / (\tau_r + \tau_l) \approx 3 \times 10^{-12}$ s (for minimal $\Gamma = 0.3$ and $A_0/A = 10$ from Fig. 6). The obtained scattering lifetime τ is practically equal to the period of electron oscillations in an external (surface) electric field $T_B = 2\pi\hbar/Fa \approx 3.3 \times 10^{-12}$ s [6].

Thus, the effect of broadening on the amplitude of oscillations in the IR absorption spectra is due to interaction of the surface multi-phonon polaritons with scattered electrons. This interaction transforms the resonance electron scattering (τ_r) in samples without preliminary surface cleaning into ordinary scattering on ionized impurities (τ_l) for the samples with preliminary surface cleaning. The transformation takes place at scattering lifetime τ equal to the period T_B of electron oscillations in a surface electric field.

5. Conclusions

We investigated the contribution of the electron-phonon interaction to the broadening parameter Γ of the Wannier-Stark ladder levels in oxidized macroporous silicon structures. The growth of the concentration of bridge-like oxygen atoms in Si-O-Si (TO phonons) after oxidation of macroporous silicon is due to reduction of the dangling bond passivation in the absence of hydrogen. In addition, the LO phonon absorption peaks are formed due to the incident radiation along the surface of cylindrical macropores (geometry of the frustrated total internal reflection).

The TO-LO phonon splitting decreases for oxide thickness of 5–50 nm and increases for oxide thickness over 50 nm. The reduction of the TO-LO phonon energy splitting corresponds to the stress relaxation in silicon oxide layer. The increase in the splitting of TO-LO phonons is associated with higher stoichiometry at the silicon-silicon oxide interface as the SiO₂ content in the SiO/SiO₂ mixture increases. A series of light absorption bands at frequencies $\omega \geq \omega_{LO}$ were explained by formation of multi-phonon polariton states as a result of the interaction of phonon polaritons of the SiO₂ film with waveguide modes in the silicon matrix.

The obtained parameter Γ of the Wannier-Stark ladder is much less than the adjacent level energy evaluated from the giant oscillations of resonance electron scattering on the surface states. We determined the effect of broadening on the oscillation amplitude in IR absorption spectra as convolution of the “nonbroadened” oscillation amplitude with Lorentz distribution. The obtained value of broaden-

ing parameter $\Gamma = 0.3 \div 0.8$ cm⁻¹ equals to that for surface phonon polaritons measured in thin films of II–VI semiconductors. Thus, the effect of broadening on the oscillation amplitude in IR absorption spectra is due to interaction of the surface multi-phonon polaritons with scattered electrons. This interaction transforms the resonance electron scattering in the samples without preliminary surface cleaning into an ordinary electron scattering on ionized impurities for the samples with preliminary surface cleaning. The transformation takes place at the scattering lifetime commensurate with the period of electron oscillations in a surface electric field.

References

1. A. Birner, R.B. Wehrspohn, U.M. Gösele, and K. Busch, “Silicon-Based photonic crystals”, *Adv. Mater.* **13**, 377–388 (2001).
2. L.A. Karachevtseva, “Two-dimensional photonic crystals as perspective materials of modern nanoelectronics”, *SPQEO* **7**, 430–435 (2004).
3. A. Glushko and L. Karachevtseva, “Photonic band structure of oxidized macroporous silicon”, *Opto-Electron. Rev.* **14**, 201–203 (2006).
4. L. Karachevtseva, V. Onyshchenko, and A. Sachenko, “Photocarrier transport in 2D macroporous silicon structures”, *Opto-Electron. Rev.* **18**, 394–399 (2010).
5. L.A. Karachevtseva, V.I. Ivanov, O.O. Lytvynenko, K.A. Parshin, and O.J. Stronska, “The impurity Franz-Keldysh effect in 2D photonic macroporous silicon structures”, *Appl. Surf. Sci.* **255**, 3328–3331 (2008).
6. L. Karachevtseva, S. Kuchmii, O. Lytvynenko, F. Sizov, O. Stronska, and A. Stroyuk, “Oscillations of light absorption in 2D macroporous silicon structures with surface nanocoatings”, *Appl. Surf. Sci.* **257**, 3331–3335 (2011).
7. L.A. Karachevtseva, S.Ya. Kuchmii, K.P. Konin, O.O. Lytvynenko, and A.L. Stroyuk, “Room temperature Wannier-Stark effect in 2D macroporous silicon structures with nanocoatings”, *Chemistry, Physics and Technology of Surface* **2**, 105–113 (2011).
8. A.G. Cullis, L.T. Canham, and P.D.J. Calcott, “The structural and luminescence properties of porous silicon”, *J. Appl. Phys.* **82**, 909–965 (1997).
9. N.H. Nickel, P. Mei, and J.B. Boyce, “On the nature of the defect passivation in polycrystalline silicon by hydrogen and oxygen plasma treatments”, *IEEE T. Electron Devices* **42**, 1559–1560 (1995).
10. N.J. Harrick, *Internal Reflection Spectroscopy*, Interscience Publishers, New York/London/Sydney, 1967.
11. A.G. Milekhin, C. Himcinschi, M. Friedrich, K. Hiller, M. Wiemer, T. Gessner, S. Schulze, and D.R.T. Zahn, “Infrared spectroscopy of bonded silicon wafers”, *Semiconductors* **40**, 1304–1313 (2006) doi:10.1134/S1063782606110108.
12. K.T. Queeney, M.K. Weldon, J.P. Chang, Y.J. Chabal, A.B. Gurevich, J. Sapjeta, and R.L. Opila, “Infrared spectroscopic analysis of the Si/SiO₂ interface structure of thermally oxidized silicon”, *J. Appl. Phys.* **87**, 1322–1330 (2000).
13. E.A. Vinogradov, “Semiconductor microcavity polaritons”, *Phys.-Usp.* **45**, 1213–1250 (2002) doi:10.1070/PU2002v045n12ABEH001189.

14. F. Priox and M. Balkanski, "Infrared measurements on CDS thin films deposited on aluminium", *Phys. Stat. Sol.* **32**, 119–126 (1969).
15. E.A. Vinogradov, G.N. Zhizhin, and V.A. Yakovlev, "Resonance between dipole oscillations of atoms and interference modes in crystalline films", *Sov. Phys. JETP* **50**, 486–490 (1979).
16. B.O. Seraphin and N. Bottka, "Band-structure analysis from electro-reflectance studies", *Phys. Rev.* **145**, 628–636 (1966).
17. R. Enderlein, "The Influence of Collisions on Franz-Keldysh Effect", *Phys. Stat. Sol.* **20**, 295–299 (1967).
18. L.K. Vodopyanov, E.A. Vinogradov, V.V. Kolotkov, and Yu.A. Mityagin, "Optical properties of cadmium telluride in the far-IR", *Sov. Phys. Solid State* **16**, 1419–1425 (1974).