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Polar optical phonons in superlattices Si/SiO$_2$

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A study was carried out of the dielectric properties of planar Si/SiO$_2$ heterostructures, which play an important role in modern electronics. Using the model of dielectric continuum, the spectra of polar phonons in Si/SiO$_2$ binary superlattices have been studied. Quartz and cristobalite lattices are considered as a structural model of the oxide layer. The dependences of polar optical phonons frequencies and the high-frequency dielectric constant tensor elements on the ratio of layer thicknesses were obtained. The results obtained open up the possibility of using spectroscopic data to characterize the structure of superlattices.

Keywords: oxide-semiconductor heterostructures, superlattices, computer modelling, dielectric continuum model, vibrational spectra.

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1. Introduction

Knowledge of the microscopic structure of a Si/SiO$_2$ interface may facilitate an improvement of quality of various devices utilizing a sequence of metal–oxide–semiconductor heterojunctions. However, many years of research involving a variety of experimental techniques [1] have not yet provided sufficiently detailed data on the atomic structure of this interface. The complication lies in the fact that an ideally ordered silicon crystal is bonded at this interface to a completely disordered amorphous oxide phase. Theoretical methods based on quantum-mechanical calculations are needed to gain an insight into the relation between the structure and properties of such objects. In most studies of this kind, superlattices (periodic layered heterostructures [2]) served as a model of a planar Si/SiO$_2$ interface. This provided an opportunity to use calculation software developed for the study of three-dimensional crystalline structures. Various methods for growth of binary superlattices (SLs) [3] have been developed in more recent times, and they were subjected to extensive experimental examination [4,5].

Considerable efforts were spent on finding a method for monitoring the quality of an interface in grown samples. Vibrational spectroscopy, which was proven to be an efficient and informative technique for the examination of semiconductor SLs [6], may serve as such a method. However, vibrational spectroscopy is efficient only if a reliable diagram for assignment of observed spectral lines to characteristic vibrational modes of typical structural fragments is available. A diagram of this kind cannot be prepared without theoretical calculations of the phonon spectrum. Prior theoretical studies have been focused mostly on the spatial and electron structure of Si/SiO$_2$ SLs and have not covered the vibrational states of these systems. The first studies into such vibrational states relied on the density functional method and have been published fairly recently [7,8].

However, the use of highly accurate quantum-mechanical calculations in modeling of the structure and vibrational spectra of heterostructures is limited by the time-consuming nature of these calculations. Novel approaches (less accurate, but physically informative and applicable to large systems) have been researched. One such approach is associated with the dielectric continuum model (DCM). which has been first proposed by S.M. Rytov in [9] for characterization of radio wave propagation in a finely layered medium. The idea to apply this model to phonons in SLs has been suggested in the early 1980s [10]. The first studies were limited to isotropic media (the case of cubic arsenide crystals) [11]. Shortly after the development of a technique for growth of nitride SLs (late 1990s), a series of studies generalizing DCM to the case of SLs of anisotropic media have been published [12].

The dielectric continuum model is a quasi-classical continuum model designed to characterize the behavior of polar optical phonons in spatially inhomogeneous systems. Within DCM, polar phonons are treated as a polarization wave accompanied by an electrical field:

$$\mathbf{E} \sim \exp(i\,\mathbf{q}\cdot\mathbf{r} + i\omega t). \qquad (1)$$

Retardation effects are neglected in this model; i.e., electrostatic fields oscillating harmonically in time, which are consistent with the classical description based on Maxwell equations for a system without free charges, are considered:

$$\operatorname{rot}\mathbf{E} = 0,\ \operatorname{div}\mathbf{D} = 0,\ \mathbf{D} = \varepsilon\,\mathbf{E}. \qquad (2)$$

A heterostructure consisting of several regions occupied by different crystalline compounds is regarded as a continuous medium with its permittivity at a given spatial point defined by the dielectric function of the corresponding crystal:

$$\varepsilon(\omega, \mathbf{q}) = \varepsilon^{\infty} \prod_{k} \frac{\omega^2_{\mathrm{LO},k}(\mathbf{q}) - \omega^2}{\omega^2_{\mathrm{TO},k}(\mathbf{q}) - \omega^2}. \tag{3}$$

Expression (3) holds true in the $\mathbf{q} \to 0$ limit. Index k in it denotes the number of a polar phonon mode, and symbols $\omega_{\mathrm{LO},k}$ and $\omega_{\mathrm{TO},k}$ represent the frequencies of longitudinal and transverse modes in the direction set by vector $\mathbf{q}$. Since oxide crystals examined here are anisotropic, the frequencies of polar phonons corresponding to different $\mathbf{q}$ directions differ, varying within the limits of TO and LO values (see Tables 1 and 2).

Let us consider a binary SL consisting of alternating layers with thicknesses d_1 and d_2 and dielectric functions ε_1 and ε_2. If we assume that the direction of alternation of heterostructure layers is aligned with axis z, the components of the dielectric constant averaged over the SL are written in the following way in the long-wavelength limit (when $1/q \gg d_1, d_2$) [11]:

$$\langle \varepsilon_{xx} \rangle = \frac{1}{d}\,(d_1\varepsilon_{xx,1} + d_2\varepsilon_{xx,2}), \tag{4}$$

$$\left\langle \frac{1}{\varepsilon_{zz}} \right\rangle = \frac{1}{d}\left(\frac{d_1}{\varepsilon_{zz,1}} + \frac{d_2}{\varepsilon_{zz,2}}\right), \tag{5}$$

where $d = d_1 + d_2$ is the SL period. It bears reminding that a frequency-dependent dielectric function is considered in DCM. Relation (4) is satisfied in the region of frequencies corresponding to phonons polarized perpendicularly to the SL axis. It follows from (4) that condition $\langle \varepsilon_{xx} \rangle = \infty$ may be fulfilled either when $\varepsilon_{xx,1} = \infty$ or when $\varepsilon_{xx,2} = \infty$. This implies that TO phonons polarized perpendicularly to the SL axis are localized in separate layers of a layered heterostructure. Relation (5) is satisfied in the region of frequencies corresponding to phonons polarized along the SL axis. It follows from (5) that condition $\langle \varepsilon_{zz} \rangle = 0$ may be fulfilled either when $\varepsilon_{zz,1} = 0$ or when $\varepsilon_{zz,2} = 0$. This implies that LO phonons polarized along the SL axis are localized in separate layers of a layered heterostructure. These conclusions were verified by experimental spectra of nitride SLs. Note that the wave vector of TO phonons polarized perpendicularly to the SL axis and LO phonons polarized parallel to it is directed along z; i.e., phonons propagating along the SL axis are considered in both cases. Such phonons are always localized in layers of a specific type. The frequencies of these phonons provide information regarding the state of materials in different layers (specifically, on elastic strain in them). However, they are less useful if one needs to analyze the SL structure (the ratio of layers thicknesses and the interface state).

In this context, phonons propagating perpendicularly to the SL axis (i.e., in the interface plane) are of a much greater interest. Among these phonons are TO ones polarized along the SL axis with their frequencies satisfying, according to (5), the condition

$$d_2\varepsilon_{zz,1} = -d_1\varepsilon_{zz,2}, \tag{6}$$

and LO phonons polarized perpendicularly to the SL axis with their frequencies satisfying, according to (4), the condition

$$d_1\varepsilon_{xx,1} = -d_2\varepsilon_{xx,2}. \tag{7}$$

Having inserted functions (3) with parameters determined from spectra of individual bulk crystals into Eqs. (6)−(7) and set ratio d_1/d_2, one may determine the frequencies of phonons propagating in the interface plane. These frequencies depend strongly on the thickness ratio of layers, which verifies their delocalized nature.

2. Results

We applied the dielectric continuum model, which was used widely in the studies of vibrational spectra of arsenide and nitride SLs, to a Si/SiO$_2$ SL. These structures are specific in that polar phonon modes are lacking in one of the materials (crystalline silicon). Therefore, the dielectric function is frequency-independent in the region of phonon frequencies and is equal to ε^{∞}. When DCM is applied to such SLs, it is assumed that ion polarization associated with atomic displacements is always localized in SiO$_2$ layers and only electron polarization is present in silicon layers. However, dielectric (silicon) layers affect polar vibrations in oxide layers. The frequencies of these bound phonon-photon states (polaritons) are specified by Eqs. (6)−(7).

2.1. Models of Si/SiO$_2$ interfaces

An important factor in the construction of a model of an interface in a planar heterostructure is the compatibility of lattice dimensions on joined surfaces of two crystals. In ideally matched materials, the positions of Si atoms in adhering planes should overlap. If they do not match but the surface densities of such sites are close, materials may adhere with insignificant elastic strain. If the surface densities are widely different, surfaces cannot be splicing.

We relied on the experimentally established fact that silicon is always structured in a cubic diamond-like lattice. Having searched through various surface options in major modifications of silica (quartz, cristobalite, and tridymite), we found four variants that may produce a stable interface. With the relaxed structure of each of these four interfaces examined and the corresponding formation energies estimated, we chose three models: one with quartz (Q) and two with cristobalite (C1 and C2). Fragments of SLs with such interfaces are shown in Figure 1.

Interface C1 is obtained by joining surfaces (001) of Si and cristobalite crystals directly. We have demonstrated [7] that, although the difference in Si−Si distances on these surfaces is significant, their direct joining is perfectly realistic, since the cristobalite lattice yields readily to compression in plane (001). Interface C1 is extremely thin and consists of a single layer of Si^{2+} atoms. Interface C2 is obtained by joining the same surfaces with one of the crystals rotated by 45°. Owing to this rotation, Si sites on joined surfaces

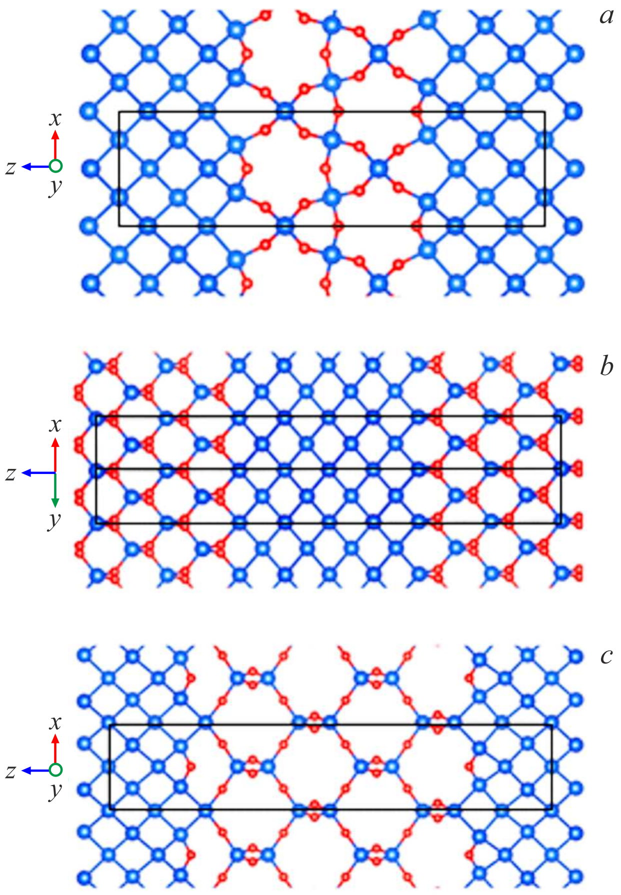

Figure 1. Positioning of silicon atoms (large circles) and oxygen atoms (small circles) in SLs with interfaces of the following types: *a* — Q, *b* — C1, and *c* — C2. The boundary of an SL supercell is indicated in black; the directions of its translation vectors are shown on the left.

become closely positioned, but Si sties on the oxide surface are matched with only one half of Si sites on the silicon surface. One half of interfacial Si atoms are left with two dangling bonds in this connection geometry. This is a strong defect that makes the structure unstable. These Si atoms may be replaced by O atoms, which leads to the formation of additional Si-O-Si bridges in the interface layer [8]. Interface C2 consists of two monolayers of Si^{2+} and Si^{1+} atoms. These Si-O-Si bridges are also present in the region of interface Q that, just as C1, consists of only a single layer of Si^{2+}.

2.2. Polar phonons in Si/SiO_2 SLs

In order to apply DCM to the SLs under study, one needs to characterize the spectrum of polar phonons polarized along the interface and perpendicularly to it. It is assumed that the oxide material in heterostructures with interfaces C1 and C2 (see Figures 1, *b* and *c*) has a structure close to that of the tetragonal cristobalite modification, so-called $\tilde{\beta}$-cristobalite with space group $I\bar{4}2d$ [13]. The principal crystallographic axis of tetragonal cristobalite is aligned with the direction of heterostructure growth. It is worth reminding that the lattice of $\tilde{\beta}$-cristobalite belongs to crystalline class D_{2d}. Therefore, modes B_2(TO) and E(LO) correspond in these structures to polar phonons propagating in the interface plane. The frequencies of polar phonons in $\tilde{\beta}$-cristobalite are listed in Table 1.

Table 1. Parameters of polar phonons in $\tilde{\beta}$-cristobalite taken from [14]

	TO, cm^{-1}	LO, cm^{-1}
B_2-mode $E \parallel z$	422 1063	497 1216
E-mode $E \perp z$	130 443 765 1073	134 482 796 1212
ε^∞	2.205	

Table 2. Parameters of polar phonons in α-quartz taken from [15]

	TO, cm^{-1}	LO, cm^{-1}
A_2-mode $E \perp z$	364 495 778 1080	388 547 790 1240
E-mode $E \parallel z$	128 265 394 450 697 795 1072 1162	128 265 401 509 697 807 1162 1235
ε^∞	2.172	

The oxide material in the model of a heterojunction with interface Q (see Figure 1, *a*) is crystallized in the structure of α-quartz with the principal axis directed along the interface. It is worth reminding that the lattice of quartz belongs to crystalline class D_3. Therefore, modes A_2(LO) and E(TO) correspond in Q-type structures to polar phonons propagating in the interface plane. The frequencies of polar phonons in quartz are listed in Table 2.

No experimental estimates of ε^∞ are available for $\tilde{\beta}$-cristobalite. This is the reason why we used the theoretically calculated value (see Table 1). To obtain a more accurate prediction, the ε^∞ value for quartz presented in Table 2 was taken from the experimental data from [16]. The ε^∞ value in a cubic silicon crystal was set equal to the experimental one (11.7 [17]).

As was already noted, the frequencies of phonons propagating in the interface plane and polarized along the

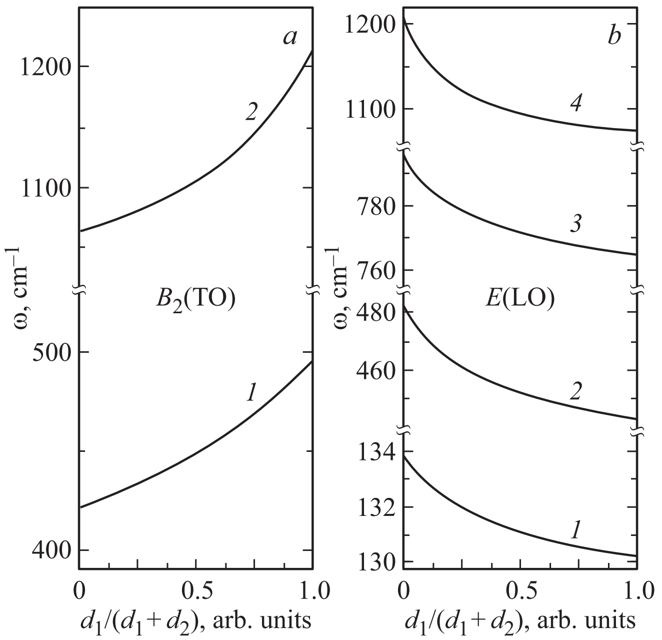

Figure 2. Frequencies of polar phonons in SLs with C1 and C2 interfaces as functions of the layer thickness ratio: d_1 is the Si layer thickness and d_2 is the SiO$_2$ layer thickness. Cases *a* and *b* correspond to polar phonons B_2(TO) and E(LO).

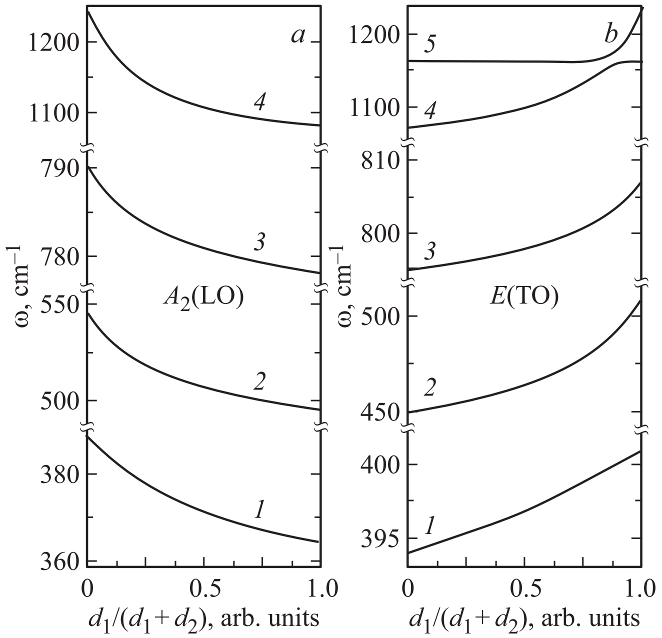

Figure 3. Frequencies of high-frequency polar phonons in SLs with Q interfaces as functions of the layer thickness ratio. Cases *a* and *b* correspond to polar phonons A_2(LO) and E(TO).

SL axis satisfy Eq. (6). These are B_2(TO) modes in the silicon/cristobalite SL and E(TO) modes in the silicon/quartz SL. At the same time, the frequencies of phonons propagating and polarized in the interface plane satisfy Eq. (7). These are E(LO) modes in the silicon/cristobalite

Table 3. Diagonal components of the dielectric tensor of a series of Si/Q SLs with different d_1 (Si) and d_2 (SiO$_2$) values

SL	ε(calc)			d_1, Å	d_2, Å	ε(DCM)	
	ε_x	ε_y	ε_x			ε_x	ε_y
2×1	8.344	8.108	4.382	10.834	8.872	8.470	4.463
1×1	6.323	6.082	3.487	5.380	8.888	6.582	3.554
1×2	4.897	4.634	2.955	5.401	17.666	5.019	3.041

SL and A_2(LO) modes in the silicon/quartz SL. Note that polar phonons with a wave vector directed along the SL axis (B_2(LO) and E(TO) modes of cristobalite and A_2(TO) and E(LO) modes in quartz) are not considered in the present study.

Having solved Eqs. (6) and (7) at various ratios of d_1 and d_2, we determined the frequencies of phonons listed above as functions of the layer thickness ratio. Dimensionless quantity $p = d_1/(d_1 + d_2)$ was chosen as a parameter characterizing the SL structure. Since index *1* corresponds to Si, it is evident that limits $p = 0$ and $p = 1$ correspond to the cases of pure SiO$_2$ and pure Si, respectively. The results are presented in Figures 2 and 3.

2.3. Refraction index anisotropy in SLs

The ideas of DCM were applied above to polar phonons. However, the key equations of this model (Eqs. (4)−(5)) are equally applicable to other excitation types. Specifically, they may be used to characterize the propagation of light waves in an off-resonance frequency interval. Within this approach, Eqs. (4)−(5) may be regarded as relations providing an opportunity to estimate elements of the SL dielectric tensor in terms of the permittivity of component materials and structural parameters d_1 and d_2.

With experimental data on dielectric constants lacking, the idea behind this approach may be verified via ab initio quantum-mechanical calculations. All the SLs considered above have been studied theoretically (see [7,8,14] for details). Let us examine the results of such calculations using the silicon/quartz (Si/Q) SL as an example. The structure, vibrational spectra, and dielectric susceptibilities of a series of Si/Q SLs with different layer thicknesses were investigated theoretically through computer modeling. The calculated values of diagonal components of the dielectric tensor of these SLs determined within the quantum-mechanical approach are denoted in Table 3 as ε(calc).

It is evident that transverse polarizabilities (ε_x, ε_y) are close for all SLs and are significantly higher than the longitudinal polarizability (ε_z). All tensor components decrease appreciably with increasing oxide layer thickness. We turned to DCM to find an explanation for these trends.

The same quantities were evaluated using formulae (4)−(5). Theoretical estimates of dielectric constants of bulk crystals ($\varepsilon_x = \varepsilon_y = \varepsilon_z = 13.391$ for silicon and $\varepsilon_x = \varepsilon_y = 2.489$, $\varepsilon_z = 2.458$ for quartz) were used to apply these relations. The values of diagonal components of the dielectric tensor of these SLs calculated by formulae (4)−(5) are denoted in Table 3 as ε(DCM). It can be seen that they agree quite closely with calculated data. Thus, it is fair to say that the dielectric continuum model provides an opportunity to reproduce both the anisotropy of the SL permittivity tensor and its changes upon variation of the layer thickness ratio. As far as we know, this results is the first example of application of DCM to characterization of the high-frequency component of the dielectric function of binary SLs.

3. Discussion

Let us first point out a general trend in the obtained results: as p increases, the frequencies of TO modes rise, while the frequencies of LO modes decrease. In the $p = 0$ limit (i. e., in the case of infinitely thin silicon layers or, alternatively, when these layers are lacking), the frequencies of SL polar modes assume the values of the corresponding modes in bulk oxide crystals. This appears to be logical and physically meaningful. In the contrary limit case of $p = 1$ (i. e., when oxide layers are infinitely thin or, alternatively, thick silicon layers are interleaved with thin oxide films), the frequencies of SL polar modes tend to the values of alternative modes in bulk oxide crystals: the frequencies of TO modes tend to the frequencies of LO modes, and vice versa. At first glance, this seems strange. However, it is worth reminding that a similar effect was observed in the spectra of AlAs/GaAs SLs [18]. In contrast to the SLs studied here, arsenide SLs feature polar phonons in both materials, but their corresponding frequency intervals are widely spaced. In view of this, optical vibrations of atoms in neighboring layers mix only weakly, and all modes are divided into AlAs-like and GaAs-like. These are the TO- and LO-like modes that depend on the layer thickness ratio in the same way as phonons in Si/SiO_2 SLs do.

An explanation for the observed mutual transformation of TO and LO modes may be provided if one takes into account the facts that each of these modes is localized in a single layer (in the present case, SiO_2 at all times) and that the problem becomes equivalent to the problem of polar vibrational states of atoms in a sample having a shape of a plane-parallel plate (slab). This problem has been examined in detail both theoretically [19] and experimentally. One of the findings made in these studies was that TO vibrations polarized perpendicularly to the slab plane transform into LO vibrations in the limit of an infinitely thin plate, while LO vibrations polarized parallel to the slab plane transform into TO vibrations. This is exactly the case in Si/SiO_2 SLs.

It should be stressed once more that heterostructures considered here differ from binary semiconductor SLs (such as GaAs/AlAs or GaN/AlN) examined earlier in having zero polar phonons in the material of one of the layers (specifically, silicon). Therefore, in the limit case when the thickness of the other layer (in the present case, the oxide layer) tends to zero, the spectrum of polar phonons in such SLs should transform into the spectrum of silicon. In other words, we need to understand that the spectrum should vanish completely in practice, and this implies that the intensities of all modes should turn to zero. What is the physical meaning of modes the frequencies of which are indicated in Figures 2 and 3 in the $p \to 1$ limit? Case $p \to 1$ corresponds to a heterosystem with bulk silicon layers separated by very thin oxide films. Polar vibrations are present in the film material, and their spectrum is fairly anisotropic. The curve values in Figures 2 and 3 at $p \to 1$ are exactly the frequencies of polar vibrations in thin oxide films separating thick silicon layers. The intensities of such modes is proportional to the film thickness and decreases in the $p \to 1$ limit.

4. Conclusion

The interface structure in Si/SiO_2 heterostructures has a strong influence on the electrooptical characteristics of functional components of silicon electronics. The issue of express nondestructive quality testing of such interfaces is crucial. Vibrational spectroscopy may be one of the methods for this. In the present study, the applicability of the dielectric continuum method to spectra of polar optical phonons in Si/SiO_2 superlattices with several types of interfaces was investigated.

Since polar phonons are lacking in a Si crystal, we proposed a modification of the mathematical framework of the dielectric continuum method for systems wherein the dielectric properties of one of the materials are characterized by a function with zero dispersion. The solutions of obtained equations for two major structural models of the Si/SiO_2 heterojunction, which present the oxide material in the form of $\tilde{\beta}$-cristobalite and α-quartz, were examined. It was found that Si/SiO_2 superlattices support polar modes localized in the bulk of an oxide layer: polar modes B_2(LO) and E(TO) in Si/cristobalite heterosystems and A_2(TO) and E(LO) polar modes in Si/quartz superlattices. Other polar modes localized at the interface are also present in the same systems: polar modes B_2(TO) and E(LO) in Si/cristobalite superlattices and A_2(LO) and E(TO) polar modes in Si/quartz superlattices. In short-period superlattices, the frequencies of modes of the latter type depend on the layer thickness ratio and may be used to probe spectroscopically the structure of the studied samples. The obtained results revealed physical meaningfulness and predictive validity of the proposed approach.

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Conflict of interest

The authors declare that they have no conflict of interest.

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