

Density-Functional Study of the Si/SiO₂ Interfaces in Short-Period Superlattices: Vibrational States and Raman Spectra

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1. Deformation potential parameters for β -cristobalite

During the epitaxial growth of planar heterostructures, due to the lattice mismatch, elastic strains inevitably arise in the layered materials. The question of the influence of the strains on the optoelectronic properties is of great interest. Estimation of the magnitude of strains and their distribution in the layers is also of decisive importance for the development of technology for the fabrication of low-dimensional structures using special strain-induced growth mechanisms. Raman spectroscopy is a standard non-destructive method for determining strains in bulk and nanostructured materials. The application of this method is based on the exact knowledge of Phonon Deformation Potentials (PDPs), which, in turn, makes it possible to determine the magnitude of deformations from phonon frequencies [S1, S2].

Within the approach based on PDPs, the effects of anisotropic deformations on phonon frequencies are described using empirical relations. In a linear approximation, the relationship between the strains $U_{\mu\nu}$ and the frequency shift $\Delta\omega_n$ of the n -th Raman-active mode caused by it is described by the expression (S1)

$$\Delta\omega_n = \sum_{\mu\nu} C_{n,\mu\nu} U_{\mu\nu} . \quad (S1)$$

The coefficients of such a relation are called PDP or deformation potentials. Estimates of these parameters have been obtained for many monatomic and binary semiconductors, including cubic crystals of Si [S3, S4]. We can use them in studies of Si/SiO₂ superlattice. With regard to the second material—various modifications of silicon oxide, such studies, as far as we know, have not been carried out. This paper aims to fill this gap.

Figure S1 shows the results of calculating the Raman spectrum and the frequency distribution of the center-center phonon modes of β -cristobalite both in the equilibrium configuration ($U_{xx}=U_{yy}=U_{zz}=0$) and for two deformed configurations: stretched by 5% along the tetragonal axis ($U_{zz}=0.05$) and axially stretched by 5% in the plane perpendicular to the tetragonal axis ($U_{xx} = U_{yy} = 0.05$). Using the calculated frequencies one can determine the DP parameters which are presented in Table S1.

Table S1. Calculated frequencies and DP parameters (in cm^{-1}) for the zone-center phonon modes of $\tilde{\beta}$ -cristobalite

Irreducible representation	Phonon frequency (ω), cm^{-1}	C_{zz}	C_{xx}
E	130	-249	-1370
A_1	309	-1139	-3138
A_2	354	390	-282
B_1	408	-670	-796
B_2	422	141	-187
E	443	-272	-404
B_1	752	106	-413
E	765	-551	-437
B_2	1063	231	221
E	1073	-422	254
A_2	1106	131	798

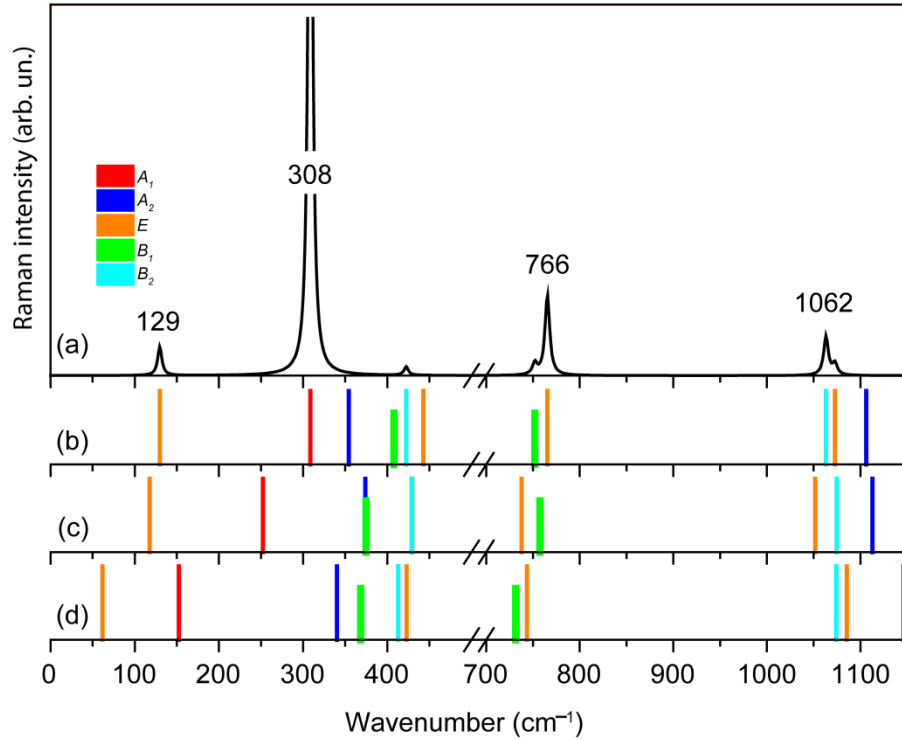


Figure S1. Raman spectrum (a) and frequency distribution of zone-center phonons in $\tilde{\beta}$ -cristobalite: for the zero strain configuration (b), for the lattice stretched by 5% along the tetragonal axis (c), and with a cell stretched by 5% in the perpendicular plane (d). Modes of different symmetry are highlighted in different colors.

It can be seen that the most Raman-intensive mode A_1 -308 is more strain-dependent than all others. The corresponding coefficients have unusually large values: $C_{zz}=-1126 \text{ cm}^{-1}$ (for uniaxial deformation U_{zz}) and $C_{xx}=-3125 \text{ cm}^{-1}$ (for axially symmetric deformation $U_{xx}=U_{yy}$). For comparison, the similar coefficients for the Raman-active mode in the Si crystal are $C_{zz}=-337 \text{ cm}^{-1}$ and $C_{xx}=-733 \text{ cm}^{-1}$, that is, approximately 4 times less [S3].

Also, the E -129 mode, for which $C_{zz}=-239 \text{ cm}^{-1}$ and $C_{xx}=-1360 \text{ cm}^{-1}$, has rather high DP values. Note that both of these modes (A_1 -308 and E -129) originate from the triply degenerate T_{2u} mode of cubic β -cristobalite, which has an imaginary frequency of $i83$ in the equilibrium configuration [S5]. Therefore, a sharp decrease in the frequency of these modes with an increase in the volume of the cell can be explained

by the approximation of the structure of $\tilde{\beta}$ -cristabolite to the structure of β -cristabolite. Other Raman active modes shown in Figure S1 depend on deformations much weaker: the corresponding DPs do not exceed in magnitude 700 cm⁻¹.

A distinctive feature of the considered spectra is the presence of modes with positive DP values. This behavior is an obvious anomaly: as the cell size increases, the phonon frequencies increase! This anomaly manifests itself most clearly in high-frequency modes (>1000 cm⁻¹) associated with the Si-O bond stretching vibrations. As it was shown above, these modes primarily involve oscillations of O atoms along the Si-O-Si bridges. That is a classic case of antisymmetric tension-compression of the bonds that form the Si-O-Si bridges. Such modes are usually referred to as $\nu_{as}(\text{SiOSi})$. There are two structural factors that affect the frequency of such vibrations: the Si-O bond length and the Si-O-Si bond angle. The influence of the first factor is determined by the universal rule—the longer the bond, the lower the force constant, the lower the frequency of the bond stretching vibration [S6]. The influence of the second factor was the subject of special studies, during which a correlation was established: the larger the Si-O-Si bond angle, the higher the frequency $\nu_{as}(\text{SiOSi})$ [S7]. The results of our calculations are shown in the Table S2.

Table S2. Variation of structural parameters of $\tilde{\beta}$ -cristobalite at different elastic strains

	Si-O (Å)	Si-O-Si (°)	$\nu_{as}(\text{SiOSi})$ (cm ⁻¹)	φ (°)
$U_{xx} = U_{yy} = U_{zz} = 0$	1.6170	146.5	1106	20.5
$U_{zz} = 0.05$	1.6205	153.0	1113	16.8
$U_{xx} = U_{yy} = 0.05$	1.6158	163.4	1146	10.1

Based on the data presented, it can be assumed that the main factor affecting the frequencies of the $\nu_{as}(\text{SiOSi})$ mode is the Si-O-Si angle. The length of the Si-O bond under lattice deformations of $\tilde{\beta}$ -cristobalite changes insignificantly and non-monotonically: when stretched along c , it slightly increases, and when stretched in the ab plane, on the contrary, it decreases! Such an anomalous behavior can be explained by the specifics of the structure: the dimensions of the $\tilde{\beta}$ -cristobalite cell in the ab plane are determined not so much by the sizes of the SiO₄ tetrahedra, but by the value of τ —the angle of rotation of the tetrahedra relative to the tetragonal axis. According to Table S2, when changing the lattice dimension in the ab plane, first of all, the angle φ changes, and not the size of the tetrahedra.

An implicit confirmation of the positive values of the DP for the ν_{as} modes in cristobalite can be the results of studying the Raman spectra of related modifications of this structure under pressure [S8]. In which it was found that the frequencies of high-frequency phonon modes under pressure (that is, during compression) decrease.

References for supporting information

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