Electronic structure of stishovite SiO$_2$

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Abstract. Electronic structure calculation of the stishovite as close packing SiO$_2$ modification was performed with the use of the linearized augmented plane wave method in framework of Wien2k code. Band diagram, total and partial density of states were calculated. X-ray emission Si K and Si L$_{2,3}$ spectra characterizing valence band were obtained. By “core hole” approximation XANES Si L$_{2,3}$ was calculated. X-ray stishovite spectra reveals good agreement with the experimental data. The explanations are given for the observed density of states and emission spectra fine structure features.

1. Introduction
Silicon dioxide is a key dielectric in the microelectronic industry [1]. Under the large variety of polymorph types of silicon dioxide (α- or β-quartz, cristobalite, tridymite, coesite etc.) stishovite takes specific place. This tetragonal SiO$_2$ phase with rutile type crystalline space structure is formed under high values of pressure and temperature. If compared with other polymorphs of silicon dioxide having 4:2 atoms coordination the stishovite has 6:3 coordination (six-coordinated silicon and three-coordinated oxygen) indicating the close packing modification of silicon dioxide. Stishovite represents rutile-like materials with such known compound as GeO$_2$, SnO$_2$, TiO$_2$ etc. [2]. Rutile compounds usually has very useful physical characteristics so they are the objects of active scientific research [3] and industrial application [4, 5].

2. Calculation details
Electronic structure calculation of stishovite have been performed using the linearized augmented plane wave method as implemented in the Wien2k code [6]. The Generalized Gradient Approximation (GGA) and modified Becke-Johnson (mBJ) potential [7] were used for the exchange-correlation energy estimation. The crystallographic parameters of stishovite were taken from Database [8] and given in table 1. The unit cell and the first Brillouin zone of stishovite are shown in figure 1.

![Figure 1](image-url)
Table 1. Crystallographic data for the stishovite [8].

| Space group          | P4$_2$/mmn |
|----------------------|------------|
| Unit cell parameters | $a, \text{Å}$ | $b, \text{Å}$ | $c, \text{Å}$ |
|                      | 4.177      | 4.177        | 2.665         |
| Coordinates of atoms | $x$ | $y$ | $z$ |
| Si$_1$               | 0           | 0            | 0             |
| Si$_2$               | 0.5         | 0.5          | 0.5           |
| O$_1$                | 0.3062      | 0.3062       | 0             |
| O$_2$                | 0.6938      | 0.6938       | 0             |
| O$_3$                | 0.1938      | 0.8062       | 0.5           |
| O$_4$                | 0.8062      | 0.1938       | 0.5           |

3. Results and discussion

The calculated in GGA approximation band structure of stishovite is given in figure 2. It can be seen that stishovite is a direct-gap dielectric, with the shortest transition at Γ point. The $E_g$ width is 5.8 eV, which well agree with the results of known 5.3 and 5.5 eV calculations [9]. The ~ 11 eV stishovite valence band contains 12 energy bands. We also performed calculations of the stishovite electronic structure using the mBJ potential [7]. This allowed us to obtain the $E_g$ width ~ 7.8 eV, which is close to the experimental value of 7.6 eV [10]. The rest results obtained by calculations using the mBJ potential are practically the same as ones obtained using the GGA approximation.

![Figure 2. Band structure of stishovite.](image-url)
Figure 3 shows the spectrum of the total electron density of states (DOS) of stishovite and the spectra of partial density silicon and oxygen atoms states (PDOS). The DOS of stishovite contains a number of local maxima, the intensity of which monotonously increases from the bottom to the top of the valence band. This is due to the fact that the dispersion of the energy bands in figure 2 is maximal at the bottom of the valence band and decreases to its top. The p-states of oxygen make the largest contribution to the full spectrum of stishovite valence band DOS. Below the valence band, at an energy of $\sim -20$ eV one can find subvalent states with the origin of oxygen s-states. In the considered range of the conduction band, the intensities of the DOS spectra of silicon and oxygen turn out to be comparable. Chemically, this is due to the substantially higher electronegativity of oxygen atoms compared to silicon atoms. The lower-energy electron states are localized on more electronegative atoms, in this considered case – oxygen. At the same time, the states distributed above should be considered as more bounded to silicon atoms. Since SiO$_2$ is a dielectric, most of the electronic states of oxygen in it are occupied by electrons, since they are located below the Fermi level. On the contrary, most of the silicon states are unoccupied, since these states are located above the Fermi level. The DOS spectrum of silicon in the valence band is clearly divided into 3 areas: s states dominate at the bottom of the valence band, p states dominate in the central part, and d states dominate at the top of the valence band. A similar distribution of the PDOS spectra contributions is related to stishovite with other rutile compounds, in particular with tin dioxide [11].

![Figure 3. Density of states of stishovite.](image-url)
In order to confirm the reliability of our results, we performed a calculation of Si K and Si L\textsubscript{2,3} X-ray emission spectra (XES) and compared them with known experimental data [12]. The results of such a comparison are presented in Fig. 4. There is a good agreement between theoretically and experimentally obtained spectra. This suggests the correctness of the approaches chosen for the modeling and the reliability of the calculations results.

According to the dipole selection rules (Δl = ±1) Si K XES represents the distribution of the silicon p-states in the valence band while at the same time Si L\textsubscript{2,3} represents densities of the s- and d- states. As it follows from the Fig.3 the intensity of Si s-states peak is higher relatively to the Si d-states peak. But according to figure 4, the intensities of the corresponding peaks in the spectrum of Si L\textsubscript{2,3} are redistributed in the reverse order: the peak at 1829.5 eV is associated with s-states and is less pronounced than the peak at 1836 eV that is associated with d-states. It is known that the intensity of the X-ray emission band can be approximated as the probability of an electron transition from the initial valence state to the final core level P(E) multiplied by the partial density of the initial valence states n(E):

\[ I(E) \sim P(E) \cdot n(E) \]

Consequently, the redistribution of intensity between the Si L\textsubscript{2,3} XES spectrum maximum in comparison with the corresponding peaks of the PDOS spectrum is associated with a significantly greater probability of transition from Si 3d to Si 2p states in comparison with the probability of Si 3s \textrightarrow Si 2p transitions.

Figure 4. Comparison of experimental [12] and calculated Si K and Si L\textsubscript{2,3} X-ray emission spectra in stishovite.
We also conducted a calculation of the Si L$_3$ X-ray absorption near edge structure (XANES) spectrum. For this purpose, we used the core hole method [3, 11, 13]. The size of the crystal super cell was chosen to be 3×3×4. The theoretically calculated spectrum was combined in a single scale with the experimental spectrum from [14] by the position of the main maximum at an energy of ~ 106.5 eV (figure 5). The calculation result shows a good agreement with the experiment by the spectra shape, the number of the observed fine structure features and the ratio of intensities between them. At the same time, the result obtained better describes the features of the fine structure of the Si L$_3$ XANES spectrum compared to the similar calculation performed in [9].

![Comparison of calculated and experimental XANES spectra of stishovite.](image)

**Figure 5.** Comparison of calculated and experimental [14] XANES Si L$_{2,3}$ spectra of stishovite.

Thus, analyzing the theoretical results obtained in the work, their internal consistency and good agreement with the experimental data, it can be concluded that the computer simulation of the electronic structure of stishovite is highly reliable.

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