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ELECTRONIC STRUCTURE OF SiO_2(111) THIN FILM*

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The electronic structure of (111) surface of β-crystobalite is investigated using the empirical tight binding method. Our calculations identify surface states in the conduction band, band gap and valence band. The surface state formed from silicon-s and p_z orbitals, which is believed to account for the structure in the O K excitation spectra, lies in the band gap. It is seen that oxygen adsorption on the surface removes surface states and gives rise to a sharp peak at about − 3.8 eV below the valence band edge.

RECENT INTEREST in SiO_2 has mainly focused on (i) interface states localized in the energy gap of Si in Si–SiO_2 junction, (ii) oxygen adsorption and oxidation of Si surfaces, (iii) interpretation of the spectra of SiO_2 itself. For these and other reasons, there has been an increasing attempt to understand the electronic structure of SiO_2. Here, for the first time, we investigate the electronic structure of SiO_2(111) thin film. Further to electronic structure of SiO_2 surface itself, this study is believed to reveal important aspects of the SiO_x metastable phase formed at the interface region. Considering the fact that the fundamental structural unit, the SiO_4 tetrahedron, determines prominent features of the spectra, SiO_2 is represented by β-crystobalite geometry.

In the present study, the empirical tight binding method as formulated by Slater and Koster [1] is used. Recent studies have shown that localized nature of bonds in semiconductors and ionic solids enables us to use this method successfully [2–5]. Here, the Hamiltonian matrix elements of orthonormalized Bloch sums are obtained in terms of energy integrals, h_{ij}, representing the interactions between neighboring atomic-like orbitals

$$H_{ij}(\mathbf{k}) = \sum_n \exp\left[i\mathbf{k}\cdot(\mathbf{R}_n + \boldsymbol{\tau}_j - \boldsymbol{\tau}_i)\right] h_{ij}(\mathbf{R}_n + \boldsymbol{\tau}_j - \boldsymbol{\tau}_i),$$

(R_n: f.c.c. translation vector, τ_i: ith atom position in the unit cell). As to energy integrals, h_{ij}, they are calculated in terms of two-center energy parameters (ss, $sp\sigma$, $pp\sigma$, $pp\pi$) determined from the first principle band structure calculations of β-crystobalite [6].

$$h_{s_1 s_2}(\mathbf{d}) = s_1 s_2(d),$$

$$h_{s_1 p_2}(\mathbf{d}) = s_1 p_2 \sigma(d)\, \mathbf{d}_0 \cdot \mathbf{t}_{p_2},$$

$$h_{p_1 p_2}(\mathbf{d}) = p_1 p_2 \sigma(d)(\mathbf{d}_0 \cdot \mathbf{t}_{p_1})(\mathbf{d}_0 \cdot \mathbf{t}_{p_2}) + p_1 p_2 \pi(d)(\mathbf{d}_0 \times \mathbf{t}_{p_1}) \cdot (\mathbf{d}_0 \times \mathbf{t}_{p_2})$$

where $\mathbf{d} = \mathbf{R}_n + \boldsymbol{\tau}_2 - \boldsymbol{\tau}_1$ represents the vector from orbital (1) to orbital (2), $\mathbf{d}_0 = \mathbf{d}/|\mathbf{d}|$ and $\mathbf{t}$ is the direction vector of the orbital (p). d-type atomic orbitals are not included, because they are known to have negligible influence on the valence band and the lower part of the conduction band of SiO_2. Values of the two-center energy parameters are listed in Table 1. It should be noted that two-center energy parameter [p(silicon) s(oxygen) σ] is taken to be 6.4 eV. In Fig. 1, the band structure and total density of states of β-crystobalite based on 12 two-center energy parameters are illustrated. From our results, which are strikingly similar to the results of first principle calculations, one is able to reveal all the features relevant for the electronic properties of SiO_2. We adjusted self-energies of Si-s and p orbitals to yield energy band gap of 9.4 eV. Previous first-principle calculations [6, 7] also predicted similar gap values.

As to composition and orbital character of the bands, the flat bands (at about − 20 eV) labelled by O_s originate from oxygen-2s orbitals. The bands ~ 6 eV above O_s bands constitute the lower part of the valence band of SiO_2. They are formed from silicon-sp^x and oxygen-p orbitals directed along Si–O–Si bond and denoted here as O_σ bands. O_π bands, at the edge of the valence band, are 2.4 eV wide. Oxygen p_x, p_y, p_z orbitals are combined to give maximum charge perpendicular to Si–O–Si chain. Because of small $pp\pi$ interaction (~ 0.3 eV) they are almost dispersionless and recognized by two overlapping peaks at − 1.3 and − 2.4 eV in the UPS spectrum of amorphous SiO_2 [8]. Lower part of the conduction band is reminiscent of silicon valence band with a smaller width due to reduced Si–Si interaction. For the sake of comparison UPS and

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Table 1. Two-center energy parameters (in eV) used in the calculation of the energy band structure of β-crystobalite

Si–Si	O–O		Si–O
$d = 0$	$d = 0$	$d = 4.78$ a.u.	$d = 2.93$ a.u.
$ss = 6.7$	$ss = -16.0$	$ss = -0.4$	$ss = -3.0$
$pp = 12.2$	$pp = -1.1$	$pp\sigma = 0.3$	$sp\sigma = -4.4$
		$pp\pi = -0.3$	$pp\sigma = 5.8$
			$pp\pi = -1.4$

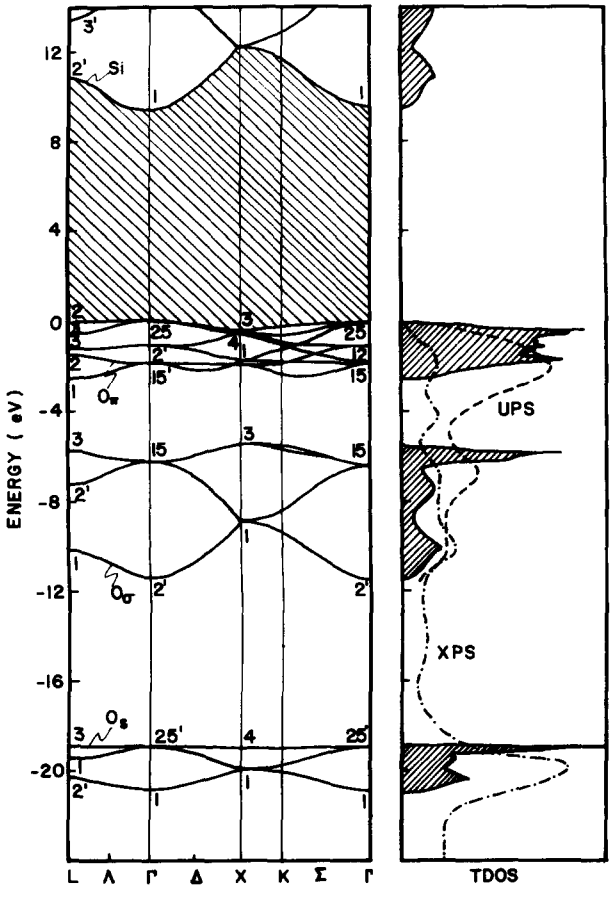


Fig. 1. Energy band structure and total density of states of β-crystobalite calculated in terms of two-center energy parameters listed in Table 1. Energies are measured relative to the valence band edge (symbols are explained in the text).

XPS spectra from [8] are reproduced in the same figure.

Using the same energy parameters we calculate energy band structure of β-crystobalite (111) surface represented by a thin film which consists of 6 Si layers and 11 oxygen layers. Due to the localized nature of the charge around Si–O–Si bond, energy parameters expressing the interactions of the surface orbitals

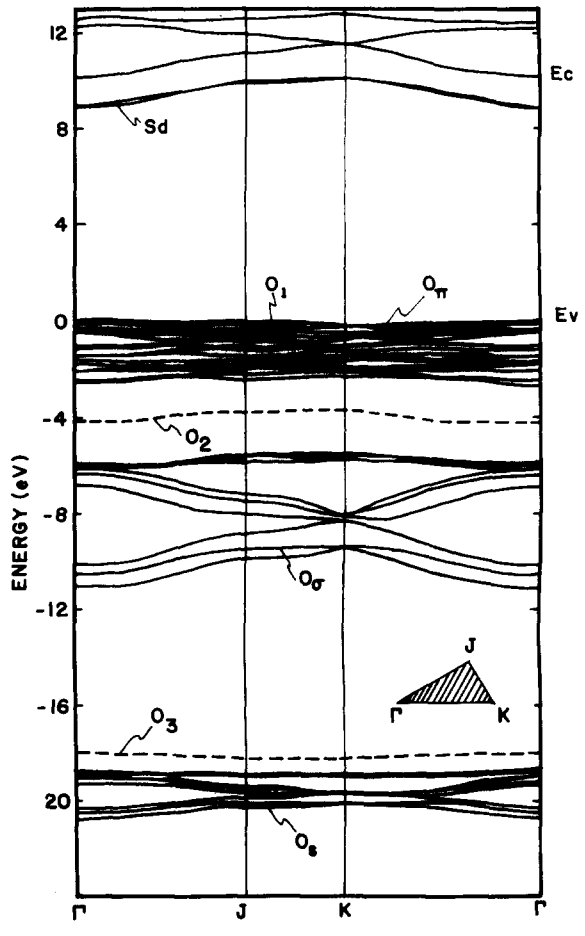


Fig. 2. Energy band structure of the ideal (111) surface of β-crystobalite represented by a thin film consisting of 6 Si layers and 11 oxygen layers. Broken lines show O_1, O_2, O_3 bands.

assumed to be unaltered. Figure 2 presents the energy band structure with the inset showing symmetry directions of the surface Brillouin zone. Closely lying bands (extending from about −21 eV) correspond to bulk β-crystobalite and exhibit all the features outlined above. The band, S_d, located in the energy gap has 60–70% charge localized at the surface and originates from the s and p_z (perpendicular to surface) of the surface silicon atoms. At the center of the surface Brillouin zone s-orbital contribution is 58%, but p_z-contribution is small (8%). As one departs from Γ, p_z-orbital contribution increases, consequently the dangling bond character becomes eminent. The dispersion of this surface state band is low, because of negligible interaction of Si-orbitals via back-bonds. Here, the energy location, especially the gap between S_d and conduction band, is of prime interest. This is certainly dependent upon the values of energy parameters. In order to understand their influence on the location of

S_d we repeated our calculation by using different silicon-s and -p self-energies. Results show that different energy parameters lead to different energy location for S_d, but the separation from the conduction band is almost maintained. Due to the top and bottom surfaces of the thin film, S_d consists of two bands with a negligible splitting, signifying considerably small interaction between two surfaces. Since S_d band is half filled, our thin film becomes metallic. Our experience from the Si(111) $-$ (2 $\times$ 1) surface [9], however, implies that the reconstruction of the SiO_2(111) surface splits these two bands producing a superlattice energy gap. As the filled band lowers, empty band may overlap the conduction band and becomes wider. Reconstruction is expected to arise mainly from the "unusual" bending of Si–O–Si chain. This, in addition, may create surface states between O_σ and O_π bands.

It is most interesting to note that S_d bands may account for the structure appearing in the Si $L_{2,3}$ and O K excitation spectra of SiO_2. Previously, this structure located at the edge of the conduction band was attributed to excitonic effects [7, 10].

In addition to localized S_d states, one expects more localized states due to the perturbation caused by the incomplete Si–O–Si chain at the surface. In fact, our calculations predict surface related states (generally resonance states) at the boundaries of O_π and O_σ bands, which are primarily localized along J–K symmetry direction. In the conduction band, states at about 12.2 eV are localized and have predominantly Si-p_z orbital character. As one departs from Γ, localization shifts to back-bonds, but additional states at about 14.8 eV start to be localized on the p_z orbitals of the surface atoms.

As a next step towards the completion of Si–O–Si chain, we went further and studied the oxygen adsorption on one of the surfaces. In the past, oxygen adsorption is used to detect surface states. One also recognizes that such a simple model can be used to describe one of the stages in the oxidation of Si surfaces. Therefore, results obtained from our calculations are believed to provide information about the oxidation. Broken lines in Fig. 2 illustrate the effect of the oxygen adsorption. It is clearly seen that oxygen atoms forming bonds with Si atoms remove surface states in the gap as well as in the conduction band. Pronounced effect of this bond appear as the bands O_1, O_2, O_3. The states of O_3 band are formed from O–2s orbitals of the adsorbed oxygen atoms. Bonding combination of silicon-s + p_z and oxygen p_z orbitals constitutes O_2 band, yielding a sharp peak at about $-$ 3.8 eV. Missing Si atom at the opposite end of Si–O–Si chain causes this band to raise above O_σ bands. In their study of SiO_2(100) surface Pollmann and Pantelides [11] reported the existence of this band in the same energy region. The peak at $-$ 3.6 eV in the X-ray emission spectra (Si, $L_{2,3}$) lies very close to the energy of the O_2 band. This peak, which could not be reproduced by any calculation on the state distribution of bulk SiO_2, has recently been attributed to the existence of elemental Si in the amorphous SiO_2 [7, 12]. Under these circumstances we believe that more experimental data need to be supplied to come up with a conclusive interpretation of the X-ray emission spectra. Finally O_1 states have the same overall structure of O_π bands. They are very much in atomic character, so that the surface is only a weak perturbation.

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