

## Surface electronic structure of silicon dioxide

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By using the empirical tight-binding method, we have investigated the surface electronic structure of silicon dioxide. The two-center energy parameters of the tight-binding Hamiltonian are obtained from the first-principles band calculations and the surfaces of silicon dioxide are represented by the ideal (111), (100), and (110) surfaces of  $\beta$  cristobalite. For Si-terminated  $\text{SiO}_2$  surfaces we find surface states in the optical gap and conduction band. Depending upon the degree of oxygen coverage the localized state in the optical gap may be half-filled or empty. In the case of the full oxygen coverage (i.e., the O-terminated  $\text{SiO}_2$  surface) these surface states are removed and new surface states originating from the oxygen atoms attached to the surface silicons are created in the valence band. Recent experimental data related to the  $\text{SiO}_2$  surface are outlined. We note that the dangling-bond surface states near the conduction-band edge are also observed experimentally. Furthermore, we examine the ultraviolet photoelectron spectroscopy and electron energy-loss spectroscopy (ELS). Our calculations favor the existence of Si-Si bonds near the  $\text{SiO}_2$  surface which account for the features lying in the lower part of the ELS spectrum.

## I. INTRODUCTION

As the metal-oxide-semiconductor transistors have found a widespread application in electronics, silicon dioxide has been studied quite extensively over the past years. Part of the research carried out thus far concentrated directly on the bulk  $\text{SiO}_2$ , and brought about data which are essential for a better understanding of the electronic structure.<sup>1-11</sup> It is now clearly known that the fundamental structural unit, the  $\text{SiO}_4$  tetrahedron, determines the prominent features of the electronic spectra. Most relevant nature of these spectra, which is common to various allotropic forms of  $\text{SiO}_2$ , as well as to amorphous silica, is that there are three kinds of bands associated with the oxygen atoms forming the  $\sim 21$ -eV-wide valence band.<sup>7-11</sup> The conduction band, on the other hand, exhibits the silicon character and is separated by a  $\sim 9$ -eV energy gap from the valence band.<sup>4,9-11</sup>

Besides the interest on the bulk electronic properties, current advances in the capability of measuring precise surface properties have stimulated many experimental and theoretical studies on the interface of Si- $\text{SiO}_2$  junctions.<sup>12-19</sup> This interface is formed while amorphous  $\text{SiO}_2$  grows thermally over the silicon surface. Due to the lattice mismatch, the manner in which the Si and  $\text{SiO}_2$  link together becomes very irregular. Consequent-

ly, as proposed by recent studies, the structure of the fundamental tetrahedron is destroyed, and a metastable phase<sup>15,20,21</sup>  $\text{SiO}_x$  ( $x < 2$ ) and even the voids are formed at the interface. Irregularities in the arrangement of atoms lying in the interface region generally control the electronic character of the junction, and therefore become the focus of attention.<sup>12,13</sup>

Our purpose in investigating the electronic energy structure of  $\text{SiO}_2$  surfaces can be summarized as follows. First of all, despite the fact that the surfaces of many tetrahedrally coordinated solids have been explored during the last decade, there is not much known about the electronic structure of  $\text{SiO}_2$  surfaces. Much debate has centered on whether surface states exist in the band gap or they are located in the valence band of  $\text{SiO}_2$ . The ultraviolet photoelectron spectroscopy (UPS) valence-band spectrum for  $\hbar\omega = 40.8$  eV, having a surface sensitivity, did not indicate any feature originating from the filled states.<sup>22</sup> On the other hand, electron transport studies<sup>23</sup> in the thermally grown layers of  $\text{SiO}_2$  showed the existence of defect states  $\sim 2$  eV below the conduction band which was ascribed to Si  $sp^3$  dangling-bond state. Furthermore, it is noted that the observed peak (at  $-3.3$  eV below the vacuum level) in the  $\text{SiO}_2$  soft-x-ray absorption spectrum may arise from the surface states.<sup>8</sup> The electron energy-loss spectra<sup>22,24-26</sup> (ELS) them-

selves have been another subject of the controversy. Previously, the structure below 10 eV in the valence-band ELS spectrum has been attributed to unoxidized Si or metastable  $\text{SiO}_x$ . Recently, based on their extensive ELS measurements, Bermudez and Ritz<sup>26</sup> proposed that an empty surface state  $\sim 2.7$  eV above the valence-band edge accounts for the same structure. A systematic study is, therefore, expected to contribute to our knowledge about the surface states of highly ionic solids. When the super Si—O—Si bond is broken, the resulting surface may be covered either by Si, or by O atoms. As a consequence, two different surface electronic structures should appear depending upon the kind of atom lying at the surface. We expect to learn various aspects of the oxidation of silicon from the O-terminated  $\text{SiO}_2$  surface.<sup>15,22,24</sup>

In  $\text{SiO}_2$  the charge is strongly localized around the Si—O—Si bond implying the highly local character of the defect states.<sup>10</sup> For this reason the amorphousness of the surface should not affect our conclusion in any essential manner. Using the same basic premise, the principal features of the  $\text{SiO}_x$  phase can also be revealed from the surfaces of  $\text{SiO}_2$  which contain incomplete tetrahedral coordination. Experimentally, the  $\text{SiO}_x$  phase can be obtained by electron irradiation or by  $\text{Ar}^+$  sputtering in ultrahigh vacuum (UHV), whereby oxygen atoms are desorbed from the surface.

Since there is no experimental data available concerning the actual positions of surface atoms, in the present study we have assumed geometries corresponding to the ideal surfaces of  $\beta$  cristobalite.<sup>27</sup> Moreover, instead of performing sophisticated calculations on the unknown surface geometry, we had rather preferred to use an empirical tight-binding method and have taken an approach to obtain fundamental aspects of the electronic structure.<sup>28</sup> Consequently, we expect that our study will serve as a guide to interpret the spectra obtained from the surfaces of  $\text{SiO}_2$ .

The organization of the rest of the paper is as follows. In Sec. II, we briefly review the empirical tight-binding (TB) method, and obtain the energy integrals from the first-principles band-structure calculation of  $\beta$  cristobalite. These energy integrals will be used throughout this work. As a prelude to surface electronic structure, in Sec. III, the energy bands and the density of states for the bulk  $\beta$  cristobalite are calculated and compared with the experimental results. We devote Sec. IV to the discussion of our results of the electronic structure of the ideal  $\text{SiO}_2(111)$  surface. The effect

of the adsorption of oxygen on the silicon-terminated (111) surface is also studied in the same section. Results for both silicon and oxygen-terminated (100) and (110) surfaces are presented in Sec. V and VI, respectively. In Sec. VII our results are discussed and compared with the available data. Finally, it is closed with our conclusions in Sec. VIII.

## II. EMPIRICAL TIGHT-BINDING ENERGY PARAMETERS

In the present study the empirical TB method is utilized as formulated by Slater and Koster.<sup>29</sup> Early applications of this method have been the interpolation scheme for the more sophisticated band-structure calculation. Later, starting from the simple chemical-bond concept the method has found a wide range of applications to explore chemical trends in the tetrahedrally coordinated semiconductors.<sup>30,31</sup> Increasing interest in the surface physics during the last decade has made the empirical TB approach one of the principal theoretical tools to investigate the electronic properties of surfaces and interfaces.<sup>32–35</sup> Great simplicity offered by this method lies in the evaluation of the Hamiltonian matrix elements<sup>36</sup>:

$$H_{ij}(\vec{k}) = \sum_{\vec{R}_n} \exp[i\vec{k} \cdot (\vec{R}_n + \vec{\tau}_j - \vec{\tau}_i)] \times h_{ij}(\vec{R}_n + \vec{\tau}_j - \vec{\tau}_i), \quad (1)$$

where  $\vec{R}$  and  $\vec{\tau}$  denote the primitive and nonprimitive translational vectors, respectively. The energy integrals describing interactions between atomiclike orbitals

$$h_{ij}(\vec{R}_n + \vec{\tau}_j - \vec{\tau}_i) = \langle \phi_i(\vec{\tau}_i) | \mathcal{H} | \phi_j(\vec{R}_n + \vec{\tau}_j) \rangle \quad (2)$$

are determined from the known quantities (such as the optical transition energies or the energy-band structure), rather than from detailed computations. Regarding the  $\alpha$  coefficient in the free-electron exchange potential it is clear that the parametrization to some extent is also inherent in several first-principles approaches.

It is worth nothing that the atomiclike orbitals are not explicitly used in the empirical TB method; hence, one is not able to calculate charge densities. However, the contribution of an orbital  $i$  in the

state  $(n, \vec{k})$

$$\theta_{in}(\vec{k}) = |a_{in}(\vec{k})|^2, \quad (3)$$

$a_{in}(\vec{k})$  is the mixing coefficient of  $i$ th Bloch sum, allows us to analyze the orbital character of each state.<sup>10</sup> Furthermore,  $\theta_{in}(\vec{k})$  is used to obtain orbital densities of states

$$D_i = \sum_n \int \delta(E - E_n(\vec{k})) \theta_{in}(\vec{k}) d\vec{k}, \quad (4)$$

and also the local density of states

$$\mathcal{L}(\nu) = \sum_{i \in \nu} D_i. \quad (5)$$

In Eq. (5) summation over  $i$  includes all the orbitals of atom  $\nu$ . Going one step further we can define the total electronic occupancy of an atom in the unit cell. This can be achieved by summing  $\theta_{in}(\vec{k})$  over the orbitals at a given atom  $\nu$ .

$$\xi_\nu = \frac{1}{N} \sum_{i \in \nu} \sum_n^{\text{occ}} \int \theta_{in}(\vec{k}) d\vec{k}. \quad (6)$$

Here  $N$ , the number of points sampled in the Brillouin zone (BZ), is used to normalize the occupancy. In the ionic solids, such as  $\text{SiO}_2$ , there is an appreciable amount of charge transfer resulting in a net charge

$$Z_\nu^* = \xi_\nu - Z_\nu \quad (7)$$

on the anion. The method outlined here is believed to consider the transfer of charge between atoms implicitly.

In this work, we have calculated the energy integrals in Eq. (1) in terms of two-center energy parameters ( $ss$ ,  $sp\sigma$ ,  $pp\sigma$ ,  $pp\pi$ ) by using the relations

$$\begin{aligned} h_{s_1 s_2}(\vec{d}) &= s_1 s_2(d), \\ h_{s_1 p_2}(\vec{d}) &= s_1 p_2 \sigma(d) (\vec{d}_0 \cdot \vec{t}_2), \\ h_{p_1 p_2}(\vec{d}) &= p_1 p_2 \sigma(d) (\vec{d}_0 \cdot \vec{t}_1) (\vec{d}_0 \cdot \vec{t}_2) \\ &\quad + p_1 p_2 \pi(d) (\vec{d}_0 \times \vec{t}_1) \cdot (\vec{d}_0 \times \vec{t}_2), \end{aligned} \quad (8)$$

where  $\vec{d} = \vec{R}_n + \vec{\tau}_2 - \vec{\tau}_1$  represents the vector from orbital (1) to orbital (2),  $\vec{d}_0 = \vec{d}/d$ , and  $\vec{t}$  is the direction vector of the orbital  $p$ . Similar to other empirical TB calculations Si  $3d$  orbitals are not included in the basis set.<sup>8,17,18</sup> Results of detailed band-structure calculations of  $\text{SiO}_2$  seem to show that correct energies can also be obtained without invoking Si  $3d$  orbitals. Despite that, how significantly Si  $3d$  orbitals participate in bonding is one

TABLE I. Energy parameters (in eV) used in the calculations of the electronic structure of  $\beta$  cristobalite.

Si-Si $d=0$	O-O $d=0$	O-O $d=4.78$ a.u.	Si-O $d=2.93$ a.u.
$ss=6.7$	$ss=-16.0$	$ss=-0.4$	$ss=-3.0$
$pp=12.2$	$pp=-1.1$	$pp\sigma=0.3$	$ss\sigma=-4.4$
		$pp\pi=-0.3$	$ps\sigma=6.4$
			$pp\sigma=5.8$
			$pp\pi=-1.4$

of the current controversies.<sup>11</sup> In the past, the intense peak at 94.5 eV in Si  $L_{2,3}$  emission spectrum was ascribed to the Si  $3d$  orbital contribution in the valence band.<sup>37</sup> Later on, various theoretical investigations have indicated contradictory results in connection with the contribution of the Si  $3d$  orbitals.<sup>38</sup>

As to the energy parameters, they are determined from the first-principles band calculations of  $\beta$  cristobalite.<sup>10</sup> For the choice of energy parameters a common procedure is followed where the empirical TB band energies are fitted to the known energies by diagonalizing the secular equation at the high-symmetry points ( $\Gamma, X, L, \dots$ ). Band structure obtained in this way may not agree with the known data as one departs from the symmetry points. To obtain realistic bands for  $\text{SiO}_2$ , the parameters, listed in Table I, are optimized throughout the BZ.

### III. ENERGY-BAND STRUCTURE OF $\beta$ CRYSTOBALITE

The energy-band structure and the total density of states calculated in terms of our parameters are illustrated in Fig. 1. The present band model, wherein  $\sim 21$ -eV-wide valence band, 9.4-eV energy gap<sup>4</sup> (optical gap), and the lower part of the conduction band are seen, reflects overall features relevant to  $\beta$  cristobalite.

For the sake of completeness here we would like to present a brief discussion of the bulk electronic structure. For a more detailed discussion the reader is suggested to refer to Refs. 8–11. In the valence band three distinct energy regions are recognized. The flat bands (at about  $-20$  eV) labeled<sup>39</sup> by  $O_s$  originate from O  $s$  orbitals and give rise to a sharp peak in the soft-x-ray spectrum (SXS).<sup>2</sup> The bands lying between  $-6$  and  $-11.5$  eV are formed from the bonding combination of Si

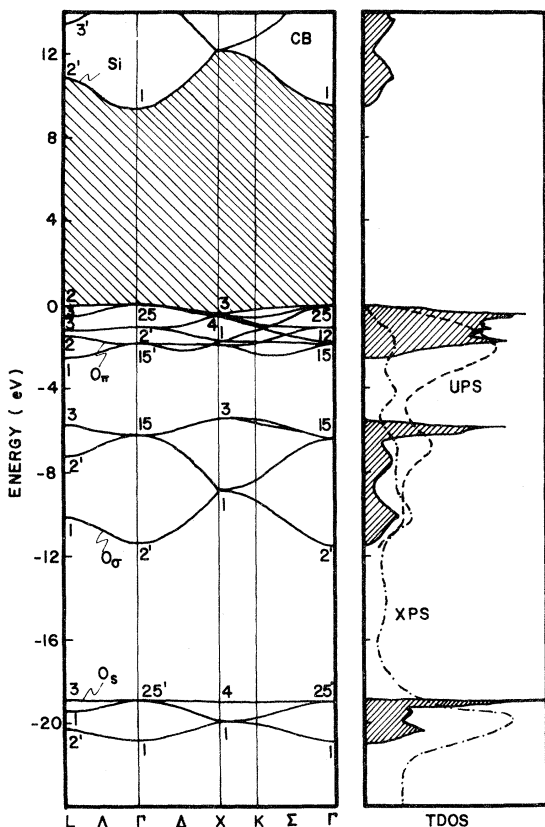


FIG. 1. Energy-band structure and total density of states of  $\beta$  cristobalite calculated in terms of parameters described in Sec. II. UPS and XPS intensities are reproduced from Ref. 5. Energies are measured relative to the valence-band edge. (For the explanation of the symbols see the text.)

( $s + p$ ) and oxygen  $p$  orbitals directed along the Si—O—Si super bond and are responsible for the binding of  $\text{SiO}_2$ . They are labeled by  $O_\sigma$  and correspond to the x-ray photoelectron spectroscopy (XPS) peak<sup>5</sup> at about  $-6$  eV. To form  $O_\pi$  bands in the upper portion of the valence-band oxygen  $p$  orbitals are combined to give maximum charge distribution perpendicular to Si—O—Si chain. Because of small ( $pp\pi$ ) interaction ( $\sim 0.3$  eV) these bands are almost dispersionless and are recognized by two overlapping peaks at  $-1.3$  and  $-2.4$  eV in the UPS spectrum.<sup>5</sup> The bending of Si—O—Si bond (the bond angle decreases from  $180^\circ$  to  $144^\circ$ , as is the case in  $\alpha$  quartz and in amorphous silica) causes the width of the  $O_\pi$  bands to increase so that the gap between  $O_\sigma$  and  $O_\pi$  becomes smaller.<sup>8,10</sup> Considering the orbital compositions, and most importantly the static effective charge of oxygen atoms (which amounts to 1.5 electrons) one

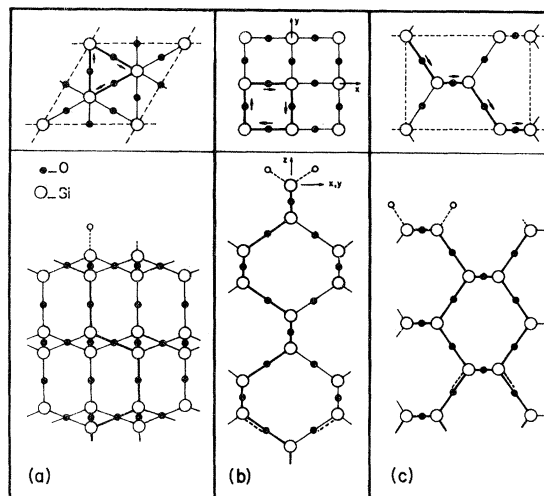


FIG. 2. Surface unit cells and the atomic arrangements of  $\beta$  cristobalite slabs used to simulate various surfaces of  $\text{SiO}_2$ . (a) ideal (111) surface, (b) ideal (100) surface, (c) ideal (110) surface. Bonds shown in dashed lines describe the O-terminated surfaces. The slab unit cell for (111) Si-terminated surface contains 6 Si and 11 O atoms, and thus 11 atomic layers. For Si-terminated (100) surface there are 9 Si and 16 O atoms, and 17 atomic layers in the slab unit cell. The slab unit cell corresponding to (110) surface contains 10 Si and 18 O atoms, and 9 atomic layers. Lengths of Si—O—Si and Si—O bonds are taken 5.86 and 2.93 a.u., respectively.

concludes that the oxygen character becomes predominant in  $O_s$ ,  $O_\sigma$ , and  $O_\pi$  bands. In contrast to that the lower part of the conduction band is reminiscent of silicon valence band.<sup>40</sup> Having discussed the bulk  $\beta$  cristobalite, let us now concentrate on the electronic structures of surfaces.

#### IV. $\text{SiO}_2(111)$ SURFACE

To explore the electronic energy structure of the  $\text{SiO}_2(111)$  surface we have used the slab model. As is shown in Fig. 2(a), our slab has the two-dimensional periodicity of the ideal (111) surface of  $\beta$  cristobalite, and consists of 11 atomic layers. According to this representation one Si—O—Si bond per surface unit cell is broken, such that the silicon atoms cover the top and the bottom surfaces of the slab. Figure 3(a) shows the energy-band structure with the inset showing the symmetry directions of the surface BZ. Closely lying bands (extending from about  $-21$  eV) correspond to bulk  $\beta$  cristobalite and depict four characteristic energy regions ( $O_s$ ,  $O_\sigma$ ,  $O_\pi$ , and the conduction

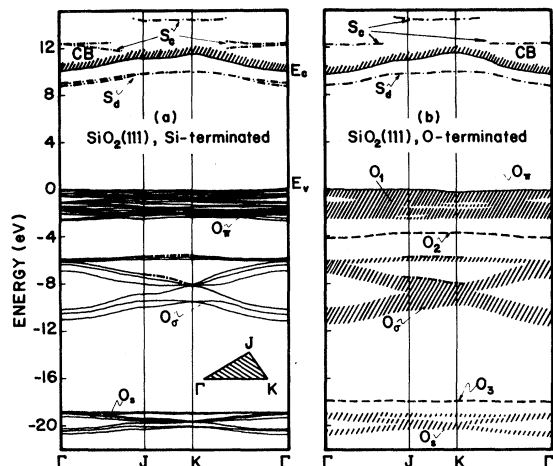


FIG. 3. Calculated energy-band structure for (a) Si-terminated  $\text{SiO}_2(111)$  surface, (b) oxygen adsorbed on the top surface. Dash-dotted lines describe surface states formed mainly from Si orbitals. Surface states created by the adsorption of oxygen atoms denoted by dashed lines. As is seen from panel b, after the oxygen adsorption Si surface states belonging to the top surface are removed, and  $O_1$ ,  $O_2$ , and  $O_3$  oxygen states are created, Si surface states corresponding to the bottom surface are maintained. Zero energy is taken as the edge of the valence band. The inset shows the symmetry directions of the surface BZ corresponding to the unit cell in Fig. 2(a).

band) of  $\text{SiO}_2$  as outlined in Sec. III. The pronounced effect of the surface appears as the bands  $S_d$ , located in the band gap. Due to the top and bottom surfaces of the slab,  $S_d$  contains two bands with a negligible splitting signifying considerably small interaction between two surfaces. States forming  $S_d$  have 60–70% charge localized at the surface and originate from  $(s+p_z)$  orbitals of the surface Si atoms. In the vicinity of the  $\Gamma$  point  $s$  orbital contribution is predominant (58% at the surface and 25% at the Si layer just below the surface), but  $p_z$  contribution is small (8%). However, as one departs from the center of the surface BZ, the  $p_z$  contribution increases and localization below the surface diminishes, consequently the dangling-bond character becomes eminent.  $S_d$  bands are half-filled, and their dispersions are low because of negligible interactions of Si atoms via backbonds. Our experience from  $\text{Si}(111)$   $(2 \times 1)$  surface,<sup>31–33</sup> however, implies that a possible reconstruction of  $\text{SiO}_2(111)$  surface produces a superlattice energy gap and hence splits the  $S_d$  bands. In concluding the discussion of the  $S_d$  states, it is appropriate to comment on its energy location, especially the gap

between  $S_d$  and the conduction band. It may be argued that the position of  $S_d$  is strongly dependent upon the values of energy parameters utilized in the calculations. In order to understand the influence of these parameters, we have carried out band-structure calculations by varying them in reasonable limits. It is observed that lowering Si  $s$  and  $p$  self-energies leads to the lowering of the conduction-band edge as well as  $S_d$ , but the energy separation between them is unaltered. In contrast to that, inducing new interaction parameters among Si atoms in the vicinity of the surface lowers  $S_d$  states towards the midgap. We will return to this point later.

In addition to  $S_d$  we found intrinsic surface states  $S_c$  in the conduction band. Near the center of the surface BZ, states of  $S_c$  stem from the surface  $\text{Si } p_z$  and the third layer Si  $s$  orbitals and hence reflect the backbonding nature. Along  $J$ - $K$  direction, however, localization shifts to the surface and  $\text{Si } p_z$  orbital character becomes dominant. At this point, a complementary remark is in order. Surface states (such as  $S_c$ ) lying above the vacuum level are not bound states. Besides, the method and the basis set used in the present study is not capable of describing the upper part of the conduction band. Our calculations predict also surface-related states in the valence band. In the  $O_\pi$  bands, they are generally surface resonances. States lying at the boundaries of  $O_\sigma$  bands are localized along  $J$ - $K$  directions and display the character of the backbonding surface state.

To investigate the adsorption of oxygen on the Si-terminated  $\text{SiO}_2(111)$  surface we proceed with the formation of Si–O bonds<sup>41</sup> sticking out of the top surface [see Fig. 2(a)]. Such a model is able to describe the O-terminated  $\text{SiO}_2(111)$  surface. Broken lines in Fig. 3(b) illustrates the effect of the oxygen atom forming a bond with each surface Si atom. It is clearly seen that the surface states are removed and instead  $O_1$ ,  $O_2$ , and  $O_3$  localized states in the valence band are created as a result of the oxygen adsorption. Taking the energies of these bands into consideration, one can deduce that  $S_d$  states are highly reactive against the oxygen atom, and that by forming Si–O bonds the energy of the surface is lowered.

Approaching from the lower part of the valence band, states of  $O_3$  result mainly from the  $2s$  orbital of adsorbed oxygen, and  $\sim 6\%$  from the surface  $\text{Si } p_z$  orbital. In the gap between  $O_\pi$  and  $O_\sigma$  bulk bands the bonding combination of the surface Si  $(s+p_z)$  and the adsorbed  $O p_z$  orbitals form the

flat  $O_2$  band. The energy of this combination is not as low as the one occurring in the super Si—O—Si bond; therefore the  $O_2$  band is pulled out of the bulk  $O_\sigma$  bands. Since the interactions between the  $p_x$  and  $p_y$  of the adsorbed oxygen and the  $\pi$  orbitals of oxygen lying at the center of the backbonds are weak, the surface does not constitute a strong perturbation. Consequently,  $O_1$  states cannot split from  $O_\pi$  bands, and become resonating states localized at certain regions of the surface BZ.

### V. $\text{SiO}_2(100)$ SURFACE

The electronic structure of the ideal (100) surface of  $\text{SiO}_2$  has been investigated by using a slab model consisting of 17 atomic layers as described in Fig. 2(b). According to this model two Si—O—Si bonds per surface unit cell are broken and an ideal (100) surface is created. Figure 4(a) presents the energy-band structure corresponding to Si terminated (100) surface. As we have already explained closely lying bands labeled by  $O_s$ ,  $O_\sigma$ ,  $O_\pi$ , and conduction band (CB) stem from bulk  $\beta$  cristobalite. Bands shown by the dash-dotted lines display the effect of the surface. Now we concentrate first on the surface states lying in the optical gap. Localized states occurring  $\sim 1.5$  eV below the conduction band form two bands belonging to the surfaces of the slab. They are labeled by  $S_{sz}$  (or  $S_d$ ), and are filled. At the center of the surface

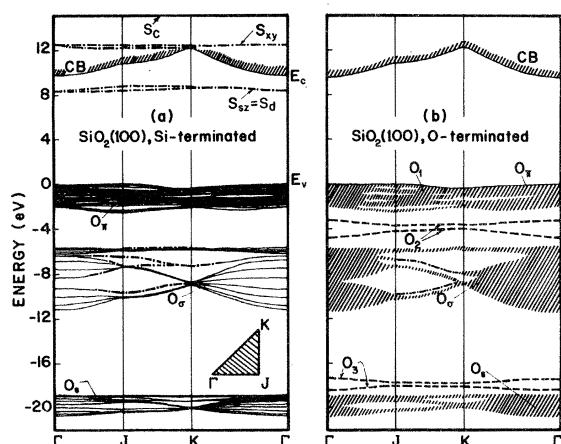


FIG. 4. Calculated energy-band structure for (a) Si-terminated  $\text{SiO}_2(100)$  surface; (b) O-terminated  $\text{SiO}_2(100)$  surface. Dash-dotted and dashed lines denote the silicon and oxygen surface states, respectively. Bulklike  $O_s$ ,  $O_\sigma$  and  $O_\pi$  bands in panel b are described by the shaded area. (Symbols are explained in the text.)

BZ these bands are degenerate and are formed from 70%  $s$  and 12%  $p_z$  orbitals of the surface silicons. As one approaches the  $J$  point, these two bands start to split because of the fourfold rotation connecting the top and bottom surfaces. At the  $J$  point 73%  $s$  and 12%  $p_z$  orbitals of the top surface contribute to the lower-lying band, whereas  $p_z$  orbital contribution of the bottom surface silicons increases to 19% in the higher-lying band. At the  $K$  point (the corner of the surface BZ) these two bands join and are formed from 72%  $s$  and 19%  $p_z$  orbitals of the surface silicons. From the symmetry point of view the top and bottom surfaces are equivalent, and therefore these two bands continue to be degenerate along the  $K$ - $\Gamma$  direction. Taking their orbital composition into account we ascribe a dangling-bond-like character to these surface bands.

Above  $S_d$ , in the conduction band, we find two flat surface bands displaying completely different character. They originate from  $p_x$  and  $p_y$  orbitals of the surface silicons, and therefore they are labeled by  $S_{xy}$ . At this point, it should be noted that the formation of  $S_d$  and  $S_{xy}$  bands from two dangling bonds of the surface silicon atom resembles the surface-state bands of the ideal Si(100) surface.<sup>42,43</sup> As one recognizes, two dangling bonds of Si(100) surface are reordered to minimize the electronic energy, such that the filled band is formed from  $p_z$  orbital with a charge distribution pointing out of the surface. On the other hand, the empty band is produced by a  $p_x$  (or  $p_y$ ) orbital which is parallel to the surface but perpendicular to the plane containing the two backbonds. Apart from  $S_d$  and  $S_{xy}$ , we see additional surface states in the conduction band. They are labeled by  $S_c$  and reflect the behavior of the Si  $p$ -type backbonding states.

In the valence band the pronounced effect of the surface is seen in the  $O_\sigma$  band region, where the states are splitted from the bulk bands and form surface bands localized along  $J$ - $K$  direction. These states are mainly produced by the oxygen  $p$  orbitals of the strengthened backbonds.

Having discussed the Si-terminated surface, we now turn to the O-terminated  $\text{SiO}_2(100)$  surface. As is seen from the electronic energy structure illustrated in Fig. 4(b), no surface states appear either in the gap, or in the conduction band. In contrast to that, localized states are found in the valence band. Since they exhibit an orbital structure similar to the ones found in O-terminated  $\text{SiO}_2(111)$  surface, we also label them by  $O_1$ ,  $O_2$ ,

and  $O_3$  in Fig. 4(b). Each surface unit cell contains two oxygen atoms forming Si—O bond, so  $O_3$  contains two and  $O_2$  four (two doubly degenerate) surface bands.<sup>44</sup> Because of the negligible effects of the surface on the lone-pair orbitals,  $O_1$  states are buried in  $O_\pi$  bands and are localized at certain regions of the surface BZ. The most significant feature of the O-terminated  $\text{SiO}_2(100)$  surface manifests itself at the edge of the valence band, whereby two bands at the edge are seemingly emptied. For a slab model having one surface O-terminated and the other surface Si-terminated,  $S_d$  bands will be emptied, whereas there will be no empty band in the valence band. Later, in Sec. VII we shall address this subject.

Further to  $O_1$ ,  $O_2$ , and  $O_3$  bands, we find surface states in the  $O_\sigma$  band region. They are produced from the  $O\ 2p$  orbitals of the backbonds and are localized along the  $J$ - $K$  direction. Comparison made between these states and the backbonding states of the Si-terminated  $\text{SiO}_2(100)$  surface [see Fig. 4(a)] reveals that the saturation of the Si dangling bonds by oxygen atoms cannot restore the bulk charge distribution, so the backbonding surface states are not removed.

## VI. $\text{SiO}_2(110)$ SURFACE

Si-terminated  $\text{SiO}_2(110)$  surface contains an equal number of Si and O atoms [see Fig. 2(c)]. From the four bonds of each surface silicon atom, two lie in the surface plane, one is connected to the second atomic layer, and one is broken, so that each surface unit cell contains two broken bonds. In Fig. 5(a) we present our results corresponding to Si-terminated  $\text{SiO}_2(110)$  surface. Features in the electronic structure do not differ very much from the surface described in Secs. IV and V. Four broken bonds of the slab unit cell (two bands for each surface) form four surface-state bands labeled by  $S_d$ . At the  $\Gamma$  point, two bands of  $S_d$  result from the  $s$  orbital of surface silicons and are located  $\sim 1.5$  eV below the conduction-band edge. Because of Si  $p$  orbital contribution the rest of the surface bands in  $S_d$  are splitted and located in the conduction band. As one approaches the corner of the surface BZ, Si  $p$  orbital contribution increases in the lower-lying  $S_d$  bands, so that four bands join at the  $K$  point. In addition to  $S_d$  bands, empty surface states in the conduction band exhibit the similar behavior of the surface bands seen in previous sections: In the lower part of the conduction band

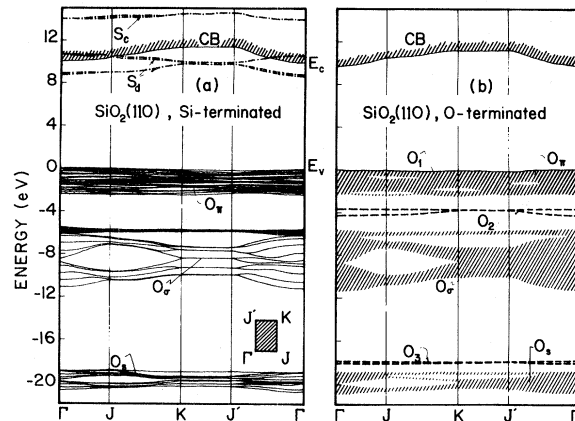


FIG. 5. Calculated energy-band structure for (a) Si-terminated  $\text{SiO}_2(110)$  surface; (b) O-terminated  $\text{SiO}_2(110)$  surface.

we find  $s$ -type surface states localized at the third atomic layer containing the other end of the backbond. Four Si  $p$ -type surface bands labeled by  $S_c$  are also seen in the upper portion of the conduction band.

Figure 5(b) illustrates our results for the O-terminated  $\text{SiO}_2(110)$  surfaces. Features are not different from the other surfaces of  $\text{SiO}_2$ ; hence the previous discussions apply also to the (110) surface of  $\text{SiO}_2$ .<sup>45</sup>

## VII. DISCUSSION

Thus far we have reported our results corresponding to the electronic structure of ideal (111), (100), and (110) surfaces of  $\text{SiO}_2$ . Most significant features common to all surfaces can be summarized as follows. For Si-terminated slab surfaces (i) localized surface-state bands displaying dangling-bond-like character lie 1–2 eV below the conduction band. These bands are half-filled and are produced mainly by the ( $s + p_z$ ) orbitals of surface silicons. In the case of (100) surface, however,  $S_d$  bands are splitted due to the reordering of the Si  $sp^3$  dangling bonds. As the filled bands  $S_{sz}$ , resulting from the Si ( $s + p_z$ ) orbitals, stay below the conduction-band edge, the empty bands  $S_{xy}$ , displaying Si  $p_x$  (or  $p_y$ ) orbital character, are raised into the conduction band. The same reordering of the bands is also seen in the ideal Si(100) surface. (ii) Additional surface-state bands originating from Si  $s$  and Si  $p$  orbitals are located in the lower and upper regions of the conduction band, respectively. (ii) Major effect of the surface on the valence band

occurs in the  $O_\sigma$  band region. Here, backbonding surface states produced by the O  $2p$  orbitals are localized along certain directions of the surface BZ.

The O-terminated  $\text{SiO}_2$  surface can be viewed as the formation of tetrahedrally directed Si—O bonds by the adsorption of oxygen atoms on the Si-terminated surface. In this case (i) surface states lying in the optical gap as well as in the conduction band are removed. (ii) New surface states arising mainly from the  $s$  and  $p$  orbitals of the surface oxygens appear instead. These states labeled by  $O_1$ ,  $O_2$ , and  $O_3$  are located in the valence band. (iii) The backbonding surface states of the Si-terminated surfaces (located in the valence band) are almost removed in the  $\text{SiO}_2(111)$  slab. However, the perturbation raised by two broken bonds of the  $\text{SiO}_2(100)$  surface seems to be strong enough to maintain the backbonding states even after the Si—O bonds are formed.

A simple analysis of the oxygen adsorption, namely the formation of a Si—O bond at the surface can be made as follows: Each atomic oxygen having six valence electrons gives rise to four bands when it saturates the surface silicon. These four bands are located below the valence-band edge, and should be filled by eight electrons. The comparison between the self-energies of the O  $s$  and  $p$  orbitals with the locations of these four bands implies that the formation of Si—O bonds are energetically favorable. Accordingly, when both surfaces of the slab are terminated by oxygen,  $S_d$  bands are removed and two empty bands are generated at the edge of the valence band. In practice, when  $\text{SiO}_2$  is cleaved in UHV, each surface created this way shall contain equal numbers of silicon and oxygen atoms. Consequently, any ideal surface of  $\text{SiO}_2$  cleaved in UHV shall display an electronic structure consisting of empty  $S_d$  surface states and completely filled valence band.

As a complementary remark to the above summary it may be appropriate to compare the surface electronic structure of  $\text{SiO}_2$  with that of compound semiconductors. Previous studies have revealed a general trend whereby the surface states related to the anion-covered surface lie in the valence band. On the contrary, the dangling-bond surface states originating from the cation-terminated surface rise with the increasing ionicity of the compound in the optical gap and become more flat.<sup>31</sup> Interestingly, our results indicate that the surfaces of  $\text{SiO}_2$  (which has both ionic and covalent components in the binding) follow the same trend.

In the context of the surface electronic structure

of  $\text{SiO}_2$ , the most important question to ask is whether or not  $S_d$  lies in the optical gap. Using a “Green’s function scattering-theoretical” approach together with the empirical TB Hamiltonian, Pollman and Pantelides<sup>46</sup> investigated the (100)  $\beta$ -cristobalite surface and have claimed that surface states related to the Si-terminated surface lie in the conduction band. Except for the position of  $S_d$  our results seem to be in fair agreement with their work. Laughlin<sup>47</sup> showed that the broken bond defects in  $\text{SiO}_2$  lead to localized states  $\sim 2$  eV below the conduction-band edge. In connection with the defect states in  $\text{SiO}_2$ , an investigation of the oxygen vacancy has revealed the occurrence of a bound state ( $E'_1$  center)  $\sim 1.5$  eV below the conduction-band edge.<sup>48</sup> Due to the localized nature of the bands and the orbital structure, we may expect that the energy of the O-vacancy bound state shall not differ appreciably from the energy of  $S_d$ .<sup>49</sup> Therefore, the existing predictions related with O-vacancy seem to confirm our prediction for the energy of  $S_d$ .

Experimentally, Williams<sup>23</sup> has studied the electron transport in thermally grown layers of  $\text{SiO}_2$ . He has introduced electrons into oxide by photoemission from the adjoining silicon crystal and found deep electron traps  $\sim 2$  eV below the conduction-band edge. These traps act like positive charged centers. In Ref. 48, it was shown how the O-vacancy state is associated with the positively charged centers in Si- $\text{SiO}_2$  junctions. EPR studies of silicon surface by Hochstrasser and Antonini<sup>50</sup> showed that unpaired electron is trapped near the surface silicon atoms.

There is more experimental evidence supporting the Si dangling-bond state near the conduction-band edge. One such significant result is reported by Mitchell and Denure,<sup>51</sup> who have studied defects in  $\text{SiO}_2$  thin films introduced by the electron irradiation. Using cathodoluminescence technique, they have found that electron irradiation enhances an optical emission peak (so-called “C band”) at 2.8 eV, which was thought to originate from a broken Si—O bond.

Auger electron spectrum (AES) obtained from the oxygen-deficient  $\text{SiO}_2$  surface (which practically corresponds to the Si-terminated surface) has brought about interesting features concerning the surface electronic structure. After the electron irradiation, a new peak at  $\sim 91$  eV is induced in the Si  $L_{2,3}$  Auger signal while the signals from oxygen atoms decrease. Comparing this new peak with the main peak in Si  $L_{2,3}VV$  AES of pure silicon, it



was concluded that Si islands are induced by the electron irradiation.<sup>52</sup> Later, Schwidtal<sup>53</sup> noted that the growth law for the “free Si” peak in the Auger spectrum is the same as that reported for the “C band” from cathodoluminescence, and both signals have the same origin. He further suggests that the radiation-induced feature arises from a Si  $L_{2,3}VD$  ( $D$  means defect) transition and this defect is a singly occupied Si dangling-bond state  $E'_s$  (here denoted by  $S_d$ ) located 2 eV below the conduction-band edge.

Taking the uncertainty in the location of the conduction-band edge (within the range of  $\pm 0.5$  eV) into account, experimental evidence discussed so far seems to support our predictions for  $S_d$ , namely the existence of the surface states originating from the surface silicons. These states are empty for a crystal cleaved in UHV and become half-filled for a Si-terminated surface (which may be equivalent to the oxygen deficiency). As we noted in Sec. IV, we have examined the influence of the energy parameters on the energy of  $S_d$  and demonstrated that the gap between  $S_d$  and the conduction band is maintained irrespective of the value of  $S_i$  and  $p$  self-energies. However, increasing interactions between surface silicon atoms, which may be interpreted as the formation of Si—Si bonds (in “free Si”) or the drastic bending of a Si—O—Si bond, lowers the localized state in the optical gap. This also implies that our calculations are physically meaningful for SiO<sub>2</sub> surfaces.

In regard to the localized-gap states it is appropriate to consider UPS, ELS, and soft-x-ray absorption spectra of SiO<sub>2</sub>. Previously, the absence of the photoemission ( $\hbar\omega = 40.8$  eV) structure in the optical gap of thermally grown SiO<sub>2</sub> was attributed to the absence of surface states near the conduction band.<sup>22,26</sup> This followed from the surface sensitivity of the UPS valence-band spectra. Considering the fact that the  $S_d$  bands of thermally grown SiO<sub>2</sub> are emptied we may easily assert that UPS results do not constitute any disagreement with our predictions. In contrast to UPS results, the observed peak ( $\sim 3$  eV below the conduction-band edge) in O  $K$  spectrum was pointed out to originate either from excitonic effects or from the surface states.<sup>8</sup> However, based on the ELS results there have been objections to the suggestions related to surface states.<sup>11</sup> The interpretation of ELS spectrum has been the center of controversy. Since the present work is concerned with the surface electronic structure of SiO<sub>2</sub>, here we confine our attention to localized surface states in the ELS

spectrum.

Ibach and Rowe have investigated ELS spectrum of thermally grown SiO<sub>2</sub> by using primary electron energies of 100 eV to excite transitions from the valence band.<sup>22</sup> They have noted that the loss spectrum did not vary for primary energies in the range 50–200 eV. This was taken as an objection to the occurrence of empty surface states near the edge of the conduction band.<sup>11</sup> On the other hand, they have employed excitonic states ( $\sim 2$  eV below the conduction band) as the final states and interpreted ELS features in terms of transitions from the valence band. It should be noted that the dangling-bond state  $S_d$  in our study happens to lie in the same energy region as that of the excitonic level. To avoid the influence of the valence band on the ELS structure, Koma and Ludeke<sup>24</sup> studied excitations from Si  $2p$  and O  $1s$  core levels and obtained an ELS spectrum which almost coincides with the valence-band ELS spectrum.<sup>22</sup> Having a single initial state they have taken a different approach in interpreting the spectrum, and proposed five distinct levels in the conduction band. Interestingly, the surface states (grouped in  $S_d, S_c$ ) found in the present study lie close to the levels assigned by Koma and Ludeke<sup>24</sup>. It should be born in mind that in the same work the localized states resulting from Si(100) ( $2 \times 1$ ) surface have been resolved, although core excitations require primary electron energies greater than 600 eV. Before the conclusion of our discussion related to the ELS spectrum we concentrate on the structure lying in the lower part of the spectrum. This structure, corresponding to transitions to empty final states above the valence-band edge, has in the past attracted great interest. Now, it is anticipated that “free Si” (or unoxidized Si) existing in SiO<sub>2</sub> may account for this structure. This argument is justified by the works of Yndurain,<sup>54</sup> and Lannoo and Allan.<sup>55</sup> Similarly, we have showed in the present study that the energy of the surface state in the optical gap may lower with the increasing interactions between surface silicons. The absolute energy of a Si—Si bond can also be estimated without performing detailed calculations. To do that we make use of the parameters of the bond orbital model.<sup>30,31,56</sup> According to this model  $sp^3$  hybrid orbitals of neighboring Si atoms are combined to yield bonding and antibonding bond orbitals. The energy of the hybrid orbital  $E_h$ , can conveniently be computed from atomic term values and found to be  $\sim -8.2$  eV. The covalent energy  $V_2$  of Si is equal to  $-2.2$  eV. Then the Si—Si bond energy is

given by  $E_h + V_2$ . Substituting the corresponding values of energies, the absolute energy of the Si—Si bond is found to be  $\sim -10.4$  eV. Using the value reported for the photoelectric threshold<sup>22</sup> of SiO<sub>2</sub> (which is equal to 10.6 eV), we show that the Si—Si bond energy should lie  $\sim 0.2$  eV above the valence-band edge. Structural changes in the vicinity of the surface may cause either the Si—Si bond to stretch, or a silicon cluster to form. In the former case the bond energy is raised above the valence-band edge.<sup>40</sup> In the latter, the Si—Si bond energy broadens into a valence band extending from  $\sim -5$  to  $\sim -17$  eV (in absolute energies). In both cases, however, electrons occupying localized levels of silicon drop to the empty band (which occurs at high oxygen coverages and lies at the edge of the valence band), and may account for the empty final states in the ELS spectrum. Recently, Bermudez and Ritz<sup>26</sup> have also concentrated on the features of ELS spectra of various SiO<sub>2</sub> samples and performed an extensive study. Aside from small changes they observed three loss peaks at 3.3, 5.0, and 6.8 eV, irrespective of electron irradiation, annealing in vacuum, or O<sub>2</sub>, H<sub>2</sub>, and Ar<sup>+</sup> sputtering. In view of these observations, they proposed an empty intrinsic surface state (2.7 eV above the valence-band edge) which was taken as a final state to interpret the ELS spectrum. Moreover, they anticipated that this intrinsic state may associate with a Si=O double bond. To see whether the Si=O double bond gives rise to an empty state above the valence-band edge of SiO<sub>2</sub>, we considered a SiO<sub>2</sub>(100) slab with each surface silicon attached to one oxygen on top of it and to the bulk SiO<sub>2</sub> by two backbonds (Si—O—Si bonds). In the framework of the method and parameters described in Sec. II, calculations performed on this slab model did not yield any empty surface state near the valence-band edge.

Finally, we turn to the surface bands, O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub>, occurring in the O-terminated surface. Although various theoretical works are in overall agreement on their locations, experimentally these states seem not to attract much attention. It is interesting to note that the peak at  $-3.6$  eV in the x-ray emission spectra lies very close to the energy of the O<sub>2</sub> band. This peak, which could not be reproduced by any calculation of the state distribu-

tion of bulk SiO<sub>2</sub>, was attributed to the existence of elemental Si in the amorphous SiO<sub>2</sub>.<sup>9,54</sup> In any case, these states are expected to participate in the transitions from the valence band which account for the features in the ELS spectrum. However, available data do not allow us to come up with a conclusive interpretation.

### VIII. CONCLUSIONS

The surface structure of thermally grown SiO<sub>2</sub> is not known clearly yet. Composition as well as structural features of surface depend upon the conditions wherein SiO<sub>2</sub> layers are formed. As to the surface of the "real" crystalline SiO<sub>2</sub>, they are believed to reconstruct. Consequently, the back bonds may exhibit bendings different than that of the bulk bonds. Using idealized surface geometry, we showed that localized states near the conduction-band edge may be half-filled, empty, or completely removed depending upon the composition of the surface. In the case of the O-terminated surface (or full coverage with oxygen), localized states appear in the valence band. Certainly, the deviations from the ideal geometry and composition are expected to affect the surface electronic structure.<sup>57</sup> Bending of the backbonds increases the interaction between first and second layers of silicon, thus causing the  $S_d$  states to shift slightly. However, our results are believed to describe the surface electronic structure of SiO<sub>2</sub>, unless a drastic deterioration in the bonding of surface atoms took place. Apart from the electronic structure corresponding to the ideal surface geometry and composition, we show that empty states originating from Si—Si bonds can be located above the valence band.

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- <sup>45</sup>Due to the same reason explained in Ref. 44, for the

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