PHYSICAL REVIEW B VOLUME 31, NUMBER 4 15 FEBRUARY 1985

Band structures of all polycrystalline forms of silicon dioxide

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(Received 5 June 1984; revised manuscript received 7 September 1984)

The band structures and density of states of all polycrystalline forms of SiO_2 with known crystal structures are calculated using a first-principles orthogonalized linear combination of atomic orbitals method. These include 4:2-coordinated polymorphs of α-quartz, β-quartz, β-tridymite, α-crystobalite, β-crystobalite, keatite, coesite, and two idealized forms of β-crystobalites, as well as the 6:3-coordinated stishovite. Linear relations between the band gaps and the average Si—O bond lengths and the minimum Si—O—Si angles are firmly established. The electronic structure of stishovite is found to be very much different from the 4:2-coordinated oxides and shows more covalency in the bonding character.

I. INTRODUCTION

Silicon dioxide exists in many polycrystalline forms as well as in a vitreous glassy state. The crystal structures of many of these polymorphs have been well determined.[1] These include α- and β-quartz, β-tridymite, α- and β-crystobalite, keatite, coesite, and stishovite.[2] The structural information for these crystals are summarized in Table I. With the exception of stishovite, all these polycrystals and the amorphous phase have local structures of fourfold tetrahedral bonding for Si and twofold bridging bonding for O. For stishovite, which has a much larger mass density, each Si atom is sixfold coordinated in the form of a distorted octahedron and each O atom is threefold bonded in the center of a planar triangle. The Si—O bond lengths and the Si—O—Si bridging angles exhibit a wide range of distribution in these polymorphs. In the amorphous state, the bond lengths and the bond angles have continuous distributions with mean values of about 1.61 Å and 147°, respectively.[3]

The electronic properties of SiO_2 have been extensively discussed in the context of simple tight-binding theory.[4] The band structure of α-quartz has been studied by several authors in recent years.[5–7] Prior to that, only the idealized β-crystobalite structure had been studied.[4,8,9] The idealized structure is obtained by inserting an O atom midway between the Si atoms in the diamond lattice and rescaling the lattice parameter accordingly, thus the Si-O-Si bridging angle in the idealized structure is always 180°. Ciraci and Batra[8] studied the idealized β-crystobalite structure (ideal A) which has the same density as the real β-crystobalite structure and with Si—O bond length equal to 1.55 Å; Schneider and Fowler[9] studied the idealized β-crystobalite structure (ideal B) which scaled to give Si—O bond length equal to 1.61 Å, same as in the α-quartz and with a very low density of 1.934 g/cm^3. Very recently, the valence-band (VB) structure of stishovite was studied for the first time by Rudra and Fowler[10] (RF) using a simple tight-binding method. The electronic structures of amorphous SiO_2 (a-SiO_2) has been studied in detail by one of us using a continuous random network (CRN) model containing 54 SiO_2 molecules in a periodic cell.[11] The purpose of this paper is to report the results of band-structure calculations on all the polymorphs of SiO_2 mentioned above plus two idealized β-crystobalite structures, ideal A and ideal B. We intend to seek any regularities in the calculated electronic structures and correlate them with the Si—O bond lengths and Si—O—Si bond angles in these crystals. Both the VB and the conduction band (CB) of stishovite are also studied in greater detail than those of Ref. 10.

II. METHOD AND APPROACH

We used a first-principles, direct-space, orthogonalized linear combination of atomic orbitals method (OLCAO) to calculate the band structures of all the polymorphs of SiO_2. The method has been adequately described in the literature[11,12] and this will not be repeated in this paper other than in a brief outline. This method of band-structure calculation has been demonstrated to be very efficient for complex crystals[13] and amorhpous structures[14] and involves no arbitrary interaction parameters.

We start with the construction of atomiclike potentials for Si and O in a α-quartz environment using a superposition of atomic charge-density model. Atomiclike basis functions are obtained by the method of contraction using Gaussian type of orbital.[15] The potential and the minimal basis set obtained are then used in the band-structure calculation using the OLCAO method.[12] Interactions up to fifth nearest neighbors are included by accurate evaluation of multicenter integrals using Gaussian transformation technique. We used the value of exchange parameter $\alpha = 0.80$ for our potential such that an indirect band gap of 8.8 eV is obtained for α-quartz which is close to the experimental value of 8.9 eV.[16] The same atomiclike potentials and basis functions are then used for the calculation of band structures of all other polymorphs. From the band structures and the wave functions obtained, the density of states (DOS) and the average effective charges for Si (Q^*_{Si}) and O atom (Q^*_O) in each polymorph are then calculated.

TABLE I. Structure and calculated properties of SiO_2 polycrystals (average bond length and bond angle in parenthesis).

Crystal Properties	(a) α-quartz	(b) β-quartz	(c) β-tridymite	(d) α-crystolbalite	(e) β-crystolbalite	(f) Keatite	(g) Coesite	(h) Stishovite	(i) Ideal A	(j) Ideal B
Lattice	Hexagonal	Hexagonal	Hexagonal	Tetragonal	Cubic	Tetragonal	Monoclinic	Tetragonal	fcc	fcc
Molecules per cell	3	3	4	4	8	12	16	2	2	2
Lattice parameters (Å)	$a=4.913$ $c=5.405$	$a=5.01$ $c=5.47$	$a=5.03$ $c=8.22$	$a=4.973$ $c=6.926$	$a=7.16$	$a=7.456$ $c=8.64$	$a=7.17$ $b=7.17$ $c=12.38$ $\gamma=120°$	$a=4.179$ $c=2.665$	$a=7.160$	$a=7.445$
Density (g/cm^3)	2.649	2.352	2.216	2.344	2.174	2.896	2.503	4.287	2.174	1.934
Si—O bonds (Å)	1.608(2) 1.611(2)	1.616(4)	1.533(2) 1.534 1.562	1.592(2) 1.596(2)	1.609(3) 1.612(1) 1.664(3) 1.649(1)	1.583 1.585 1.605 1.612 1.570 1.612(2)	1.600 1.615 1.611 1.641 1.590 1.612 1.616 1.619	1.757(4) 1.810(2)	1.55	1.61
	(1.610)	(1.616)	(1.541)	(1.594)	(1.635)	(1.595)	(1.613)	(1.775)	(1.550)	(1.610)
Si—O—Si angle (deg)	1.440	146.9	180.0	1.48.9	180.0(4) 137.2(12)	155.8 149.3	180.0(4) 143.5(4) 144.7(8) 139.0(8) 148.2(8)		180.0	180.0
					(147.9)	(152.6)	(148.4)			
E_g (eV)	8.80 $K \rightarrow \Gamma$	8.82 $A \rightarrow \Gamma$	11.15 $\Gamma \rightarrow \Gamma$	9.44 $\Gamma \rightarrow \Gamma$	8.51 $\Gamma \rightarrow \Gamma$	9.30 $\Gamma \rightarrow \Gamma$	8.37 $\Gamma \rightarrow \Gamma$	7.51 $\Gamma \rightarrow \Gamma$	10.95 $\Gamma \rightarrow \Gamma$	9.18 $\Gamma \rightarrow \Gamma$
Q^*_{Si} (electron)	0.947	0.898	0.664	0.865	0.892	0.862	0.979	1.383	0.698	0.816
Q^*_{O} (electron)	7.526	7.543	7.649	7.568	7.423	7.558	7.508	7.293	7.608	7.547
Ring structure	6	6	6	6	6	5	4		6	6

III. RESULTS AND DISCUSSION

A. α-quartz

The band structures and DOS of α-quartz have been studied by several groups: Chelikowsky and Schlüter (CS) used the self-consistent pseudopotential method;[5] Calabrese and Fowler (CF)[6] used a mixed basis to calculate the band structures at several high-symmetry **k** points and then used a tight-binding interpolation scheme to determine the complete VB structure and DOS. Laughlin, Joannopoulos, and Chadi[7] (LJC), using a tight-binding method with parameters fitted to experiment and pseudopotential results of CS calculated the band structure of α-quartz and DOS of a-SiO$_2$ represented by the Bethe lattice. We used a first-principles OLCAO method with a minimal basis to calculate the DOS of α-quartz. Prior to these studies, only the idealized structure of β-crystobalite with linear Si-O-Si configuration had been studied with the contention that the electronic structures thus calculated would be similar to the α-quartz. These studies include a simple two-parameter tight-binding study by Pantelides and Harrison,[4] a mixed-basis calculation by Schneider and Fowler[8] similar to CF, and a first-principles LCAO calculation by Ciraci and Batra[9] using a method very similar to ours.

The band structure and DOS calculated by the present method are shown in Figs. 1(a) and 2(a), respectively. The experimentally measured x-ray photoemission spectrum (XPS) for α-quartz is also plotted for comparison.[17] The agreement can be considered to be quite good, considering the facts that the theoretical DOS curve takes neither the instrumental broadening effects nor the different optical-absorption cross section[18] for electrons of different l quantum numbers into account. Furthermore, it appears that the four-peak structure in the calculated DOS of the O $2p$ bonding band between -5 and -10 eV is in agreement with the XPS data.[17] This is quite important because different polymorphs show quite different DOS features in this region which will be discussed in the following section.

In comparing our results with previous studies on α-quartz, we find that our calculated bandwidths are smaller than CF (Ref. 6) and much smaller than CS (Ref. 5). This may be partly due to the minimal basis nature of our calculation. On the other hand, comparable bandwidths for idealized β-crystobalite were obtained by CB (Ref. 8) using a method similar to ours. Our calculated O $2s$ peak locates at about -17 eV. Early experimental work put this peak at about -20.5 (Ref. 19) to -21 eV (Ref. 20). We think this discrepancy is due to the final-state screening effect that is occurring in detecting the corelike O $2s$ level. In the XPS type of experiment in which a core hole is created, the positively charged nuclei of that atom will exert a stronger effective Coulomb potential, thus shift down the level to a higher binding energy for at least a few eV.[21] The pseudopotential calculation[5] gives the O $2s$ peak at -25.5 eV. The calculation of CF (Ref. 6) shows three sharp peaks for O $2s$ between -21 and -23 eV with DOS features very different from CS and the present work. We find an indirect band gap of 8.8 eV from $K\rightarrow\Gamma$ for α-quartz; CF found a direct band gap of 6.3 eV at Γ and CS found an indirect band gap of 9.2 eV from $M\rightarrow\Gamma$. In our calculation, the top of the VB at M is only 0.016 eV below that of K, while Γ is only 0.137 eV below that of K. There are two more symmetry points with their top of VB energies between K and Γ. They are A (-0.05 eV) and L (-0.112 eV). The differences in the top of VB energies at these four points are sufficiently small; it will not be surprising that their relative order may change in more accurate calculations. The CB minimum is at Γ in all calculations on α-quartz.

The above comparison indicates that serious discrepancy still exists among the different band-structure calcula-

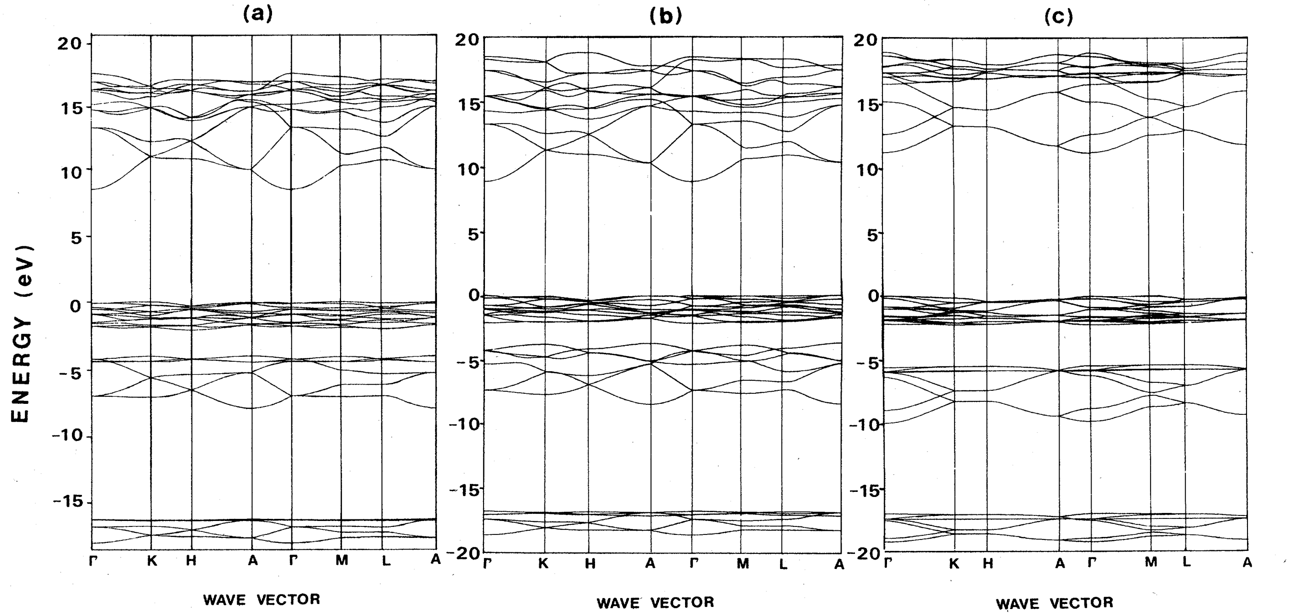

FIG. 1. Band structures of (a) α-quartz, (b) β-quartz, and (c) β-tridymite.

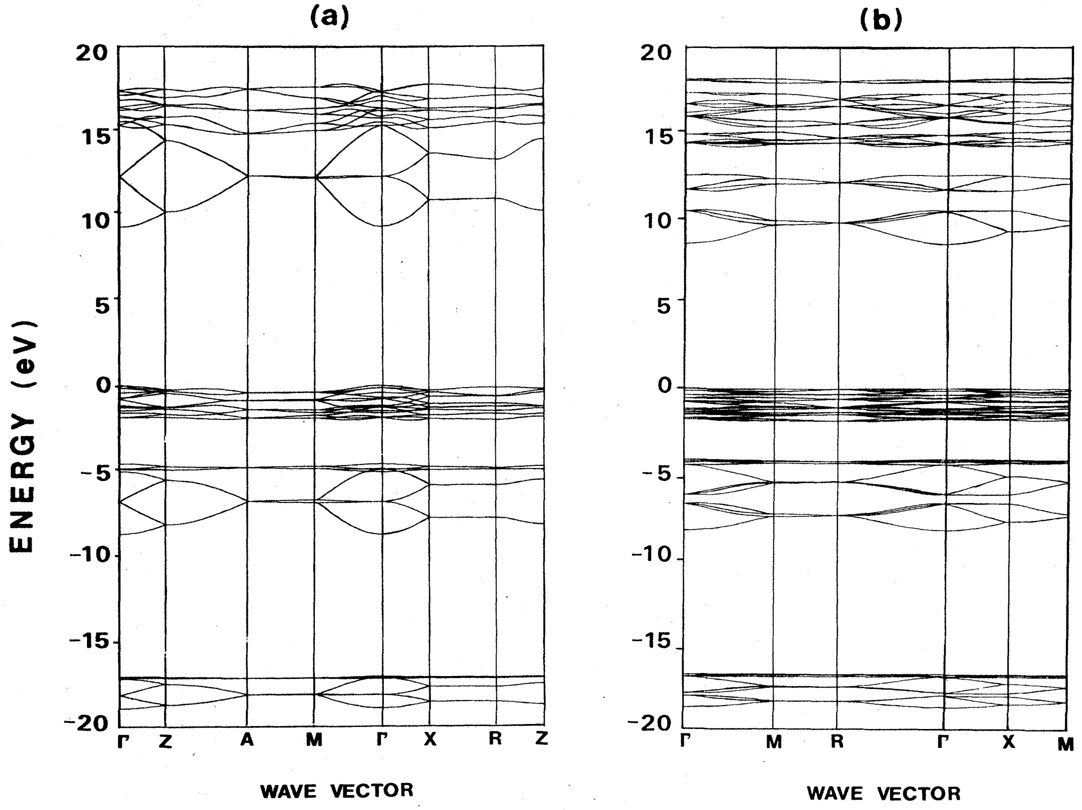

FIG. 2. Band structures of (a) α-crystobalite and (b) β-crystobalite.

tions on α-quartz using different methods. It will be very worthwhile to have more accurate calculations on α-quartz in order to resolve some of these controversies.

B. Other 4:2-coordinated polymorphs

The calculated band structures along the symmetry axes of the Brillouin zone for β-quartz and β-tridymite are shown in Figs. 1(b) and 1(c). Those of α- and β-crystobalite are shown in Fig. 2. The band structures of keatite and coesite are not plotted because, due to the complexity of these crystals, there are too many bands involved and little additional information will be added. The band structures of ideal A and ideal B structures are also not presented because these are hypothetical structures and have been studied before.[8,9] However, the DOS, which we consider to be a more important quantity, are calculated for all the 4:2-coordinated polymorphs and are shown in Fig. 3 together with that of α-quartz. Detailed examination of Fig. 3 shows considerable differences in DOS features for both the lower O 2*p* bands (σ bands) and the upper nonbonding O 2*p* bands (lone pairs). These differences are due to the slightly different bond lengths and bond angles in these crystals. Let us compare the DOS of O 2*p* bands of α-quartz and β-crystobalite as an example. For α-quartz, the upper band consists of a major peak at −0.40 eV and a weak peak at −1.70 eV; the lower band consists of a sharp peak at −4.24 eV and three smaller subpeaks at −5.20, −6.02, and −6.98 eV, respectively. For β-cyrstobalite, the upper band consists of a major peak at −1.44 eV and a minor peak at −0.32 eV while the lower band has only three structures: a sharp one at −4.25 eV and smaller but well-resolved ones at −5.51 and −7.34 eV, respectively. This difference in DOS must result from the difference in short-range order. β-crystobalite has an average Si—O bond length of 1.64 Å compared to 1.61 Å in α-quartz and two types of Si—O—Si bridging angle, 137.2° (75%) and 180° (25%). In α-quartz, all the bridging angles are equal to 144°. The DOS of O 2*s* bands with their centroids near −18 eV show much less deviation among different crystals. Another conspicuous feature that can be identified from Fig. 3 is that three polymorphs, namely β-tridymite, β-crystobalite, and coesite, all have very sharp nonbonding O 2*p* peaks at −1.82, −1.44, and −0.93 eV, respectively. Similar sharp peaks are also found in the DOS of ideal A and ideal B structures (not shown here). These are precisely the polymorphs which have 180° Si—O—Si angles. We may conclude that linear Si—O—Si configuration tend to give flat bands and consequently induce sharp O 2*p* nonbonding peaks. The various features in the VB DOS of all the 4:2-coordinated polymorphs are summarized in Table II.

In Table I we also summarize the calculated band gaps, ring structures, and the effective charges on Si and O atoms. Also listed are the Si—O bond lengths and Si—O—Si bridging angles. In order to make some detailed analysis of the effect of local short-range order on the electronic structures, all bond lengths and bridging angles are listed in addition to their mean values. With the ex-

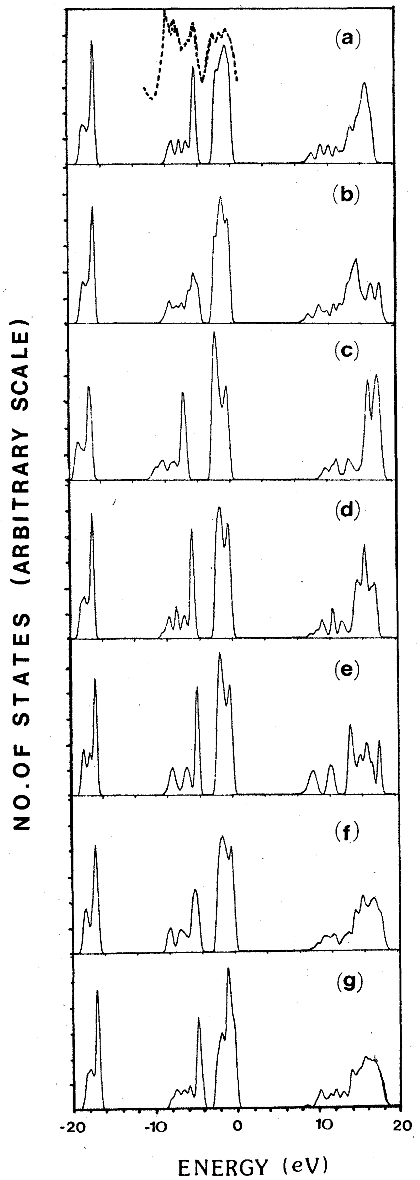

FIG. 3. Density of states of 4:2-coordinated polymorphs: (a) α-quartz, (b) β-quartz, (c) β-tridymite, (d) α-crystobalite, (e) β-crystobalite, and (f) keatite, and (g) coesite. The dotted line is the experimental data of Ref. 17 (as presented in Ref. 7) in arbitrary units.

TABLE II. Comparison of VB DOS features for 4:2-coordinated SiO_2 polymorphs.

Crystal	Peak positions (eV) O $2p$ nonbonding	 O $2p$ bonding
α-quartz	−0.40 (major)	−4.24 (major)
	−1.70 (minor)	−5.20
		−6.02 (minor)
		−6.98
β-quartz	−0.41 (minor)	−4.58 (major)
	−1.18 (major)	−5.97
	−1.96 (minor)	−6.74 (minor)
		−7.52
β-tridymite	−0.39 (minor)	−5.77 (major)
	−1.82 (major)	−6.87 (minor)
		−8.29
α-crystobalite	−0.47 (minor)	−4.82 (major)
	−1.45 (major)	−5.80
		−6.79 (minor)
		−7.77
β-crystobalite	−0.32 (minor)	−4.25
	−1.44 (major)	−5.51 (major)
		−7.34
Keatite	−0.31 (minor)	−4.81 (major)
	−1.30 (major)	−6.63 (minor)
		−7.90 (major)
Coesite	−0.25 (shoulder)	−4.62 (major)
	−0.93 (major)	−5.77
	−1.82 (minor)	−6.53 (minor)
		−7.42

ception of α- and β-quartz which have indirect band gaps of 8.80 eV ($K \rightarrow \Gamma$) and 8.82 eV ($A \rightarrow \Gamma$), respectively, all crystals including the ideal A and ideal B have direct band gaps at Γ.

We find significant correlations between the band gap E_g and the Si—O bond lengths and Si—O—Si bond angles. In Fig. 4 we plot the E_g against Si—O bond length. The horizontal error bars indicate the maximum and the minimum Si—O bond in a particular crystal. There is an excellent linear correlation with a slope of -0.35×10^2 eV/Å. In Fig. 5 we plot E_g against Si—O—Si angle; the horizontal error bars indicate the maximum and the minimum bridging angle. The linear correlation with average bridging angle is not as clear as in the case of average bond length; however, if we only consider the *minimum bridging angle* instead of the average bridging angle and delete the data for ideal B, a much better linear correlation with a slope of 0.065 eV/deg can be established. Since in the network type of structure, the Si—O bond lengths and O bridging angles are not completely independent, probably the short Si—O bond length is associated with a large Si—O—Si angle and vice versa. The above correlation analysis indicates that Si-O bond length has a more dominating effect on the electronic structures than the Si—O—Si angle. This point, which has been discussed in the context of electronic structures of a-SiO_2 (Ref. 11) is generally not well recognized.

Attempts are also made to correlate the effective atomic charges Q^*_{Si} and Q^*_{O} with bond lengths and bond angles. We find only qualitative correlation with effective charges, namely, short Si—O bond length and large Si—O—Si angle are associated with small Q^*_{Si} and large Q^*_{O} and vice versa. The effective charges obtained from our band-structure calculations are more ionic than the molecular orbital calculations on disiloxy groups.[22] This is probably due to the more localized nature of the wave functions in the molecular studies, but may also due to quite different approaches in the electronic structure calculations. As discussed above, the bond angles and bond lengths are not independent of each other in crystalline and amorphous phases; conclusions reached about their relative importance based on isolated molecular studies

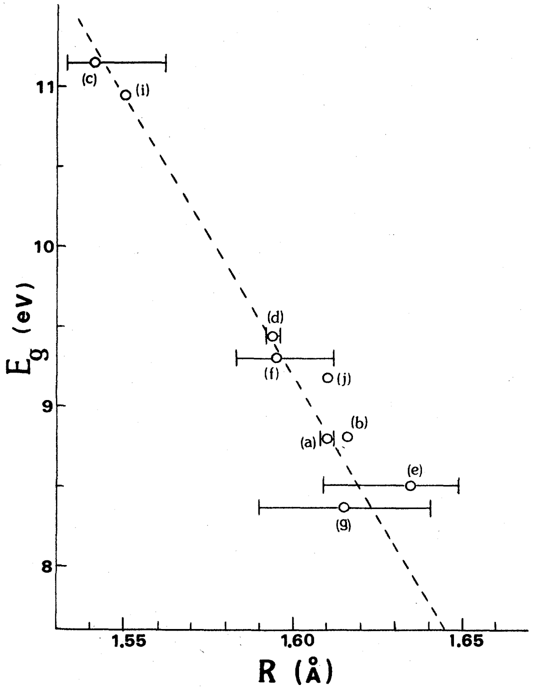

FIG. 4. Correlation plot of band gap E_g vs Si—O bond length in 4:2-coordinated polymorphs: labels (a)—(g) same as in Fig. 3; (i) ideal A; (j) ideal B. Horizontal error bars indicate minimum and maximum bond lengths.

may not be conclusive. Most of these polymorphs have six-member ring structures. Keatite has a five-member ring structure and coesite has four-member ring structure. Our calculated results on DOS and band gaps fail to establish any correlations with ring structures. It appears that the ring structure *per se* plays no crucial role in determining the electronic structures except those already reflected in the bond lengths and bond angles. From all the correlated studies discussed above, the ideal B structure is always far from any possible correlational link except in the case of E_g versus bond-length study. This may indicate that structures similar to this hypothetical ultralow-density form may never occur in nature.

C. Stishovite

Although the existence of stishovite phase of SiO_2 has been known for some time,[23,24] accurate determination of atomic positions has been achieved only recently.[2] Based on the newly determined structures, Rudra and Fowler[10] (RF) calculated the first VB structures of stishovite using a simple tight-binding method. We used the first-principles OLCAO method to calculate the band structures and DOS of stishovite. The results are shown in Figs. 6 and 7, respectively. A direct band gap of 7.51 eV at Γ is found which is smaller than the gap values of any of the 4:2-coordinated polymorphs listed in Table I. Similar to RF, we found no gap within the O2*p* bands, and the general shape of VB from the two calculations are similar. The major difference appears to be that our bands are narrower. The bands are sufficiently complicated to give rise

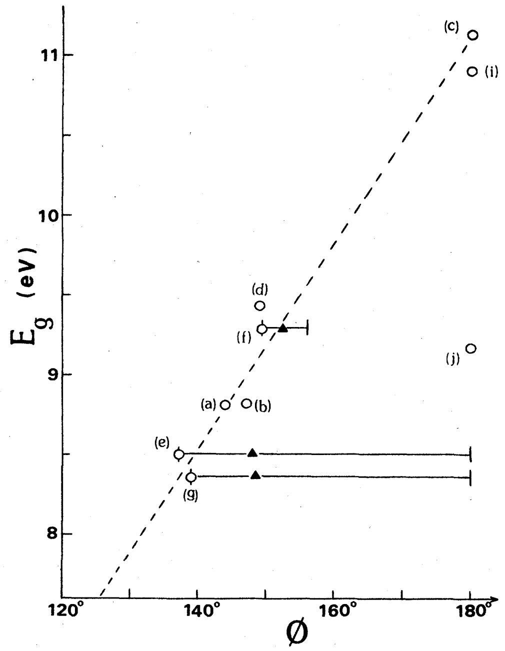

FIG. 5. Correlation plot of band gap E_g vs Si—O—Si bridging angle in 4:2-coordinated polymorphs. Notations are the same as Fig. 4. Horizontal error bars indicate minimum and maximum bond angles.

to multiple structures in the DOS. For O 2*p* bands, we find a series of major peaks at −1.40, −3.57, −5.23, −6.56, −7.90, and −8.90 eV plus a few smaller structures. The O 2*s* bands show structures at −17.41, −18.91, −19.91, and −21.0 eV. These DOS features are

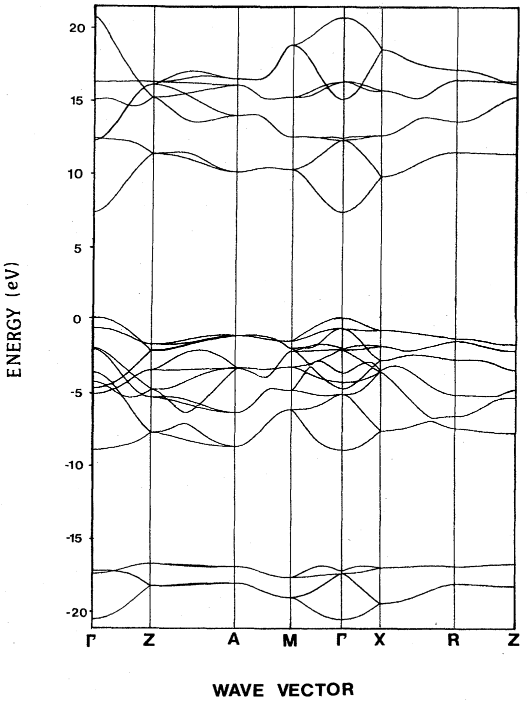

FIG. 6. Band structure of stishovite.

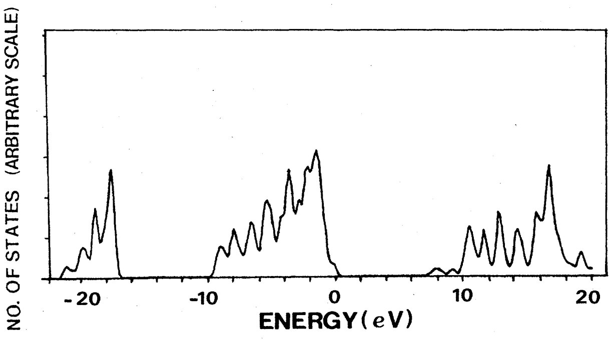

FIG. 7. Density of states of stishovite.

quite different from those obtained by RF; for example, RF's calculations give only two structures in the DOS of O 2*s* band. In comparing with the 4:2-coordinated SiO_2 polymorphs of Secs. III A and III B, the bandwidths of stishovite are much larger, reflecting an increased interaction due to increased coordination number. The calculated effective charges per atom are also quite different from the 4:2-coordinated polymorphs A and B. We obtained $Q^*_{Si}=1.38$ electrons and $Q^*_{O}=7.29$ electrons, while the largest Q^*_{Si} and the smallest Q^*_{O} of all the 4:2-coordinated polymorphs are 0.98 electron (coesite) and 7.42 electrons (β-crystobalite), respectively. This clearly indicates an increased covalent bonding character in stishovite. The electron effective mass at Γ for stishovite is found to be similar to that of α-quartz.

IV. CONCLUSION

We have calculated the band structures for all polycrystalline forms of SiO_2 with known crystal parameters. With the exception of α-quartz and stishovite, this is the first time the electronic structures of these polymorphs have been elucidated. The real β-crystobalite structure is studied instead of hypothetical structures studied before and substantially different electronic structures are demonstrated. For α-quartz, comparison with other existing calculations and experimental measurement shows only general agreement with some substantial differences still exists. Further detailed studies using more accurate procedures will be very helpful. In the case of the 4:2-coordinated SiO_2, a strong linear correlation is established between the band gap and the Si—O bond length, and to a lesser extent, between the band gap and the minimum Si—O—Si bridging angle. For the high-density-phase stishovite, detailed band structure is calculated using a first-principles method and compared with the other only existing empirical calculation. Because of increased coordination number in stishovite, it has more covalent bonding character than the 4:2-bonded polymorphs, and has a quite different electronic structure. We expect similar differences to be found between the octahedrally coordinated and tetrahedrally coordinated GeO_2.

In an earlier study of electronic structures of *a*-SiO_2,[11] we employed a CRN model in which all the SiO_2 molecules are 4:2 coordinated. In this model of *a*-SiO_2, the bond lengths and bond angles assume a continuous distribution with maximum at 1.61 Å and 147°, respectively. It has been pointed out previously that the electronic structures of *a*-SiO_2 depend more on the distribution of bond length than on bond angle;[11] this argument is further reenforced by the present systematic study on all polycrystalline forms of SiO_2 in this paper. The DOS of *a*-SiO_2 calculated actually resembles that of coesite [Fig. 3(g)] and is quite different from β-crystobalite. Recently, Phillips[25] argued that the CRN model is not the correct structure for *a*-SiO_2, and proposed a cluster model for *a*-SiO_2 which consists of large clusters of β-crystobalite of about 50-60 Å diameter in size. As discussed in Sec. III B, the DOS of β-crystobalite is quite different from that of either α-quartz or the CRN model of *a*-SiO_2. Accurate photoemission experiments with sufficient high resolution may be able to resolve this controversial yet important issue. It is also possible that 6:3-coordinated SiO_2 molecules may exist in the amorphous phase. As previously pointed out in Ref. 10, if these threefold oxygens are present in sufficient amount, the gap in the O 2*p* VB will disappear and the gap between the VB and CB will decrease. It is not clear, however, to what extent such threefold oxygens will affect the localized states near the valence-band edges of *a*-SiO_2.[11] Further detailed studies in this direction will be most interesting in understanding certain properties of both crystalline and amorphous forms of silicon dioxide.

ACKNOWLEDGMENTS

We thank Professor W. B. Fowler for providing us with information on his work on stishovite prior to publication. This research was supported by Department of Energy Contract Nos. DE-AC02-79ER10462 and DE-FG02-84ER45170.

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