

Computer Study of the Ideal and Real SiO₂/Si(100) Interfaces

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The AM1 semi-empirical method combined with the geometry optimization procedure was used to study the atomic structure of ideal and real SiO₂/Si(100) interfaces. It was shown that the average Si-O distances and bond angles in silica near the SiO₂/Si interface are close to the bulk silica values. Using *ab initio* local density approach it was found that the SiO₂/Si interface generates acceptor states in the silicon substrate near the interface. Just at the interface the energy gap is absent due to the partially unsaturated silicon bonds, although the silica forbidden gap of 4-5 eV appears at a few angstrom distance from the interface rapidly approaching 8 eV of bulk silica.

1. Introduction

It is known that the native oxide film on the silicon surface has the electronic structure close to that of bulk amorphous silica (*a*-SiO₂) even at thicknesses less than 1 nm [1, 2]. The operation of a MOS transistor, whose gate insulator film thickness was nearly 2 nm, was confirmed recently [3], and the technologists continue to work on reduction of thickness of the oxide layer. Studies aimed at the reduction of the lateral size of the devices are also performed gradually moving to the nanometer scale. However, there is a shortage of information on the electronic structure of such small silica particles placed upon the silicon surface. First of all it is important to know whether a wide forbidden gap is preserved. In the works [4, 5] the electronic structure of nanometer sized silica particles (*n*-fold SiO₂ rings) placed upon the Si(100) surface was studied without any optimization effects. It had been found that the interaction of the 6- and 4-fold planar SiO₂ rings with the silicon surface changes the electronic structure of the silica particle very weakly and the surface insulator bandgap of 7-8 eV was remaining in its density of states. The electronic structure of the 3-fold planar

ring which contacted the silicon surface undergoes a significant reconstruction. Its surface bandgap was 3.7 eV (instead of 7.6 eV for the free particle).

In this work the $\text{SiO}_2/\text{Si}(100)$ interface is studied using the atomic geometry optimization in both silica and silicon contacters. The $\text{SiO}_2/\text{Si}(100)$ interface is formed by placing some amount of oxygen and silicon atoms above the $\text{Si}(100)$ - 2×1 surface and optimizing the whole atomic structure. Two cases are studied: namely, the ideal and real cases. In the ideal case O and Si atoms are placed in a special regular way to saturate all $\text{Si}(100)$ surface bonds. In the real case their initial placements are random, thus silicon surface bonds are not saturated completely.

2. Methods of calculations

To study the atomic geometry evolutions the advanced semiempirical quantum-chemical method AM1 (Austin Model 1) [6] was used. It is a version of the modified intermediate neglect of differential overlap (MINDO) [7, 8, 9], realized in the frame of the CLUSTER-Z1 package [10, 11]. This package allows to optimize atomic configurations by the minimization of the total energy gradients over all atomic coordinates. Therefore, we can simulate self-formation of equilibrium particles from some chaotic atomic clusters.

To calculate the electronic structure the discrete-variational local-density approximation (LDA) method in the pseudopotential version [12] was used. All densities of states (DOS) were represented by superpositions of the Gaussian functions centered on each energy level. The Fermi energy was obtained integrating the total DOS to make the integral equal to the number of electrons. The basis set of the O $2s$, $2p$ and Si $3s$, $3p$ numerical pseudo-wave-functions and the Hedin-Lundqvist exchange-correlation potential [13] were used.

Semiempirical methods are faster than *ab initio* methods, but their accuracy is limited by the need to choose the correct set of parameters. Therefore, the ability of a semiempirical method to describe an arbitrary configuration of atoms must be verified.

To verify the AM1 method for Si-O interactions the test calculations of the oxygen chemo-adsorption on the $\text{Si}(100)$ - 2×1 surface were carried out recently [14]. As found by Uchiyama and Tsukada [16] using the local density functional formalism, the back-bond sites of the dimer-atoms are the most stable positions for the adsorption of single oxygen atoms. In the work [14] the same result was obtained.

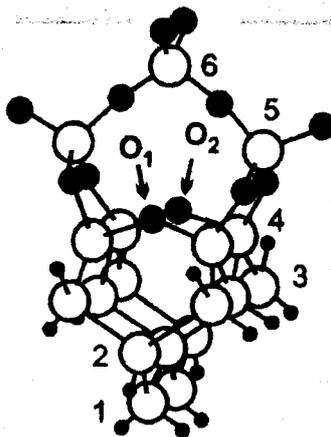


Figure 1. Atomic scheme of the ideal $\text{SiO}_2/\text{Si}(100)$ cluster system. Large black circles are oxygen atoms, small black circles are H atoms which terminate broken Si bonds. Silicon atoms are presented by the white circles. The numbers 1-7 correspond to the panels 1-7 of Fig.2.

3. Ideal $\text{SiO}_2/\text{Si}(100)$ interface

To simulate the ideal $\text{SiO}_2/\text{Si}(100)$ interface the $\text{Si}_{15}\text{H}_{14}$ cluster was taken as a model of the $\text{Si}(100)$ surface. This cluster consists of 15 Si atoms organized in four atomic layers where broken Si bonds (except the surface ones) are terminated with 16 H atoms. Initially all Si atoms were placed in ideal positions and all Si-H distances were set to the equilibrium value equal to 1.46 Å. During the optimization procedure all H atoms were fixed.

Oxygen and silicon atoms were placed in succession above the silicon cluster (atom by atom) and the total atomic structure was optimized resulting in the formation of the closed Si-O ring-like structure. The overall view of the ideal optimized $\text{SiO}_2/\text{Si}(100)$ cluster system is shown in Fig.1. The silica part of the system consists of 12 oxygen atoms and 3 silicon atoms. Two oxygen atoms (O_1 and O_2) make bridges between Si dimer atoms and other oxygen atoms (together with three silicon atoms) simulate a border cell of the SiO_2 net. No one of Si atoms has dangling bonds in this system.

No doubt, the ideal $\text{SiO}_2/\text{Si}(100)$ interface may be modelled by many different ways. However, the above model allow us to compare directly our present results with the results of the works [4, 5] in which the interaction of the $\text{Si}_{15}\text{H}_{14}$ cluster with single SiO_2 rings (Fig.3) was studied without any optimization.

First of all, some words about Si-O distances and O-Si-O angles. In Table 1 our present results are compared with the *ab initio* LDA results [4] obtained for

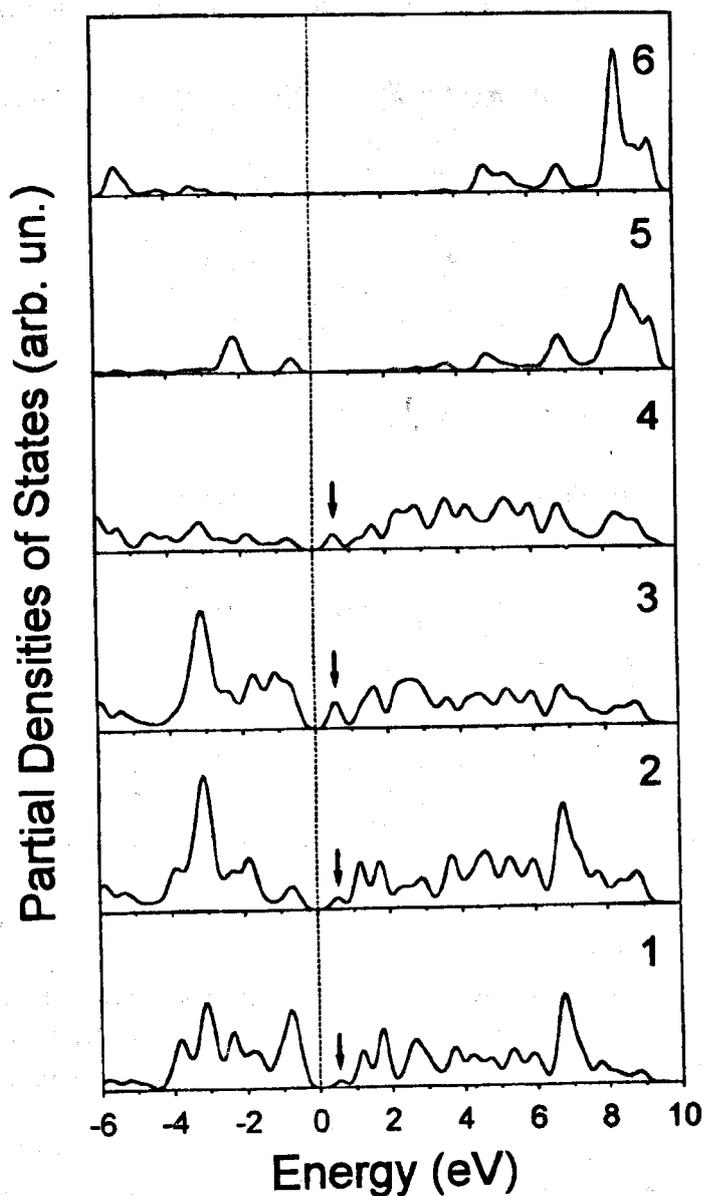


Figure 2. Electronic structure of the ideal $\text{SiO}_2/\text{Si}(100)$ cluster system. The vertical dotted line corresponds to the Fermi energy position. The panels 1-7 are numbered as Si atoms in Fig.1.

the 4-, 5-, and 6-fold planar SiO_2 rings. Calculated results of Rino *et al.* [15] and experimental bulk values [17] are also presented there. We note that our present average O-Si-O angle is closer to experimental bulk data than reported n -fold ring values. However, our average Si-O bond length 1.66 Å is larger by

n	Rino <i>et al.</i> [15]			Previous values (LDA) [4]			Ideal SiO ₂ /Si (average)	Bulk SiO ₂ [17]
	4	5	6	4	5	6		
$d(\text{Si-O})$	1.62	1.62	1.62	1.61	1.62	1.67	1.66	1.61
$\phi(\text{O-Si-O})$	104	108	108.5	106	107	112	109.5	109

Table 1. Bond lengths $d(\text{Si-O})$ and bond angles $\phi(\text{O-Si-O})$ in n -fold SiO₂ rings and in the ideal SiO₂/Si(100) system.

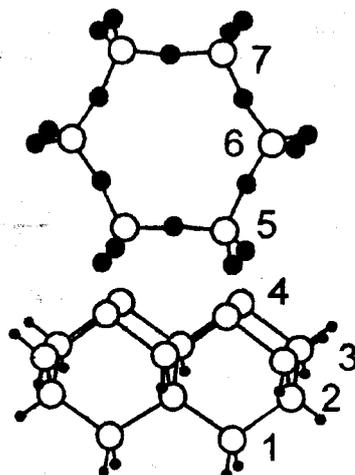


Figure 3. Atomic scheme of the six-fold SiO₂ ring/Si(100) cluster system. Large black circles are oxygen atoms, small black circles are H atoms which terminate broken Si bonds. Silicon atoms are shown by the white circles. The numbers 1-7 correspond to the panels 1-7 of Fig.4.

0.05 Å.

Now let us consider the electronic structure. As noted above, to calculate the electronic states of the SiO₂/Si(100) cluster system we used the *ab initio* LDA method. Figure 2 shows the densities of electronic states projected on Si atoms of the silicon substrate (panels 1-4) and SiO₂ chain (panels 5-7). Panel number correspond to the numbers of Si atoms in Fig.1. Previous unoptimized results are presented in Fig.4.

We see that the optimization modifies the electronic structure of the ideal SiO₂/Si(100) interface, especially the electronic structure of the silicon part of the system. First of all, the density of states of the optimized cluster has no states at the Fermi level (panel 4), and this is due to the absence of unsaturated

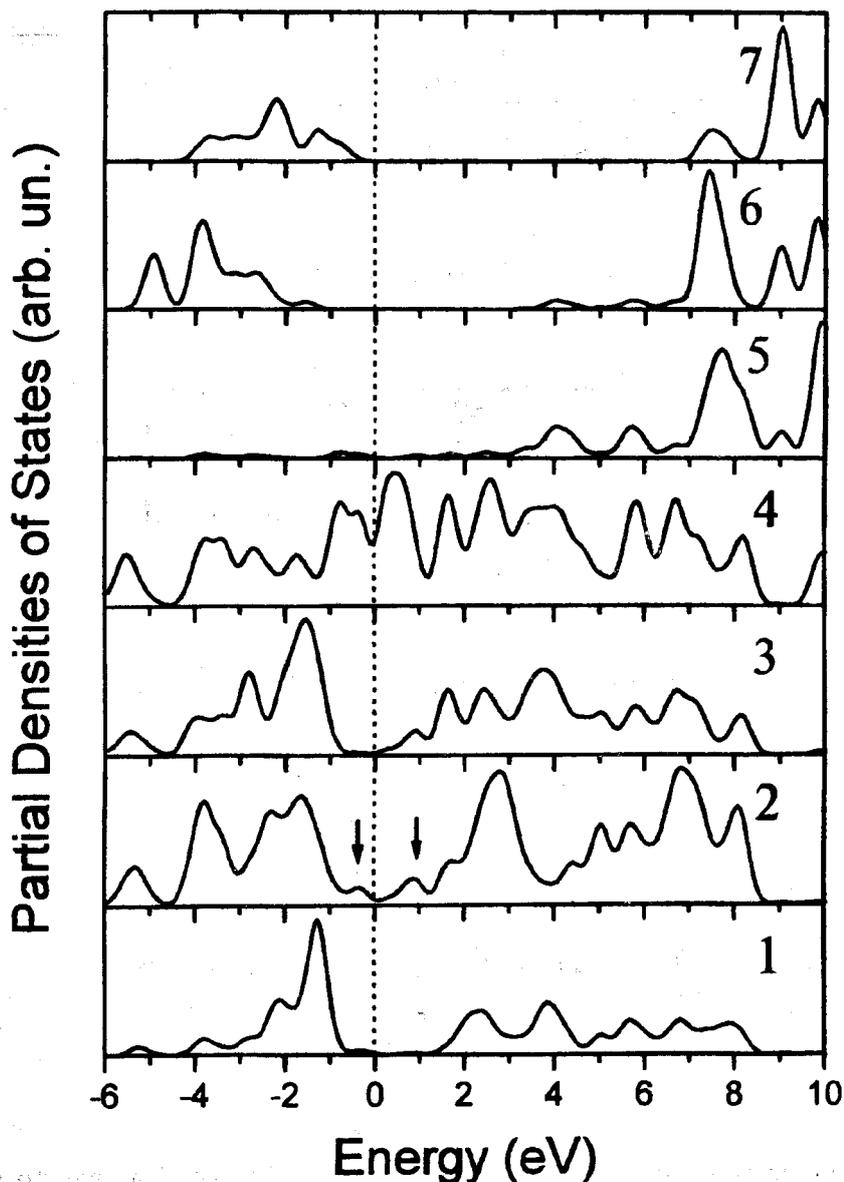


Figure 4. Electronic structure of the six-fold SiO_2 ring/Si(100) cluster system. The vertical dotted line corresponds to the Fermi energy position. The panels 1-7 are numbered as Si atoms in Fig.3.

interface silicon bonds. Interface states (marked by arrows) are seen only above the Fermi level in the panels 1-3. However, the total shape of the valence band of silicon (panels 1-4) is modified rather noticeably because of the strong interaction between silicon and SiO_2 . In other words, the ideal $\text{SiO}_2/\text{Si}(100)$

	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
SiO ₂ /Si(100)	4	3	3	1	2	1
Free SiO ₂ [14]	8	5	2	2	1	0

Table 2. Statistics (the average numbers) of n -fold Si-O rings in the silica part of the ideal SiO₂/Si(100) system and in the free silica particle of the same size (27 SiO₂ molecules).

interface shows itself as an acceptor.

Comparing the panels 5,6 of Fig.2 and the panels 5-7 of Fig.4 we note that the optimization of the ideal SiO₂/Si(100) interface leads to the reduction of the forbidden energy gap in the electronic states of the silica Si atoms. It is 5.5 eV instead of 7.9 eV which was obtained without optimization [5].

4. Real SiO₂/Si(100) interface

The real SiO₂/Si(100) interface was formed in the following way. Twenty seven SiO₂ molecules were placed randomly above the Si(100) cluster (Si₆₅H₅₄) where the 2×1 superstructure was formed previously. Then the CLUSTER-Z1 optimization procedure was applied to obtain equilibrium atomic geometries. The CLUSTER-Z1 optimization procedure does not contain any temperature effects and does not lead the system to the global energy minimum but to a local one only. Therefore, in reality, our equilibrium atomic geometries are quasi-equilibrium. To study how the final atomic geometry of the SiO₂/Si(100) interface depends on the initial molecular placement we repeated the calculations for five different random distributions of SiO₂ molecules. A typical final image of the silica-Si interface is shown in Fig.5.

4.1 Statistics of n -fold Si-O rings

Table 2 presents the statistics of n -fold Si-O rings in the silica part of the silica-Si interface system in comparison with the results obtained for the free silica particle of the same size [14]. One can see that in the SiO₂/Si system the numbers of 2-fold and 3-fold rings are less than in the free silica particles, but the numbers of 4-, 6-, and 7-fold rings are greater. This fact correlates with the model calculations of Rino *et al.* [15] where the six-fold rings were found to dominate in bulk silica, as well as with the results of Grunthaner *et al.* [18] where it was argued that the four-fold rings predominate in thin oxide films.

4.2 Interatomic distances

Interatomic distances in the amorphous state are usually described by the

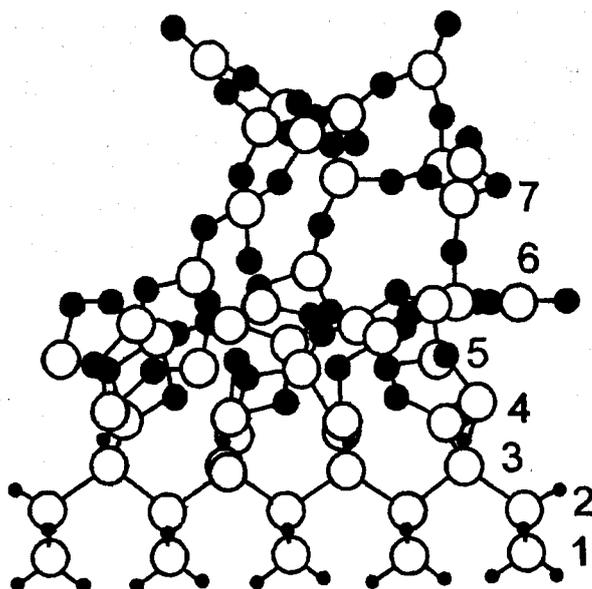


Figure 5. Atomic scheme of the real $\text{SiO}_2/\text{Si}(100)$ cluster system. Large black circles are oxygen atoms, small black circles are H atoms which terminate broken Si bonds. Silicon atoms are presented by the white circles. The numbers 1-7 correspond to the panels 1-7 of Fig.8.

pair distribution functions, $g_{\alpha\beta}(r)$, where α and β correspond to different kinds of atoms. This function expresses the probability to find a β atom at a distance r from an α -atom. The pair distribution functions, $g_{\text{Si-Si}}(r)$, $g_{\text{Si-O}}(r)$ and $g_{\text{O-O}}(r)$, for amorphous bulk silica were calculated by Rino *et al.* [15]. They are shown in Fig.6(a). For nanometer sized silica particles these functions were calculated in the work [14]. The results are presented in Fig.6(b). The present results are shown in Fig.6(c).

Analyzing the plots of Fig.6 we note that on the whole the pair distribution functions of the silica particles formed on the silicon surface are very close to those of free silica particles. In both cases the Si-O bond lengths lie between 1.55 and 1.95 Å. The shortest bonds (1.55 to 1.65 Å) correspond to a single O atom bonded only to one Si neighbour. The majority of inward Si-O bond lengths lie between 1.7 and 1.8 Å. The longest bonds (1.8 to 1.95 Å) correspond to atoms of Si-O zigzag chains which connect different rings.

The distributions of the shortest Si-Si distances (near 3 Å) in Fig.6(b,c) are bimodal. The first peak (≈ 2.7 Å) corresponds to two-fold rings, the second peak (≈ 3.3 Å) displays the Si-Si distances in all other n -fold rings with $n > 2$. The number of the two-fold rings in our SiO_2/Si system is less than in the free

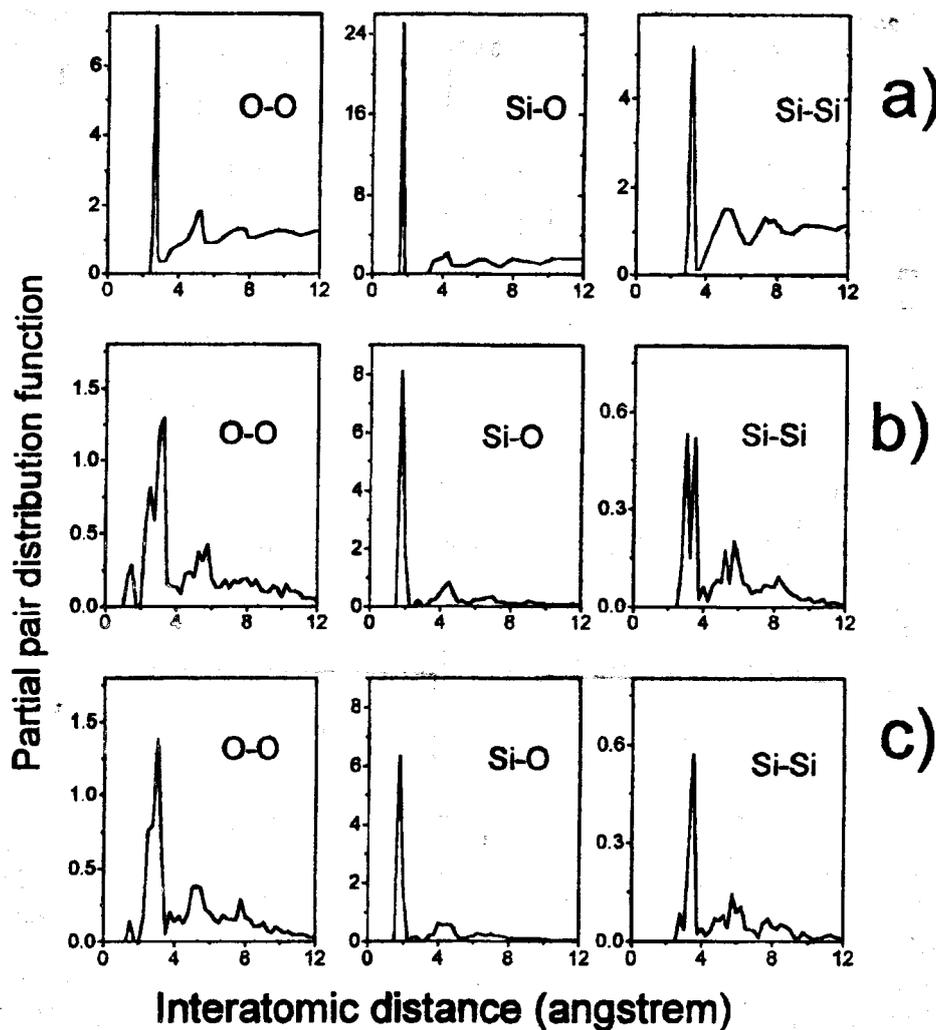


Figure 6. Pair distribution functions for various SiO_2 systems.

silica particle, therefore the amplitude of the first peak in Fig.6(c) is smaller than that in Fig.6(b).

Plots of the O-O distributions in Fig.6(b,c) look like the Rino model results except the region near 1.3 \AA where a small additional peak is observed. This peak is due to directly bonded O-O pairs which are the structure defects in silica. This peak decreases as we go from the free silica particles (Fig.6b) to the SiO_2/Si system (Fig.6c), where the number of O-O pairs is lower. Bifurcation of the main first peak (Fig.6b near 3 \AA) is the same as the described above for the Si-Si bifurcation. Namely, the left shoulder of this peak (near 2.2 \AA) corresponds to O-O distances in two-fold rings, the right shoulder (near 3.1 \AA)

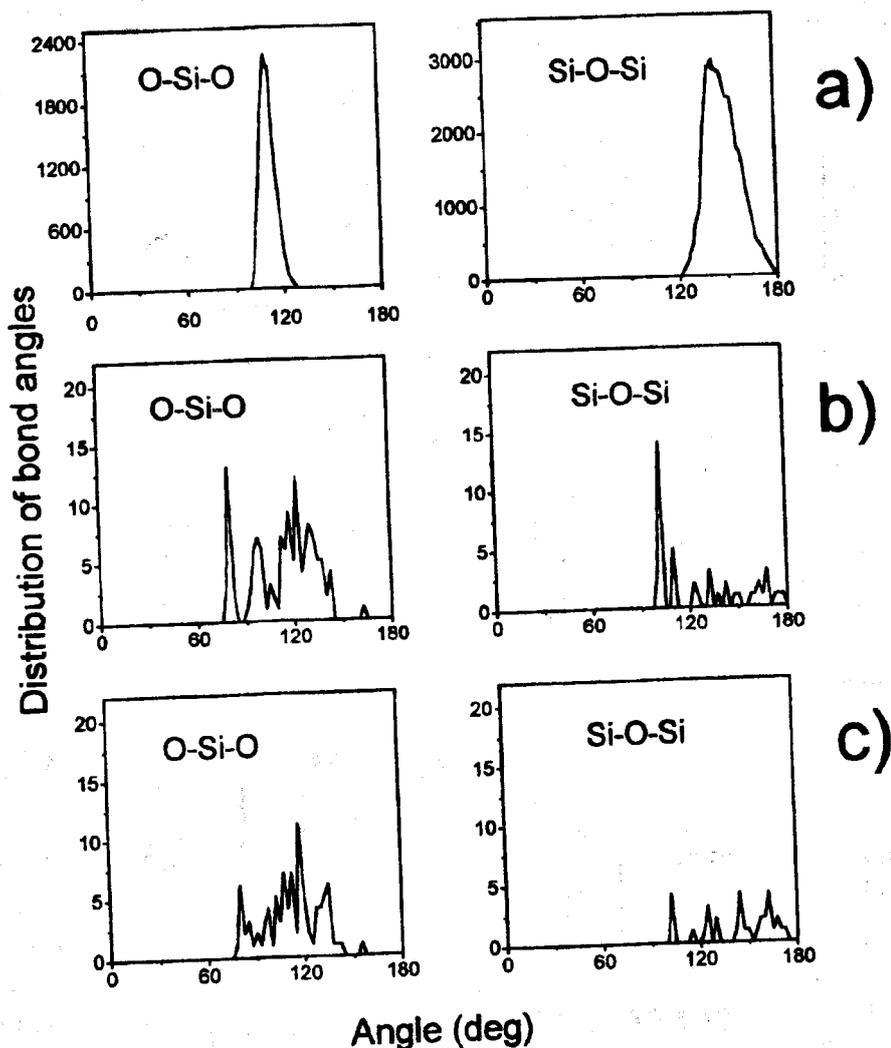


Figure 7. Distribution of bond angles for various SiO_2 systems.

are the larger O-O distances in larger rings. This bifurcation is practically absent in the SiO_2/Si case (Fig.6c).

4.3 Bond angle distributions

So far as Si-O bonds predominate in silica, the most important bond angles are O-Si-O and Si-O-Si angles. Fig.7(a) presents the results of Rino *et al.* [15] for a model of amorphous silica. They calculated the average O-Si-O angle of 109° and the Si-O-Si angle of 142° in agreement with experiments [19, 20]. The results for free silica particles [14] are shown in Fig. 7(b), and the present results for the SiO_2/Si system are plotted in Fig. 7(c).

The O-Si-O bond angles in the free silica particles and in the SiO_2/Si system

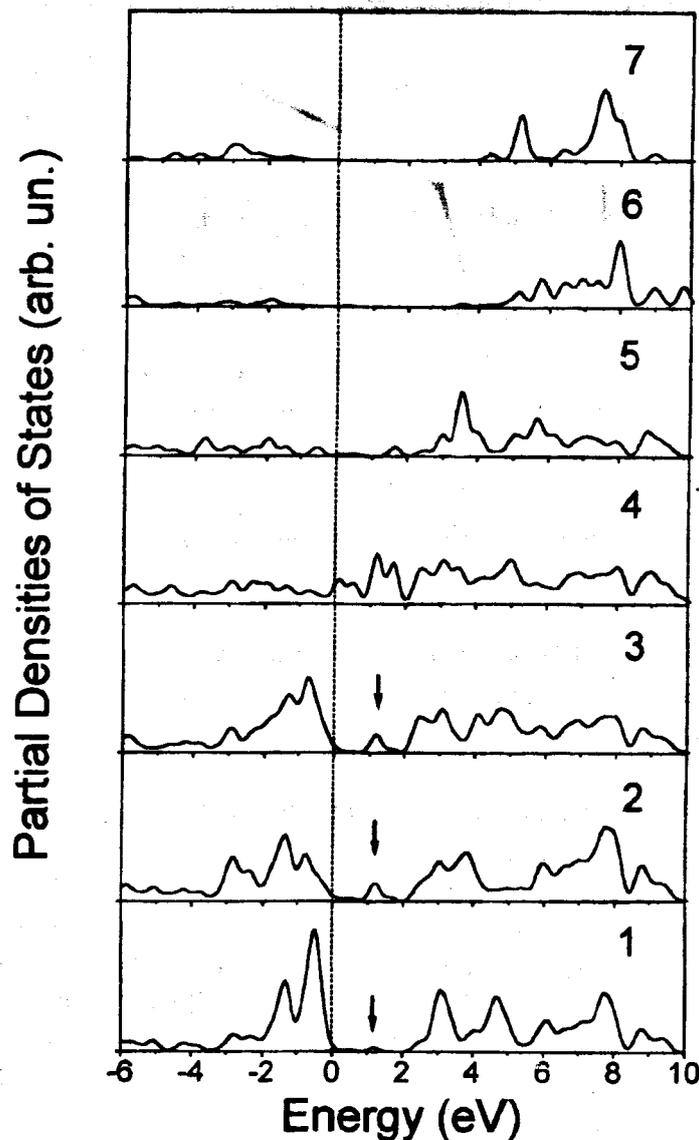


Figure 8. Electronic structure of the six-fold SiO_2 ring/ $\text{Si}(100)$ cluster system. The vertical dotted line corresponds to the Fermi energy position. The panels 1–7 are numbered as Si atoms in Fig.5.

are range from 70 to 160° . A separate peak near 75° is formed by inward-inward O-O pairs of 2-fold rings. The number of 2-fold rings in the SiO_2/Si system is less than in free SiO_2 particles, thus this peak in Fig.7c is lower than in Fig.7b.

The largest angles ($> 120^\circ$) correspond to inward-outward O-O pairs of all kinds of rings, and, on the whole, the larger angles are concentrated near 120°

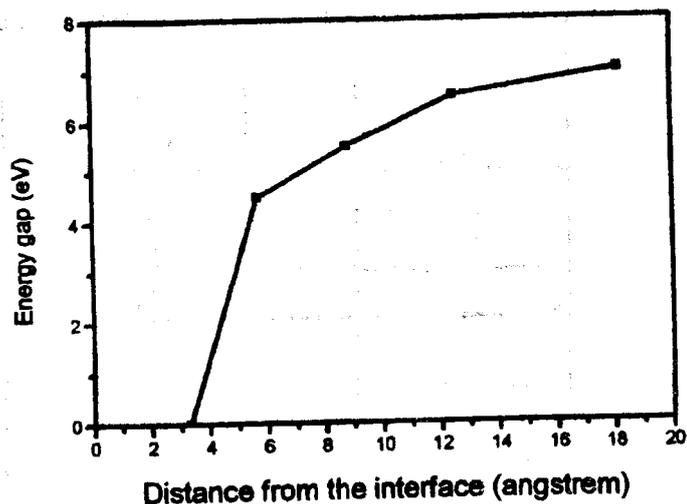


Figure 9. Dependence of the silica forbidden gap width on the distance from the silicon substrate.

in the free silica particle case, but their average value in the SiO_2/Si system is 110° which is close to the Rino model data (Fig.7a).

Outward O-atoms do not participate in the formation of Si-O-Si bond angles, thus the Si-O-Si bond angle distributions are easier for interpretation than the above O-Si-O ones. Peaks near 105° correspond to the 2-fold rings which are absent in bulk silica and dominate in free silica particles. Other angles are located around 150° in agreement with 145° of Rino *et al.* [15].

4.4 Electronic structure Electronic structure of the real $\text{SiO}_2/\text{Si}(100)$ interface calculated using the LDA approach is shown in Fig.8. Similar to Figs.2 and 4 the panels 1-4 present the partial DOS of silicon substrate atomic layers (counting from Si "bulk" to interface). The DOS at the panels 5-7 were plotted for Si atoms situated within the silica part of the system (3.3, 5.7, and 8.8 Å from the silicon substrate, respectively).

Comparing Fig.8 with Figs.2 and 4 we note that the electronic structure of silicon far from the real $\text{SiO}_2/\text{Si}(100)$ interface (the panel 1) is practically the same as in the $\text{SiO}_2\text{-ring}/\text{Si}(100)$ case. In other words, a simple $\text{SiO}_2\text{-ring}/\text{Si}(100)$ model [4] ignoring any atomic optimization describes the electronic structure of the deep silicon layers better than the ideal model with atomic optimization. Moving up from the panel 1 to the panel 3 of Fig.8 we see that the semiconductor energy gap of the silicon substrate has an acceptor state (marked by an arrow), just like it was in the ideal interface case (Fig.2). Just at the interface (panels 4 and 5) the energy gap vanishes, but then—in panels 6 and 7—the forbidden insulator energy gap appears and increases up to 5.5 eV. The whole

picture of the dependence of the silica forbidden gap on the distance from the silicon substrate is shown in Fig.9. It is clear that the forbidden gap aspires tends to some limit, and this limit is about 8 eV.

5. Conclusion

In summary, the present calculations show that the SiO₂/Si interface generates acceptor states in the silicon substrate near the interface. Just at the interface the energy gap is absent due to the partially unsaturated silicon bonds, although the silica forbidden gap of 4–5 eV appears at a few angstrom distance from the interface approaching 8 eV in the bulk silica. Average Si-O distances and bond angles in silica near the SiO₂/Si interface are close to the bulk silica values.

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