

Nonparametrized calculation of the electronic and vibrational structure of amorphous SiO_x

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A nonparametrized calculation of both the electronic and vibrational structures of SiO_x for the complete range of oxygen concentration is presented. The equilibrium atomic geometries, charge distributions, and force constants between the atoms are calculated from first principles. It is found that the equilibrium distance and force constants between silicon and oxygen at the Si-O-Si bond depend on the local geometry and the oxygen concentration. The calculated photoemission response as well as the infrared absorption are in good agreement with experimental data.

Amorphous oxides of silicon that are nonstoichiometric are found in many different situations. In some cases, as in oxidized silicon surfaces, the presence of SiO_x at the interface is difficult to avoid, and is responsible for the electronic properties of this interface. In other cases, the oxygen content can be controlled to produce samples of the desired composition in order to tailor the electronic properties of the material such as the optical-gap width, conductivity, etc. From the experimental point of view there have been optical absorption, infrared, Raman, and photoemission (at both ultraviolet and x-ray regimes) studies that have helped to identify the basic geometrical structure of the amorphous alloy.¹⁻⁵ From the theoretical point of view, however, the lack of periodicity and the disordered composition make the study of these and similar alloys rather complicated, and thus far only parametrized calculations have been reported.⁶

In this work we present nonparametrized calculations of the electronic and vibrational structure of SiO_x for the whole range of oxygen concentrations. So far nonparametrized calculations involving oxygen have been reported in the literature for either crystalline SiO₂ (Ref. 7) or impurities in crystalline silicon.⁸⁻¹⁰ The present calculations are based on a recently developed method to calculate total energies and charge distributions in real space from first principles.^{11,12} A similar method to ours has been developed by van Beest, Kramer, and van Santen¹³ to calculate force fields for silicas and aluminophosphates. Our method is based in the Hartree-Fock approximation which allows us to obtain atomic configurations, as well as Hamiltonian matrix elements between atomic orbitals, and force constants between the atoms. We consider only valence electrons, the effect of the core electrons being accounted for by the inclusion of nonlocal pseudopotentials. The minimal basis considered here contains only one 3s and three 3p orbitals per silicon atom and one 2s and three 2p per oxygen atom.

To establish the bond distances and to calculate the Hamiltonian matrix elements that enter in the calculations, as well as the force constants between the atoms, we have performed a series of total-energy calculations in clusters of atoms for different atomic configurations. We deal with clusters such that the silicon atoms in a particu-

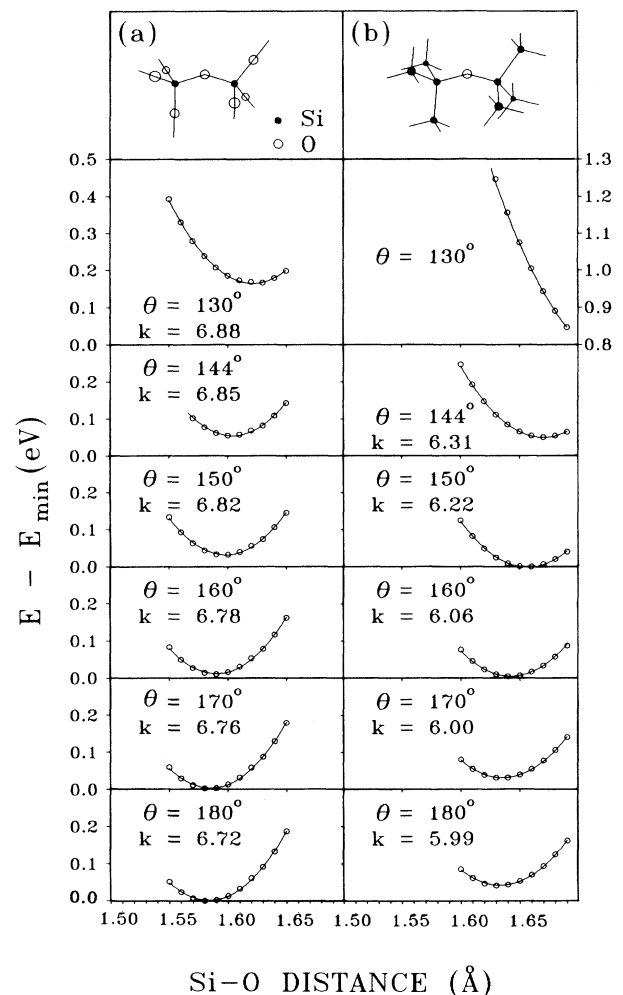


FIG. 1. Total energy (per Si-O-Si unit) vs Si-O distance for different Si-O-Si bond angles. The lines represent parabolic fits to the calculated total energies. The value (in units of 10^5 dyn/cm) of the stretching Si-O force constant is also indicated. (a) Total energy when all the Si-Si bonds are mediated by oxygen. (b) Total energy when all the Si-Si bonds are direct except the one considered.

TABLE I. Structural parameters of various crystalline forms of SiO₂. The calculated values are indicated in parenthesis.

Phase	θ (deg)	Si-O (Å)
Coesite	120	1.60-1.63(1.64)
α quartz	144	1.61(1.61)
α cristobalite	147	1.59(1.60)
β cristobalite	180	1.55(1.58)

lar Si-O-Si bond are bonded to one, two, and three bridging oxygen atoms while keeping the tetrahedral coordination. In particular, the results of the calculations for silicon clusters in which all the silicon-silicon bonds are mediated by oxygen atoms and clusters in which there is only one single Si-O-Si bond are shown in Fig. 1. Several points are worth noticing in this figure: (i) The energy difference for different values of the Si-O-Si angle are very small, showing why this angle varies from 120° to 180° for the different SiO₂ crystalline structures.¹⁴ (ii) The equilibrium Si-O distance is similar to the values for crystalline SiO₂. (iii) The larger the Si-O-Si angle the smaller the equilibrium Si-O distance in agreement with SiO₂ crystalline data. In Table I we show the structural parameters for various crystalline forms of silica¹⁴ along with our results. (iv) For a given Si-O-Si bond angle the equilibrium Si-O distance is smaller if the silicon atoms are surrounded by four oxygen atoms. (v) The stretch-

ing-force constant for Si-O is smaller for an isolated Si-O-Si unit in silicon than for a SiO₂-like configuration for a given Si-O-Si bond angle.

Once the equilibrium geometry for each atomic configuration is obtained, we pick up the corresponding Hamiltonian matrix elements between orbitals in nearest-neighbor atoms to calculate the electronic structure of infinite systems. Taking into account the above results we have calculated the valence electrons' density of states and the charge distribution of SiO_x in the Bethe-lattice approximation. To handle the random distribution of atoms in the alloy we have used the average-Green's-function method developed by Vergés and co-workers¹⁵⁻¹⁸ for a Bethe lattice of variable coordination. In the calculations we keep the Si-O-Si bond angle constant at a nominal value of 144° and the silicon-silicon distance fixed to the pure-silicon calculated value of 2.33 Å. Deviations from the nominal Si-O-Si bond angle yield

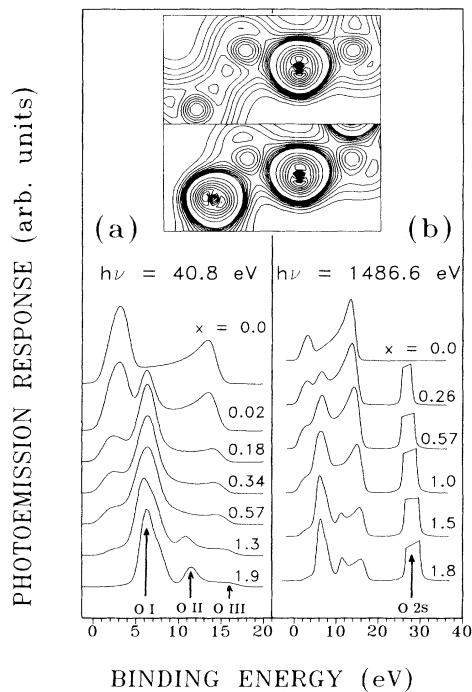


FIG. 2. Calculated photoemission response of SiO_x for different values of x for $\theta=144^\circ$ assuming nearest-neighbor interactions only in the Bethe lattice. (a) Ultraviolet response, (b) x-ray response. The main features of the spectra are indicated. The inset shows the electronic charge distributions for a single O impurity in silicon and for SiO₂.

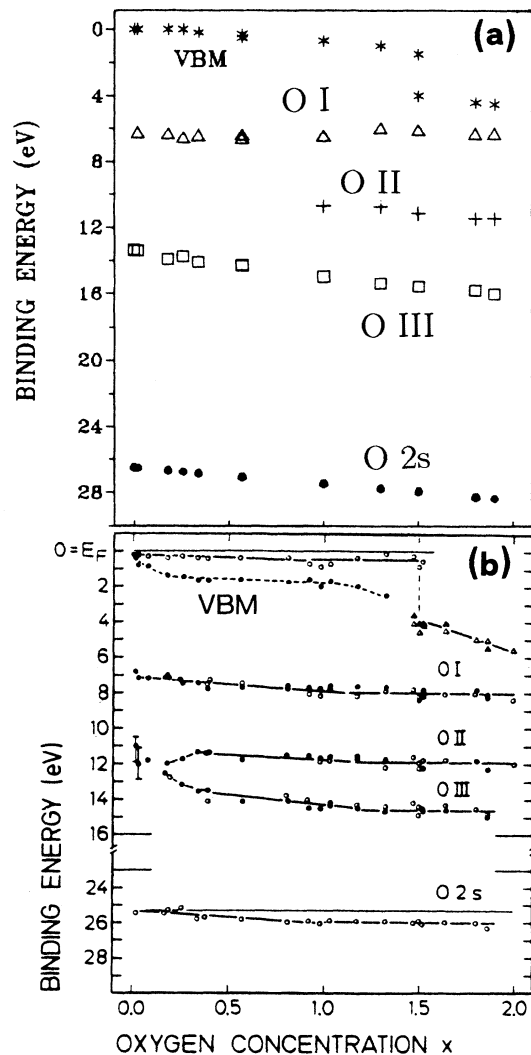


FIG. 3. Variation of the electronic spectra main features of SiO_x with the oxygen concentration. (a) Calculated results. (b) Experimental results of Bell and Ley (Ref. 4).

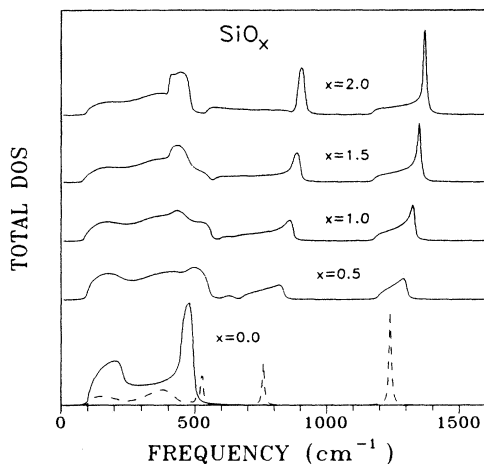


FIG. 4. Phonon densities of states for SiO_x for different values of x for $\theta = 144^\circ$. When $x = 0$ the dashed line shows the density of states of an O atom in silicon.

only minor changes in the density-of-states curves. The results of the calculated ultraviolet and x-ray photoemission response for the oxygen concentrations considered by Bell and Ley⁴ are shown in Fig. 2. The spectra are calculated by weighting the partial density of states of the valence band with the appropriate matrix elements. In order to compare with experimental data we have calculated the variation of the main spectral features with the oxygen content. Results of our calculations along with the experimental results of Bell and Ley⁴ are shown in Fig. 3. The agreement between theory and experiments stresses the appropriateness of our approximation. The variation of the Hamiltonian matrix elements and different Si-O distances with the atomic environment (which, in turn, depends on x) play a very important role in the structure and peak positions of the density-of-states curves. The jump of the top of the valence band at $x = 1.5$ corresponds essentially to the silicon percolation threshold as discussed in Ref. 6.

With the force constants obtained previously, we have calculated the phonon density of states of SiO_x as function of x . We have used the same method as in the electronic case.

The results for the Born model with the calculated central and noncentral force constants between nearest-neighbor atoms are shown in Fig. 4. It is important to notice the weakening of the Si-O stretching mode with the decrease of the oxygen content. This is due to the fact that the Si-O force constant becomes weaker when the Si-O-Si bond is surrounded by silicon atoms instead of oxygen ones, as in SiO_2 (see Fig. 1). The variation of the stretching-mode frequency with the oxygen content has been observed experimentally.³ Although the calculated vibrational modes are harder than the experimental ones,

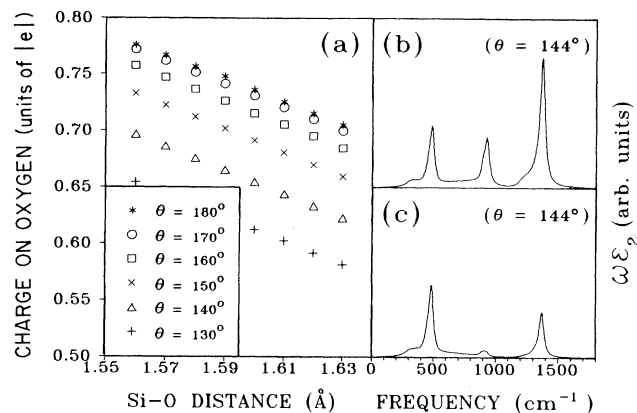


FIG. 5. Infrared absorption of amorphous SiO_2 . In (a) the variation of the electronic charge at the oxygen atom with the Si-O distance is shown. The slope of the straight lines gives the dynamic-charge parameter. (b) Infrared absorption when only static charges are considered. (c) Infrared absorption including dynamic charges.

the relative weakening of the stretching Si-O mode is well accounted for in the calculation.

We have also calculated the infrared absorption for SiO_2 . To calculate the matrix elements that enter in this calculation we have studied the variation of the charge transferred from silicon to oxygen as a function of the Si-O distance and the Si-O-Si angle [Fig. 5(a)]. The linear variation of the charge transferred with the bond distance allows a reliable linear fit to the calculated values yielding the values $\partial Q/\partial d = -0.53 \text{ e}/\text{\AA}$ and $\partial Q/\partial \theta = 0.132 \text{ e}/\text{rad}$ for $\theta = 144^\circ$. In Figs. 5(b) and 5(c) we show the results for the ir calculation taking into account static charges only, and both static and dynamic charges, respectively. We see that inclusion of dynamic charges improves the results very much, as they are in excellent agreement with experimental data.¹⁹ The intensity of the bending mode near 900 cm^{-1} is much weaker than the other two modes due essentially to the fact that the variation of the charge transfer with the Si-O-Si angle is much smaller than its variation with the Si-O distance.

We have presented a nonparametrized calculation for the amorphous SiO_x alloy. The method is reliable and allows us to obtain information on both the electronic and vibrational structure of the compound that cannot be obtained using parametrized approaches. This work represents the first unified description of this alloy.

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