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Photoemission Measurements of the Valence Levels of Amorphous SiO_2 †

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The complete valence band in amorphous SiO_2 has been examined by photoelectron spectroscopy at photon energies of 21.2, 26.9, 40.8, and 1486.6 eV. The spectra show emission from an 11.2-eV-wide *p*-derived valence band and from the oxygen 2*s* level at 20.2 eV below the valence-band edge. Four pieces of structure in the *p* bands are related to the single bonding and the two nonbonding orbitals of the O^{--} ion. A narrow, nonbonding level found at the valence-band edge may cause lattice trapping of valence-band holes.

Amorphous SiO_2 is of considerable technological and theoretical interest, although little is known about the electronic structure of the material. A knowledge of the valence-band structure is important to current studies of radiation damage, electronic structure of various defects, and interface properties for amorphous SiO_2. Several recent theoretical calculations[1-3] have contributed to an understanding of SiO_2 in terms of molecular clusters, but large uncertainties remain because such basic parameters as the principal structure and width of the valence band have not been determined experimentally. Optical measurements[4-6] have fixed the band gap at about 9.0 eV. However, past ultraviolet photoemission studies of wide-gap insulators such as SiO_2 have been limited because of the high photon energy necessary to excite electrons into vacuum. A recent extension of ultraviolet photoemission spectroscopy (UPS) to a photon energy of 40.8 eV has enabled us to probe, for the first time, the entire width of the valence band in amorphous SiO_2.

We present photoelectron spectra from amorphous SiO_2 which display a valence-band width of 11.2 eV and four clearly discernable pieces of structure.[7] The valence band, described in terms of a simple basis of wave functions on the O^{--} ion, comprises one bonding and two nonbonding oxygen orbitals. This identification of valence-band structure is based on UPS, x-ray photoemission spectroscopy (XPS), and soft x-ray spectroscopy (SXS) data. A narrow, nonbonding orbital which lies at the valence-band edge indicates a low hole mobility. Valence-band holes which have been lattice trapped in this narrow band may explain the positive charge induced by ionizing radiation in SiO_2.

The UPS energy distributions were measured by using a cylindrical electrostatic-deflection energy analyzer, with a windowless capillary discharge in He or Ne gas as a light source.[8] Photoemission distributions for $\hbar\omega = 21.2$, 26.9, and 40.8 eV were obtained from a 150-Å film of amorphous SiO_2 which was thermally grown on (100) silicon. Spectra obtained from sputter-deposited films of amorphous SiO_2 were essentially identical to those from the oxidized silicon. During the measurements, care was taken to minimize charging of the insulating samples. The salient features in the UPS measurements were found to be insensitive to vacuum conditions.

Several emission spectra for amorphous SiO_2

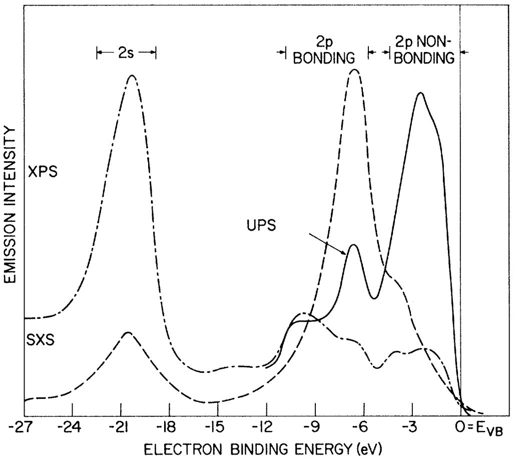

FIG. 1. Emission spectra for amorphous SiO_2 are displayed as a function of energy below the valence-band edge at $E=0$. Here UPS is the ultraviolet photoelectron distribution for $\hbar\omega=40.8$ eV, XPS is the x-ray photoelectron distribution for $\hbar\omega=1486.6$ eV, and SXS is soft x-ray emission measured by Fischer (Ref. 9).

are shown in Fig. 1, in which $E=0$ corresponds to the valence-band edge. In the UPS distribution for $\hbar\omega=40.8$ eV, an 11.2-eV-wide valence band is distinctly apparent. At the valence-band edge there are two overlapping peaks, at $E=-1.3$ and -2.4 eV, which we associate with the two nonbonding oxygen p orbitals as discussed below. The peak and lower shoulder found below the nonbonding bands are attributed to a broad band derived from Si-O bonding orbitals, which extend from -5.5 to -11.2 eV. Other UPS distributions measured at $\hbar\omega=21.2$ and 26.9 eV display the same general features seen at 40.8 eV. In each case, a minimum is found near $E=-5$ eV, between the bonding and nonbonding orbitals. The XPS spectrum[9] for $\hbar\omega=1486.6$ eV shows an 11-eV-wide valence band which is also split into the two groups corresponding to bonding and nonbonding orbitals. The XPS emission from the valence band is weak relative to that from the lower-lying oxygen $2s^2$ level at $E=-20.2$ eV. This amplitude variation is due to the energy-dependent transition probabilities which weight the components of the emission spectra. Even though optical transitions do not conserve crystal momentum in amorphous materials, the matrix element coupling does vary from band to band. Thus, the observed spectra do not determine the true density of states, but instead they show a weighted or optical density of states.

In order to facilitate our interpretation of spectra from SiO_2, a soft x-ray emission spectrum[10] (labeled SXS) is shown in Fig. 1. This measurement, which corresponds to Si $K\beta$ emission, is sensitive to wave functions of p symmetry in the region of the Si core. The peak appearing at $E=-20.2$ eV in the SXS spectrum is identified as the O $2s^2$ level, confirming the identification by Nagel.[11,12] Emission from the bonding and the nonbonding bands is seen at -6.5 and -3.6 eV, respectively, but the top of the bonding band dominates because of its large p-symmetry overlap with the Si $1s^2$ wave function.

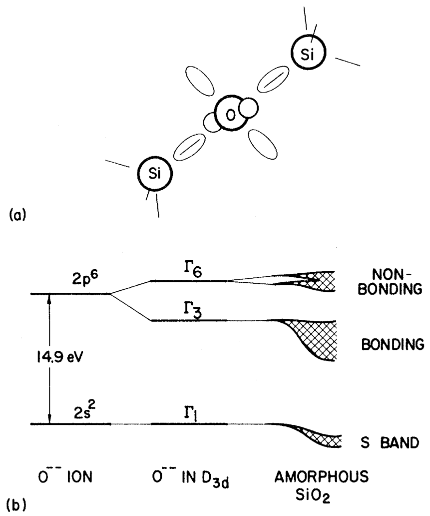

FIG. 2. Structure and energy levels of SiO_2. (a) The line Si-O-Si in cubic SiO_2 is straight, while this line in amorphous SiO_2 is bent to about 150°. (b) Energy levels shown are O^{--} in free space, O^{--} in the group D_{3d}, and the valence band of amorphous SiO_2.

The structure of amorphous SiO_2 can be understood in terms of β-crystobalite, in which the SiO_4 tetrahedra occupying the points of the diamond lattice are connected by straight Si-O-Si chains. Oxygen in this lattice occupies the sites of D_{3d} symmetry shown in Fig. 2(a). In the amorphous SiO_2, the Si-O-Si chain is bent[13] to an angle of about 150°. The electronic levels in the amorphous structure are conveniently described with the O^{--} $2s^22p^6$ orbitals as a basis. As displayed in Fig. 2(b) the s and p orbitals of the O^{--} ion in free space are separated[14] by 14.9 eV. In the D_{3d} symmetry of β-crystobalite, the $2p^6$ degeneracy is split to produce two nonbonding orbitals (Γ_6) which are perpendicualr to the Si-O-Si chain, and one bonding orbital (Γ_3) which links the Si and O centers. The s orbitals remain as the Γ_1 level in D_{3d}. In going to the amorphous structure, the electronic levels found in D_{3d} broaden into bands as shown in Fig. 2. Also, by symmetry considerations, the Γ_6 level is shown to split into two nonbonding bands, corresponding to nonbonding orbitals which lie perpendicular to and parallel to a plane determined by the Si-O-Si chain. The two nonbonding bands, the bonding bands, and the deep-lying *s* band, described in terms of an O^{--}-ion basis, are equivalent to those found theoretically by Reilly[2] who used hybrid Si orbitals and atomic O orbitals as a basis. Reilly's determination of the energy levels of SiO_2 using linear combinations of atomic and molecular orbitals shows two nonbonding levels at the valence-band edge, split by about 2 eV, with a bonding level at about 12 eV below the valence-band edge. The oxygen 2*s* level was placed at about 24 eV below the band edge.

Details of the emission spectra from SiO_2 can be identified in terms of the bands in Fig. 2(b). The two peaks at the valence-band edge have a total width at half-maximum of only 3.2 eV, presumably because of the small overlap between the nonbonding orbitals. The bonding band, seen to extend from about -5.5 to -11.2 eV in the emission spectra, is considerably broader than either of the nonbonding bands because of the larger overlap of bonding orbitals. The conduction band, which begins at 9.0 eV above the top of the valence band,[6] includes the Si-O antibonding orbitals. The similarity of the reflectivity spectra[5] of amorphous SiO_2 and α-quartz[5] indicates that the overall valence-band structure of the two should be very similar. It is significant that the nonbonding levels at the valence-band edge are quite narrow, since this introduces the possibility that low-energy holes are lattice trapped to form an immobile center on an oxygen site. As we have suggested,[7] the positive charge found in SiO_2 films which have been exposed to ionizing radiation may be due to lattice trapping of holes produced by pair creation. Also, because of lattice trapping the mobility of thermal holes in SiO_2 is expected to be low.

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