High-Resolution X-Ray Photoelectron Spectroscopy as a Probe of Local Atomic Structure: Application to Amorphous SiO_2 and the Si-SiO_2 Interface

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(Received 19 June 1979)

The chemical structure of thin SiO_2 films and SiO_2-Si interfaces has been investigated using high-resolution x-ray photoelectron spectroscopy. The data are consistent with a continuous random network of four-, six-, seven-, and eight-member rings of SiO_4 tetrahedra joined together by bridging oxygens. This distribution changes substantially within 30 Å of the SiO_2-Si interface. The near-interface region is comprised of Si_2O_3, SiO, and Si_2O. This structure is interpreted by means of a structure-induced—charge-transfer model.

In this Letter we report the results of a comprehensive high-resolution XPS (x-ray photoelectron spectroscopy) investigation[1] which exploits core-level chemical shifts for a study of the local chemical and structural environment of amorphous SiO_2 (a-SiO_2), and of the transitional region between monocrystalline silicon and bulk SiO_2. Such a use of core-level chemical shifts has been made possible for the first time via a combination of (1) the concept of structure-induced redistribution of valence charge, (2) spectral reconstruction procedures, and (3) new chemical profiling techniques.

It is well known that changes in the valence charge distribution cause the core-level binding energies to shift (chemical shift). Although the development of this subject[2] has taken place in the context of valence charge redistribution induced by the presence of new chemical species, changes in the local atomic arrangements (geometry) can also induce such charge redistribution. This concept[3] of structure-induced charge transfer (SICT) takes on particular significance in the context of network glasses, e.g., a-SiO_2, believed[3,4] to consist of an interconnecting ring system of three to eight SiO_4 tetrahedral units that are joined together via bridging oxygens with a range of Si-O-Si bond angles (θ). The charge distribution in the Si-O bond, as well as in the ring, will thus be dependent upon θ and the ring size n. The concept is of equal importance and relevance to semiconductor-dielectric interfaces since at such interfaces one expects not only various oxidation states of a given species, but also the presence of strained structural environments.[3] The possibility of obtaining structural information from the chemical shifts due to SICT thus depends upon (a) theoretical estimate of the expected range of charge transfers and the attendant chemical shifts, and (b) the ability to experimentally resolve such shifts. This requires sufficiently high-resolution data which allows the use of new spectral reconstruction techniques capable of resolving fine structure under peak envelopes.

In Fig. 1 is shown the calculated charge transfer Δn from silicon to oxygen (per Si-O bond) as a function of θ. The details of the calculations are reported elsewhere.[5] We briefly note that

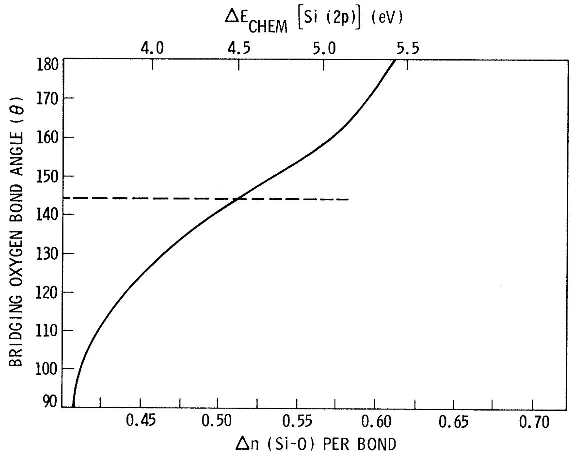

FIG. 1. The silicon-to-oxygen fractional charge transfer per bond (Δn) as a function of the Si-O-Si bond angle (θ). The upper scale shows the corresponding Si $2p$ chemical shift.

they were carried out using the empirical tight-binding method, and employing a nine-atom (three silicon and six oxygen) cluster as the unit cell. All interactions up to second nearest neighbors are retained. The parameters were determined by fitting to the pseudopotential calculations[6] for α-quartz, to which the cluster unit cell reduces for the appropriate θ value of 144°. Some perspective on the range of θ and the size of ring structures (n) expected in $a = \mathrm{SiO_2}$ can be gained[7] by noting the mean values of θ and n reported for several polymorphs. For instance, $\theta = 144°$ and $n = 6$ for α-quartz; $\theta = 120°$ and $n = 4$ for coesite; $\theta \geq 165°$ and $n = 7$, 8, and 9 for β-cristobalite; and $\theta = 154°$ and $n = 5$, 7, and 8 for keatite. Note that larger values of θ occur in polymorphs with larger ring sizes. The variations of the tight-binding parameters with θ and with the various atomic distances involved (Si-O, O-O, etc.) were modeled according to geometrical relationships and the $(1/\gamma^2)$ distance dependence of such matrix elements established in the literature. Any first-principles attempt to calculate the attendant shifts in the core-level binding energies (such as Si 2p and O 1s) are fraught with ambiguities. Consequently, using experimental information in a manner to be discussed in the following, we obtain a reasonably reliable conversion factor which, for the Si 2p chemical shift, gives the scale shown in the upper part of Fig. 1. The increase in the chemical shift of Si 2p with increasing Δn is, of course, due to the loss of charge from Si to oxygen. It also demands, however, that the chemical shifts on oxygen (e.g., O 1s) should be in the opposite direction.

The experimental studies were conducted employing a modified HP5950A spectrometer, described elsewhere.[8] A series of 3–6-Ω-cm ⟨100⟩ n-type silicon wafers was prepared, following a standardized peroxide-based cleaning procedure, and then oxidized in HCl-cleaned quartz tubes with dry oxygen at 1000 °C with no anneal.[8] A wet-chemical-etching procedure was used to depth profile these samples. This method used HF/ethanol etchants, millisecond exposure times, and a high-purity dry N_2 ambient to minimize perturbations of the sample chemistry. All spectra were taken at 300 °K with control of the secondary-electron background to minimize charging effects and establish near-flat-band conditions. Spectrometer resolution was better than 0.35 eV (full width at half maximum) and the analysis chamber pressure was in the 10^{-10}-Torr range.

In Fig. 2 are plotted the relative positions of the peaks for O 1s, Si 2p in the oxide, and Si 2p in the silicon substrate as a function of oxide thickness. Measurements out to 1000-Å-thick oxides were also obtained, and continue to give a constant limiting value [in curve of Fig. 2(a)] of 429.90± 0.02 eV. The variation of the indicated peak separations for oxide thickness less than ~ 50 Å is reflective of chemical-bonding variations, as shown in the following. Variation of the substrate Si 2p position is caused by silicon–surface-potential changes. Care has been taken[1] to make sure that final-state relaxation and dielectric-boundary effects do not alter the results presented in the following.

The observed XPS spectra may be understood as a sequential convolution of the natural line shape for the electron level, the chemical distribution function (CDF) representing different chemical states within the sampled volume, and an instrument broadening function followed by the addition of Poisson noise. Since the natural line characteristics, the instrument broadening function, and some aspects of the noise process can all be determined with reasonable (though varying) precision, it is possible to execute a number of information-retrieval operations in an effort to reconstruct the non–instrumentally-broadened spectrum and possibly the CDF. The detailed procedure has recently been developed,[9] and, in brief, exploits linear prediction based on the experimentally well-known terms of the decon-

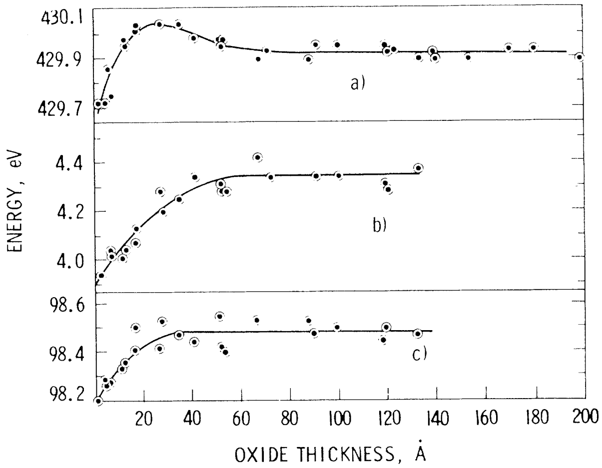

FIG. 2. (a) Separation of the Si 2p and O 1s lines in the oxide; (b) separation of the Si 2p line of the oxide from that of the substrate; and (c) position of the substrate Si 2p line.

volved Fourier transform (FT) of the spectrum using a maximum-entropy approach.[10,11] Having examined[9] the procedure critically and in detail, we find that it restores peak positions and slowly varying line shapes with great precision.

In Fig. 3, we show the result of such deconvolution of O 1*s* and Si 2*p* spectra obtained from 49- and 23-Å oxides. The initial spectra have a power signal-to-noise ratio (S/N) greater than 200:1. For clarity, the silicon-substrate spectra have been subtracted from the figure. In these spectral reconstructions, the instrument function and the spin-orbit doublet are removed. A broad Gaussian component of 1.0 eV was found to be common to both the 49- and 23-Å oxide results for Si 2*p* and O 1*s* lines. Removal of these three components left the Lorentzian line shape and other slowly varying functions in the restored results.

The deconvolved peaks in Fig. 3 can be interpreted in a consistent manner within the SICT concept discussed above. To convert calculated variations of electron-charge transfer into observed binding-energy shifts, we assume a linear relation between them and obtain the scale factor from the data. Assigning the most intense Si 2*p* peak in thick SiO_2 (> 49Å) (positioned at 4.5-eV higher binding energy relative to the substrate line) to Si^{4+} in six-membered rings with an average Si-O-Si bond angle of 144°, we obtain a scale factor of 2.2 eV/electron. Use of this scale factor places the second-most-intense peak in the upper curve of Fig. 3(b) at a bond angle of 125°, which suggests four-membered rings. The smaller peak at higher binding energy relative to 144° suggests contributions from nearly linear Si-O-Si bonds with angles > 165°, which may be associated with seven-, eight-, and nine-membered rings, and possibly from a nonbridging oxygen. As noted, a prediction of the SICT model and, consequently, a crucial test of its validity, is that the behavior of the core levels on oxygen must be the mirror image of Si 2*p*. This feature is well borne out in the results of Fig. 3(a). The peaks of the O 1*s* spectrum are found to be separated by an amount 20% greater than that within the Si 2*p* manifold. Thus, the picture emerging for bulk amorphous SiO_2 is one of a continuous random network of SiO_4 tetrahedra whose probability distribution as a function of the Si-O-Si bond angle and the ring size is peaked at $\theta = 125°$ ($n=4$), $\theta = 144°$ ($n=6$), and $\theta \geq 165°$ ($n = 7, 8, 9$).

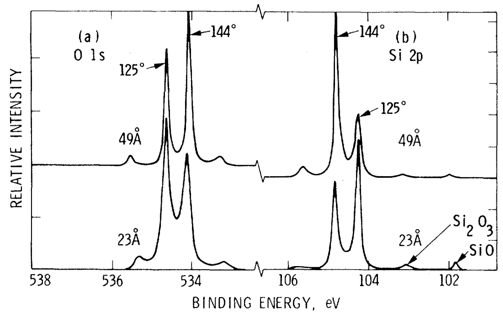

FIG. 3. (a) Deconvolved O 1*s* spectra for 49- and 23-Å oxide thickness and (b) deconvolved Si 2*p* spectra for the same oxides as (a). Substrate contribution has been removed for clarity.

Turning now to the 23-Å oxide, we note that the intensity of the Si 2*p* peaks for $\theta = 125°$ and $\theta = 144°$ [Fig. 3(b)] is reversed, though the energy positions are essentially the same. The implied shift in the ring size and bridging-oxygen bond-angle distribution towards smaller values is expected for the strained nature of the Si-SiO_2 interfacial region. Such a region necessarily demands shifts towards smaller bridging-oxygen bond angles and attendant ring size to allow for a reasonably smooth change in structure from bulk SiO_2 to elemental silicon. Once again, validity of the SICT model demands that the behavior of the O 1*s* peaks corresponding to the 23-Å oxide must be the mirror image of the Si 2*p* peaks, as is clearly borne out by Fig. 3(a).

In the interfacial region (23-Å oxide), discrete structures are also observed in the Si 2*p* and O 1*s* levels corresponding to intermediate oxidation states of silicon. If the charge transfer per Si-O bond is taken to be independent of the number of such bonds, then a first estimate of the bridging bond angles corresponding to these intermediate-oxidation-state peaks can be obtained. The peak at 103.1 eV ($\Delta E_{\text{chem}} = 2.8$ eV) would correspond to Si_2O_3 with θ between 90°–100°. The peak at 101.8 eV ($\Delta E_{\text{chem}} = 1.5$ eV) is approximately 0.2 eV too low to correspond to the predicted value for SiO with a 90°–100° bond angle. The linear independence of the Si-O charge transfer would thus appear to be only approximate, but sufficient to unambiguously identify the existence of Si^{3+} and Si^{2+} oxidation states at the Si-SiO_2 interface. Although not shown in Fig. 3, a Si 2*p* peak corresponding to Si^{1+} (Si_2O) is found at 100.9 ($\Delta E_{\text{chem}} = 0.6$ eV).

Finally, we note that in the thickness region of 0–30 Å, the change in Fig. 2(c) indicates a modification of the substrate surface potential consistent with the net removal of 4×10^{10} positive charges/cm^2. In experiments involving irradiation of these samples with electrons with kinetic energy > 8 eV, we find conversion of 125° Si^{4+} to Si^{3+} states. These states cause a change in substrate Si $2p$ line position and are steadily annealed under the conditions of the XPS experiment. It therefore appears that strained 125° SiO$_2$ bonds can be converted to fixed charge centers in the region of the interface. Si^{3+} sites in close proximity to nonbridging oxygens may constitute a primary mechanism of oxide charge buildup.

This work was sponsored in part by the National Aeronautics and Space Administration under Contract No. NAS7-100 and by the Defense Advanced Research Projects Agency through the National Bureau of Standards, Order No. 611377. One of us (A.M.) acknowledges receipt of an Alfred P. Sloan Foundation Fellowship.

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[1] Details provided in F. J. Grunthaner, P. J. Grunthaner, R. P. Vasquez, B. F. Lewis, J. Maserjian, and A. Madhukar, to be published.

[2] See, for example, articles by D. A. Shirley [*Photoemission in Solids I: General Principles,* Topics in Applied Physics, edited by L. Ley and M. Cardona (Springer-Verlay, New York, 1978), Vol. 26] and M. Cardona and L. Ley (*ibid.*).

[3] Preliminary results introducing this notion are reported in the papers by R. N. Nucho and A. Madhukar, in *The Physics of SiO$_2$ and Its Interfaces*, edited by S. T. Pantelides (Pergamon, New York, 1978), p. 60; F. J. Grunthaner and J. Maserjian, *ibid.*, p. 389.

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Semiconductor Heterojunction Interfaces: Nontransitivity of Energy-band Discontiuities

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(Received 18 September 1979)

A direct experimental test has revealed that heterojunction energy-band discontinuities are nontransitive. This result was obtained by an x-ray photoemission-spectroscopy investigation of abrupt (110) interfaces in the heterojunction series Ge/CuBr, CuBr/GaAs, and GaAs/Ge. The sum of the valence-band discontinuities for these intefaces is 0.64 ± 0.05 eV, a large deviation from the zero sum expected by transitivity.

A fundamental feature of an abrupt semiconductor heterojunction is the discontinuity in the valence band and conduction band, ΔE_v and ΔE_c, that arises from the bandgap change ΔE_g across the interface. Theoretical models[1-3] have been proposed to predict ΔE_v (or ΔE_c); these models have as a common feature a transitive relationship for the band discontinuities. In general, such models express a band discontinuity as the difference in an energy associated with each individual semiconductor. The widely used electron-affinity rule,[1] whereby $\Delta E_c(A/B) = |\chi^A - \chi^B|$, is an example of a transitive model; χ is the respective electron affinity of semiconductors A and B which form the junction A/B. Transitivity, if true, is appealing for the relative simplicity brought to the resulting models; implied is that interface properties *per se* need not be investigated to predict ΔE_γ and ΔE_c.

A transitive model has the property that if $\Delta E_v(A/B)$, $\Delta E_v(B/C)$, and $\Delta E_v(C/A)$ are the valence-band discontinuities associated with heterojunction interfaces from semiconductors A, B, and C, the relationship

$$\Delta E_v(A/B) + \Delta E_v(B/C) + \Delta E_v(C/A) = 0 \qquad (1)$$

must be valid. Since $\Delta E_v + \Delta E_c = \Delta E_g$, any conclusions drawn for ΔE_v can always be expressed in terms of ΔE_c. An experimental test of Eq. (1) is thus a test of transitivity.

The electronic properties of relatively few abrupt heterojunctions have been studied experi-