## Photoemission study of $SiO_x$ ( $0 \le x \le 2$ ) alloys

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Photoemission measurements of the core and valence levels and of the plasmon energies of SiO,  $(0 \le x \le 2)$  are presented. The samples were prepared in situ as thin films by sputter deposition of Si in an Ar-O<sub>2</sub> mixture. The Si 2p core-level spectra are analyzed in terms of five chemically shifted components corresponding to the basic Si bonding units Si— $(Si_{4-n}O_n)$ , with n = 0, 1, ..., 4. The concentration of these bonding units as a function of oxygen concentration is essentially in agreement with the random-bonding model. However, some separation into oxygen- and silicon-rich phases is also evident at intermediate stoichiometries. Plasmon energies increase from 17 eV (x = 0) monotonously to 20.8 eV (x = 2). The energies are analyzed in terms of the film density. Partial densities of oxygen- and silicon-derived valence states were obtained by using x-ray and uv excitation. A three-peak structure of mainly O 2p-derived states is observed over the whole concentration range. It is characteristic of the local bonding environment of oxygen in the form of a Si-O-Si bridge bond. The valence-band width and, in particular, the valence-band maximum (VBM) depend on the connectivity of the network structure. An abrupt shift of the VBM by 3.5 eV to greater binding energies at  $x_c = 1.5$  marks the disappearance of the Si—Si bonding states which define the valence-band maximum at low x. For oxygen concentration greater than  $x_{c_1}$  the valenceband maximum is defined by the onset of the O 2p lone-pair states. Structures of the valence bands are discussed in the light of recent band-structure calculations. The Fermi level is seen to shift by 0.7 eV between x = 0 and x = 2 towards the conduction-band edge. The natural valence-band offset between a-Si and a-SiO<sub>2</sub> was determined to be 4.5 eV.

## I. INTRODUCTION

Nonstoichiometric oxides of silicon are encountered in a variety of experimental situations, including the thin boundary layer between crystalline silicon and its thermally grown oxide,  $^{1-8}$  in samples of silicon monoxide deposited by electron beam evaporation,<sup>9</sup> and on the surface of slightly oxidized silicon.<sup>10-12</sup> The technological significance of these oxides (hereafter, SiO<sub>x</sub> alloys) is partially based on the somewhat controversial evidence that a thin layer of the alloy can remain at the Si/SiO<sub>2</sub> interface after thermal oxidation of Si. The thickness and composition of such a boundary layer have not been fully established, 1-7, 13, 14 although in the present picture it is believed that its thickness extends no more than one to two monolayers in carefully prepared samples.<sup>1,14</sup> Since the electronic properties of this layer could affect the performance of metal-oxide-semiconductor (MOS) devices which have gate oxides, the present trend to reduce the dimensions of these structures places critical demands on the quality of the oxide.<sup>15,16</sup> Ideally, the oxide would be stoichiometric up to the Si substrate. On the other hand, efforts to produce high-quality oxides on Si should be guided by the extent to which the properties of oxygenrich alloys differ from those of SiO<sub>2</sub>.

In addition to the technologically motivated interest, the  $SiO_x$  alloys provide an ideal model system for studying the evolution of the electronic structure from the semiconductor amorphous silicon (*a*-Si) to the insulator amorphous SiO<sub>2</sub> (*a*-SiO<sub>2</sub>). Theoretical calculations based on the Bethe-lattice approximation for the structure in conjunction with the tight-binding method have been done by Martinez and Yndurain,<sup>17,18</sup> and Ching has calculated the electronic structure of  $SiO_x$  for a number of continuous-random-network-model structures using a first-principles method.<sup>19</sup> In this study, we seek to understand the developments in the electronic structure of  $SiO_x$  alloys resulting from controlled changes in the oxygen concentration, and in particular, how the electronic structures of  $SiO_x$  differ from that of pure *a*-Si and *a*-SiO<sub>2</sub>.

The basic structure of the silicon-oxygen bond in  $SiO_x$ alloys can be compared to that in a-SiO<sub>2</sub>. In the case of a-SiO<sub>2</sub>, Si-O<sub>4</sub> tetrahedra are linked together by "bridging" oxygen atoms.<sup>1</sup> The high-resolution scattering studies of Mozzi and Warren<sup>20</sup> have shown that the Si tetrahedral angle is essentially preserved in a-SiO<sub>2</sub>, but the Si-O-Si bridging bond angle has a distribution centered about 144°. Galeener<sup>21</sup> has derived a similar angular distribution for the Si-O-Si bridging angle in a-SiO<sub>2</sub> from simple geometrical arguments based on excluded volumes. In the case of SiO<sub>x</sub>, two models<sup>9</sup> have been suggested for the structure based on fourfoldbonded Si and twofold-bonded O. The first is the random-bonding model (RBM) or continuous-randomnetwork model, in which there is a statistical distribution of five basic bonding units, Si— $(Si_{4-n}O_n)$ , n = 0, 1, ..., 4. In these tetrahedral units, a Si atom is bonded to four other atoms of either Si or O, and the O atoms are each bonded to two Si atoms of different tetrahedra. For simplicity, we shall designate the basic  $Si_{4-n}O_n$ ) bonding units as the Si— $O_n$  units, and refer to the n = 1, 2, 3units as the suboxides. The relationship between the overall concentration x and the concentrations of the individual units in the RBM have been determined by Hübner<sup>9</sup> and also by Martinez and Yndurain.<sup>17</sup> The individual concentrations can be derived from considerations based on the statistical replacement of Si—Si bonds in amorphous Si by Si—O—Si bonds while maintaining the fourfold coordination of Si and the twofold coordination of O. We shall discuss these concentrations in more detail in Sec. III. The second model for the network is the mixture model (MM), in which the alloy is expected to be composed of randomly arranged clusters of Si and SiO<sub>2</sub> of varying sizes.<sup>9,22</sup> In this model, the concentrations of the two species have simple linear relationships to the overall concentration x. Hübner<sup>9</sup> has correlated the preparation conditions of SiO<sub>x</sub> with the type of network the samples seem to obey.

In the formation of the Si-O bond, a charge transfer from Si to O of between 0.25e and 0.55e occurs, 1,23-25and this decrease in electronic density on the Si atom increases the binding energies of each of the Si core levels.<sup>26</sup> The x-ray photoemission spectroscopy (XPS) studies of oxidized Si by Hollinger and Himpsel,  $^{6,7,11,12}$  by Grunthaner *et al.*,  $^{1,4,8}$  and by Garner *et al.*,  $^{10}$  indicate that there is a shift of the Si core levels toward higher binding energies of about 1 eV per silicon-oxygen bond, and this shift is in part a result of the chemical shift due to charge transfer. It is thus possible to use an analysis of the Si core-level spectrum to distinguish between the RBM and the MM. If the alloys have random-bonding structure, the Si core-level spectra will be composed of a superposition of five peaks corresponding to the five possible  $Si - O_n$  bonding units. If, on the other hand, the material consists of two phases, there will be only two peaks in the Si core-level spectra corresponding to the a-Si and the chemically shifted Si core level of SiO<sub>2</sub>. Such an analysis of the Si 2p core-level spectra has been used in the past<sup>1-6</sup> to determine the concentrations of the suboxides in the boundary region of thermally grown oxides on crystalline Si and in an analysis of  $SiN_x$ .<sup>27</sup> We shall also use this method in our analysis of Si 2p core-level measurements to be given below.

The band gap in  $SiO_x$  has been measured by Holzenkämpfer and co-workers<sup>28</sup> and calculated by Martinez and Yndurain<sup>17</sup> and by Zuther.<sup>29</sup> It increases nonlinearly by about 7 eV from 1.5 to 8.5 eV as x increases from 0 to 2, but most of this increase occurs in a region of concentration  $1.5 \le x \le 2.0$ . This would suggest that the optical properties of the material are mostly siliconlike over  $\frac{3}{4}$  of the concentration range. Zuther<sup>29</sup> has calculated the dielectric functions  $\epsilon_1$  and  $\epsilon_2$  of SiO<sub>x</sub> based on an effective-medium approximation and the RBM structure and these results indicate that up to x = 1.25, the dielectric properties of SiO<sub>x</sub> are dominated by the Si network but for greater concentrations they are  $SiO_2$ -like. Zuther interpreted these results in terms of a percolation threshold for connected Si-Si and SiO<sub>2</sub> chains around an oxygen concentration of x = 1.25. A percolation threshold of this kind in  $SiO_x$  alloys has also been proposed by Martinez and Yndurain<sup>17</sup> and by Hübner<sup>9</sup> and calculated to be at the oxygen concentration x = 1.33 and 1.25, respectively.

These previous studies and their predictions about the

electronic properties of SiO<sub>x</sub> alloys have motivated us to undertake systematic measurements of the electronic structure of the SiO<sub>x</sub> system using photoemission.<sup>30</sup> The present study should be complementary to previous photoemission measurements on oxidized Si, which have been concerned primarily with surface oxidation of Si and the electronic structure of the Si/SiO<sub>2</sub> interface. Among the questions we seek to answer in this study are (1) is the network randomly bonded or mixture dominated, (2) how does the oxygen concentration influence the electronic structure, and in particular the valence-band maximum of SiO<sub>x</sub> alloys, and (3) where are the Si defect states for *a*-SiO<sub>2</sub> located in energy?

We have made alloys of amorphous  $SiO_x$  over the entire composition range from pure a-Si to a-SiO<sub>2</sub>. We have used photoemission to measure the electronic structure of the valence band and core levels and have combined these measurements with an analysis of the Si 2p and O 1s core levels to deduce information about the structure of the network. We shall show that our samples are essentially randomly bonded with a minimum of clustering, and that the electronic structure of the alloys is dominated in certain regions of concentration by either connected Si-Si chains or connected SiO<sub>2</sub> chains. In Sec. II we discuss the experimental details of the sample preparation and measurement. In Sec. III we undertake an analysis of the Si 2p and O 1s core levels in order to derive information about the network structure. In Sec. III we present measurements of the valence band, discuss its evolution with changes in oxygen concentration, and relate the structure to results of published band-structure calculations. In Sec. IV we summarize the results of the experiment and draw conclusions about the relationship between the network structure and the electronic properties.

## **II. EXPERIMENT**

Samples were prepared as thin films by dc sputtering a crystalline Si target in a mixture of argon and oxygen. Due to the strong reactivity of Si with oxygen, we have found that when the fractional pressure of oxygen is  $10^{-4}$ , essentially stoichiometric SiO<sub>2</sub> is obtained. We have made samples of specific composition using diluted oxygen previously prepared in a mixture chamber connected to the sputter chamber. With a target voltage of 1 kV and 0.5 mbar pressure, the sputter current was about 5 mA and this provided a deposition rate of about 5 Å/min with our geometry. All samples were prepared *in situ* in a sputter chamber attached to the spectrometer, and transferred under ultrahigh vacuum (UHV) to the analyzer, where the pressure was maintained at about  $10^{-10}$  Torr during the measurements.

We have found it necessary to maintain several experimental conditions in order to produce films of good quality. First, in order to ensure uniformity of composition, the samples were prepared under continuous flow by pumping off the sputter gas with a turbomolecular pump. Second, we maintained the gas flow and the discharge for 1 h before starting to deposit the film. We found this necessary to ensure that the flow and discharge were in equilibrium, and to remove by sputtering any oxide which might have built up on the target prior to the flow adjustments. During this equilibration time, the substrate was protected from exposure to the sputter beam. Finally, we have found that charging of the samples during measurement was a serious problem for thicker films having compositions in excess of x = 1.2. We eliminated this problem through strict control of the film thickness. The samples were deposited on sputtered films of molybdenum on stainless-steel sample holders. By periodically monitoring the core levels of the substrate with XPS, we were able to determine empirically the amount of time required to deposit a  $SiO_x$  film for a given composition which was thick enough to cover the substrate, yet thin enough to prevent charging during measurement.

All measurements were made on a VG Instruments model ESCA3 equipped with an aluminum x-ray anode and a monochromatized He lamp. We have used the Al  $K\alpha$  excitation ( $h\nu = 1486.6$  eV) for XPS measurements and HeI (hv=21.2 eV) and HeII (hv=40.8 eV) for the ultraviolet photoemission spectroscopy (UPS) measurements. We determine the concentration of the samples by comparing the integrated intensities of the O 1s core level to the Si 2p core level for each sample. This ratio was calibrated by measuring the same quantity for a sample of natural quartz, for which we found  $\int I(O \ 1s) / \int I(Si \ 2p) = 7.4$ . In the following, we shall refer to the concentration determined in this way as x(O)1s). Binding energies reported here are with respect to the Fermi level, which was determined by sputter coating a layer of molybdenum over the sample after all measurements were completed. We estimate the overall accuracy of the XPS measurements to be 0.1, and 0.05 eV for the UPS measurements.

#### **III. RESULTS AND DISCUSSION**

## A. The Si 2p and 0 1s core levels

We begin the data analysis with the Si 2p core levels. In Fig. 1 we show Si 2p core-level spectra obtained with Al  $K\alpha$  excitation for selected concentrations. At x=0, the Si 2p core level in a-Si is located at 99.6 eV binding energy and appears symmetric due to the resolution of 1.2 eV, i.e., the spin-orbit splitting of 0.6 eV is not resolved. The addition of oxygen in the alloys introduces intensity at higher binding energy with a concomitant decrease in the intensity at lower binding energy. This is due to a chemical shift of the Si 2p core level arising from a charge transfer from Si to O as more Si-O bonds are added in the alloy. At the highest concentrations, this trend eventually develops into one line shifted to 104 eV in binding energy. The overall shift of the Si 2p center of gravity from 99.6 eV at x = 0 to 104 eV at x = 2 indicates the changing environment of a Si atom over the concentration range. Each Si atom is bonded to four Si atoms in a-Si and to four O atoms in a-SiO<sub>2</sub>. This shift is consistent with the previously reported chemical shift of about 1 eV per silicon-oxygen bond.<sup>1,3-7</sup>

The broadening and continuous variation in the shape of the Si 2p core level provides a means for excluding the



FIG. 1. Si 2p core-level spectra in SiO<sub>x</sub> for selected oxygen concentrations x obtained with Al K $\alpha$  excitation. Dots are the measured data and the solid line is the result of a least-squares fit. Individual peaks in the least-squares fits are designated for x = 0.34 by integers corresponding to the number of Si—O bonds. The center of gravity is designated by tic marks. The zero of energy is the Fermi level.

MM as the basic network structure. If the MM were appropriate, the Si 2p core levels for all concentrations would be characterized by two peaks of roughly 2 eV width separated by 4 eV in binding energy as mentioned in Sec. I; but we do not observe this behavior. We attribute the asymmetrical broadening of the Si 2p core level at intermediate concentrations to a superposition of five peaks corresponding to the Si 2p core levels of each of the Si— $O_n$  basic bonding units in the RBM. We have per-formed an analysis<sup>4,6,27</sup> of the Si 2p core levels in which the individual spectra were fitted to a superposition of five Gaussian lines of the same width and spacing. Gaussian line shapes were chosen since it was found that the Si 2p core level in a-Si could be well fitted with this line shape due to the amorphous broadening of the lines and the resolution of the measurements. The choice of equivalent spacing is based on the principle of the addi-tivity of chemical shifts. $^{30-33}$  Fits were performed using the position of the n = 0 (nonshifted) peak, the width, and the spacing as free parameters. The least-squares method was used to obtain the intensities of the five individual components by minimizing the  $\chi^2$  for each sample. On the other hand, the same line spacing was used for all samples, so that effectively some 25 spectra were fitted simultaneously. In Fig. 1 we show the results of the fit by plotting the resulting line shape and the individual components under the corresponding spectra. Beginning at

x = 0, only the n = 0 peak is present and for increasing x, the suboxide peaks appear and change in relative intensity. At the highest concentrations, we find that, as expected, only the n = 3 and 4 peaks are represented. In our analysis, we obtain the best fit for all samples using a spacing or chemical shift per silicon-oxygen bond of  $1.05\pm0.03$  eV, and a peak width which increases linearly from 1.9 eV full width at half maximum (FWHM) at x = 0 to 2.15 eV FWHM at x = 1.0, and is constant at this value for  $1.0 \le x \le 2.0$ .

Two methods are used to check the validity of the RBM for our samples. The first is to compare the intensities of the individual components with those predicted by the RBM and the MM. The RBM, the intensities  $I_n$  of the components Si—O<sub>n</sub>  $(n=0,1,\ldots,4)$  are given by<sup>9,17</sup>

$$I_n(x) = \frac{4!}{(4-n)!n!} (x/2)^n (1-x/2)^{4-n} , \qquad (1)$$

whereas in the MM the intensities are simply

$$I_0 = 1 - x/2$$
 and  $I_4 = x/2$ . (2)

In Fig. 2(a) we show the component intensities as calculated in the RBM and the MM and in Fig. 2(b) we have plotted the component intensities as obtained from the fit. From the two plots it can be seen that the component intensities obtained from the fit agree better with the RBM than with the MM. This conclusion is also based on our attempts to fit spectra at various compositions using only two components as required in the MM. Such fits yield very poor results for the overall line shapes. However, it is also apparent from the comparison between Figs. 2(a)



FIG. 2. (a) Solid lines are relative concentrations of the basic bonding units in the random-bonding model (RBM) and dashed lines are relative concentrations of the Si and SiO<sub>2</sub> components in the mixture model (MM). (b) Relative concentrations of the basic bonding units vs oxygen concentration, as obtained from the least-squares fits.

and 2(b) that at intermediate oxygen concentrations the Si—O<sub>0</sub> and Si—O<sub>3</sub> components are emphasized at the expense of the Si—O<sub>2</sub> configuration. This tendency towards a certain degree of phase separation into oxygenrich and oxygen-poor regions is directly evident in the two peaked structures of the Si 2p spectra for x = 0.57 and 0.81.

Another check on the network structure is obtained from a second method to determine the oxygen concentration. The concentration is determined by summing the individual component intensities, each multiplied by the number of oxygen atoms per component, and normalizing this to the sum of the component intensities. This quotient represents the concentration of O bonded to Si in the samples as reflected in the Si 2p spectra:

$$x(\text{Si } 2p) = \frac{1}{2} \frac{\sum_{n}^{N} I_n n}{\sum_{n} I_n}$$
 (3)

The factor  $\frac{1}{2}$  is included since each oxygen atom is shared by two Si atoms. We shall refer to the concentration obtained in this way as x(Si 2p). In Fig. 3 we have plotted x(Si 2p) versus the absolute oxygen concentration x(O 1s) obtained from integrating the core-level intensities. These two measures of the concentration are in essential agreement apart from a 10% overestimation of x(Si 2p) in the intermediate concentration region. This result confirms that our analysis of the core-level spectra is correct on the level of our accuracy. It also excludes the possibility of small concentrations of nonbonded oxygen, because nonbonded oxygen would lead to an underestimation of x(Si 2p).

It is possible to remove the 10% overestimation of x(Si 2p) through a corresponding 10% increase in the chemical shift (peak spacing) in the intermediate concentration range. An increase of this order in the chemical shift can be realized through a small increase in the Si—O—Si bridging bond angle, as suggested by Nucho and Madhukar<sup>25,34</sup> and by Grunthaner and Grunthaner<sup>1</sup> in connec-



FIG. 3. Oxygen concentration x(Si 2p) from the leastsquares fits vs oxygen concentration x(O 1s) as derived from the ratio of the intensities of the O 1s and Si 2p core levels.

tion with a-SiO<sub>2</sub>, and by Grunthaner and Maserjian for the Si/SiO<sub>2</sub> interface.<sup>35</sup> The basis of the argument given by Grunthaner and Grunthaner is that variations in the Si-O-Si bond angle directly affect the hybridization of the bond in  $a-SiO_2$  and this rehybridization can lead to significant variations in the chemical shift. They have supported these observations by a comparison between variations in the XPS chemical shift and the variations in the nuclear magnetic resonance (NMR) shift measured by Dupree and Pettifer<sup>36</sup> in a-SiO<sub>2</sub> and by Dupree *et al.*<sup>37</sup> in SiO. According to this comparison an increase of about 5° in the bridging bond angle can produce an increase in the Si 2p chemical shift of about 0.1 eV per Si-O bond. The result of increasing the chemical shift in our fits by 0.1 eV while maintaining the position of the Si 2p n = 0component would be to increase the n = 1 and 2 components at the expense of the n = 3,4 components. The effect of this shift in the relative concentrations of the components would also bring the component intensities into better agreement with those calculated from the RBM as shown in Fig. 2, and would tend to reduce the degree of phase separation. In view of these observations, it appears that the chemical shift may be underestimated in the intermediate concentration range, and the basis of the deviations is the variation of the Si-O-Si bridging bond angle by approximately 5° throughout this range.<sup>38</sup>

From the least-squares fits, it is possible to obtain the most likely position of the unshifted Si  $2p_0$  component. In Fig. 4 we have plotted the Si  $2p_0$  component position and the positions of various other features of the spectra as functions of the oxygen concentration. We find that the binding energy of the Si  $2p_0$  peaks shifts continuously by about 0.7 eV to greater binding energy over the concentration range from x = 0 to x = 2. The rather sharp O 2s valence peak located at 26 eV in binding energy undergoes the same shift. By comparison, the O 1s core level is observed to shift by about 1.1 eV over this range. We do not, however, observe an asymmetry in the O 1s corelevel spectra at any concentrations that would indicate the presence of additional chemically shifted components for this core level. In addition, we have measured the  $O_{KLL}$  Auger spectra over a wide range of compositions and find that the spectral shape does not vary with concentration. This is consistent with the expectation that oxygen atoms experience the same local environment bridging the Si-O<sub>n</sub> tetrahedra at all concentrations, and so, to first order, the O core levels undergo no additional chemical shift with increasing x. Therefore we attribute the shift of the Si  $2p_0$  core level, the shift of the O 2s peak, and approximately two-thirds of the shift of the O 1s core level to a movement of the Fermi level towards the conduction band by 0.7 eV as x increases from 0 to 2.

The previous argument discounting the possibility of a first-order chemical shift in the O 1s core level can be extended to explain the additional 0.4 eV shift of this level. As mentioned earlier, the charge transfer of about 0.5e per Si—O bond is the basis for the shift of all Si core levels to greater binding energy. By the same token, the charge transfer from Si to O is expected to produce a shift of the O 1s level to smaller binding energy. Of course, if oxygen atoms always occupy bridging positions



FIG. 4. The binding energies of core levels and various features of the valence bands vs oxygen concentration. The zero of energy is the Fermi level. Open symbols are XPS results, closed symbols are UPS results.  $[Si 2p]_{c.g.}$  refers to the center of gravity of the Si 2p spectrum.

in the network throughout all concentrations this firstorder shift cannot be detected from the XPS core-level measurements. However, for increasing oxygen concentration, an individual oxygen atom will have an increasing number of next-nearest-neighbor oxygen atoms. An effect of the increased number of next-nearest-neighbor oxygen bonds would be to decrease the charge transfer to individual oxygen atoms, leading to a decrease in the first-order chemical shift of the oxygen core levels which appears as a net shift to higher binding energy. This socalled inductive effect could explain the additional O 1s core-level shift to greater binding energy. Chemical shifts, first order or inductive, of the outermost O 2s valence orbital are expected to be much smaller, in agreement with our observation. It is also worth mentioning that the effective dielectric constant of the alloys decreases with increasing oxygen concentration, and this may lead to a decrease of any relaxation effects which might be present at low concentrations. This can also produce a net shift of the O 1s core level to greater binding energy with increasing oxygen concentration.

### **B.** Plasmon losses

Following the photoelectric excitation of bound electrons, the outgoing electrons can suffer inelastic losses to collective oscillations and single particle excitations. The collective excitations, plasmons, show up as broad, smooth replicas of the photoelectron peaks shifted to lower kinetic energy by an amount equal to the plasmon energy  $\hbar\omega_p$  (Ref. 39) which is about 20 eV for a-SiO<sub>2</sub>. The onset of single particle excitations can also be observed in the form of a step at an energy equal to the band gap  $E_g$  below the core level. In Fig. 5 we show selected spectra for the O 1s plasmon losses. The plasmon losses result in the broad peak centered at 17 eV below the main line for low x, which shifts to higher binding energies with increasing concentration. At large x, the spectra have a more complicated structure due to the onset of the single particle excitations at energies  $E_{g}$ and  $2E_g$  below the main line, with  $E_g \approx 9$  eV. In Fig. 6 we plot the Si 2p and O 1s plasmon energies versus oxygen concentration. At higher concentrations  $(x \ge 0.7)$ there appears to be a systematic difference in our determination of the plasmon energies for the O 1s and Si 2p core levels in excess of an estimated 0.5 eV accuracy. This difference is produced in part by a distortion of the O 1s plasmon loss spectra due to the  $2E_g$  onset. This onset produces a discernible peak in the O 1s plasmon spectra at a position slightly higher than the average position of the broad loss structure. In the low-intensity Si 2p,2s loss spectra the structures due to  $E_g$  and  $2E_g$  are not discernible and  $\hbar \omega_p$  is identified with the average position of the loss structure. Corrections in  $\hbar\omega_n$  (O 1s) that take this effect into account are indicated by arrows in Fig. 6 and they remove the discrepancy over most of the concentration range. Small deviations between 1.0 < x < 1.5may again be indicative of a slight phase separation such



FIG. 5. O 1s plasmon loss spectra for selected concentrations. Loss maxima (arrows) and the onset of single particle excitations at  $E_g$  and  $2E_g$  are indicated.



FIG. 6. Si 2p, Si 2s, and O 1s plasmon energies vs oxygen concentration. Arrows indicate corrections in the O 1s plasmon energies that are necessary due to the interference of single particle excitations (compare Fig. 5).

that the O 1s losses sample preferentially oxygen-rich regions and the Si 2p losses Si-rich regions.

It is possible to derive the density of our samples from the measurements of the plasmon energies. In the freeelectron approximation,<sup>40</sup> the plasmon energy is related to the valence electron density as

$$(\hbar\omega_n)^2 = (\hbar^2 e^2 / m \pi) N_n$$
, (4)

where *m* is the electron mass, *e* is the electron charge, and  $\hbar$  is Planck's constant.  $N_v$ , the valence electron density, is related to the mass density  $\rho$  via

$$N_{v} = \rho L_{A} (n_{\rm Si} + x n_{\rm O}) / (A_{\rm Si} + x A_{\rm O}) , \qquad (5)$$

where  $L_A$  is Avogadro's number. In this expression,  $A_{Si}$ and  $A_0$  are the atomic weights of Si and O, which are 28.1 and 16.0, respectively. The number of valence electrons of Si is  $n_{\rm Si} = 4$  and  $n_{\rm O}$  is the number of valence electrons of O. In Fig. 7 we have plotted the densities of the films derived from these equations using the Si 2p plasmon energies. The application of the free-electron formula [Eqs. (4) and (5)] to determine the mass density  $\rho$ of the films meets with a difficulty because the binding energy of the O 2s valence electrons ( $E_{g} \approx 26 \text{ eV}$ ) is close to that of the plasmon energy of  $\sim 20 \text{ eV}$ . The contribution of these bound electrons to the dielectric function will reduce the plasmon energy compared to the free-electron value.<sup>41</sup> The density determined from the true plasmon energy via Eqs. (4) and (5) with  $n_0 = 4$  (upper curve in Fig. 7) will thus overestimate  $\rho$ . Inclusion of the O 2s electrons in the free-electron formula, on the other hand, will underestimate  $\rho$ . The two curves in Fig. 7 represent thus upper and lower bounds for the film densities as estimated from the free-electron approximation for the plasmon energies. A minimum appears in the density at about x = 1, due to an essentially linear dependence of the plasmon energy on concentration. This is similar to the behavior previously reported for the densities of SiN<sub>x</sub> films.<sup>27</sup> At x = 0, we find the density  $\rho = 2.4$  g/cm<sup>3</sup>, which is close to the previously reported densities of 2.1-2.3  $g/cm^3$  for a-Si as indicated by the double arrow in Fig. 7. These values were derived from x-ray analyses and weigh-



FIG. 7. Mass density of  $SiO_x$  films vs oxygen concentration as calculated from the Si 2p plasmon energies. Upper and lower curves result from using  $n_0 = 4$  and 6 oxygen valence electrons, respectively.  $\triangle$  is the density of  $SiO_{1.97}$  from Ref. 45, and  $\blacktriangle$  is the density of  $SiO_2$  from Ref. 46. The vertical double arrow indicates the range of densities reported for *a*-Si films (see text).

ing experiments on *a*-Si films prepared in various ways.<sup>42-44</sup> The densities of our films at concentrations  $x \approx 2$  are 2.0-2.6, which are within 10-18% of the densities reported for an O-rich SiO<sub>x</sub> film<sup>45</sup> and for *a*-SiO<sub>2</sub>.<sup>46</sup> Thus it appears that, at least at the extreme concentrations, the free-electron theory of the plasmon oscillations with the inclusion of the O 2s electron is a fair approximation in this system.

## C. The valence-band spectra

In Figs. 8 and 9 we present UPS and XPS valence-band (VB) spectra for selected  $SiO_x$  alloys. The features of these spectra can be best understood by referring to the structure of the SiO<sub>2</sub> valence band, which is well established through the photoemission studies of Fischer et al.<sup>47</sup> and of DiStefano and Eastman,<sup>48</sup> the photoemis-sion studies of thermally oxidized silicon,<sup>7,11,49</sup> and through various band-structure calculations.<sup>25,50,51</sup> Our He II results for the highest concentrations shown in Fig. 8 typify that structure. It consists of basically three peaks, which we label O-I, O-II, and O-III. The peak O-I, located at approximately  $E_F - 7.5$  eV, corresponds to the O 2p nonbonding states occupied by a single pair of electrons. The O 2p lone-pair orbital is perpendicular to the Si—O—Si bonding plane in the  $\alpha$ -quartz<sup>25, 50, 51</sup> and a-SiO<sub>2</sub> (Refs. 25 and 50) compounds. The peaks O-II and O-III correspond to O 2p (Si 3p, Si 3s) bonding states,<sup>47,48</sup> with mainly O 2p character due to the strong polarity of the Si-O bond. The corresponding antibonding states with largely Si 2p and Si 2s character form the conduction band and have been probed by x-ray absorption in SiO and SiO<sub>2</sub>.  $^{52}$  The basic three-peaked structure in the UPS VB spectra of our samples is retained down to about x = 0.3; for lower concentrations, the O-II and O-III peaks merge to form a broad peak centered at about  $E_F - 12$  eV. The corelike O 2s states are observed throughout the concentration range  $x \ge 0$  at about  $E_F$ -26 eV as shown in the XPS spectra of Fig. 9. The differences in the relative intensities of the O-I-O-III peaks in the XPS and UPS spectra are due to differences in photoemission cross section for the different states as a



FIG. 8.  $SiO_x$  He II valence-band spectra for selected concentrations x. The valence-band maximum (VBM) is indicated on each spectra. The zero of energy is the Fermi level.



FIG. 9. Al  $K\alpha$  valence-band spectra for selected SiO<sub>x</sub> samples after stripping the Al  $K\alpha$  satellite and subtracting a fourth-order polynomial background. The O 2s peak has been truncated to emphasize the structure below 20 eV. Tic marks designate the valence-band maximum. The zero of energy is the Fermi level.

function of photon energy. Specifically, the O-II and O-III peaks are more pronounced in the XPS spectra partly because of the factor of 10 greater photoemission crosssection ratio  $\sigma(\text{Si } 3p)/\sigma$  (O 2p) at hv=1486.6 eV compared to its value at hv=40.8 eV, and in addition, the ratio  $\sigma(\text{Si } 3s)/\sigma$  (Si 3p) is greater by a factor of 60 at hv=1486.6 eV compared to its value at hv=40.8 eV.<sup>53</sup>

For large x, the valence-band maximum (VBM) is defined by the onset of the O 2p lone-pair peak (O-I) ~4-5 eV below  $E_F$ , as in SiO<sub>2</sub>. This edge is observed to shift slightly to lower binding energies with decreasing x in the range  $x \ge 1.5$  (see Fig. 4). In addition, the width of the O-I peak narrows with decreasing x by about 1 eV over the whole range in x due to a decrease in the interaction between neighboring lone-pair orbitals. Beginning at x = 1.5, a shoulder appears at  $E_F - 0.7$  eV (Figs. 8 and 9) which increases in intensity and develops into the Si 3p bonding states that define the VBM in a-Si.<sup>54</sup> By extrapolating the leading edge of this shoulder to the baseline, we obtain the VBM, which shifts to lower binding energies with decreasing concentration as indicated by the tic marks in Figs. 8 and 9. The Si 3p bonding character of the states at the VBM is verified by the greater intensity of these states as measured by XPS (see Fig. 9). This enhancement of the Si 3p states leads to overall lower binding-energy estimates of the VBM from the XPS measurements in the concentration range x = 0-1.5, yet we consider the estimates from XPS to be more reliable due to the higher sensitivity of XPS to the Si 3p states.

We have summarized the results of our valence-band measurements by plotting in Fig. 4 the locations of various features of the valence band over the whole concentration range. From this plot, several things can be observed. First, we find that the position of the VBM defined by the Si-Si bonding states varies little from the a-Si position in the composition range x = 0 to about x = 1.5. This result supports the prediction of Martinez and Yndurain<sup>17</sup> that Si-Si chains of at least ten atoms can lead to a VBM essentially fixed in energy. Above the critical concentration  $x_c = 1.5$ , the VBM makes an abrupt transition to higher binding energy due to the vanishing of the Si-Si bonding states. This is an indication that above  $x_c$  the network consists of essentially SiO<sub>2</sub> chains with Si as an isolated impurity. The abrupt change in the energy of the VBM by 3.5 eV at  $x_c = 1.5$  gives this stoichiometry the character of a percolation threshold. Below and up to  $x_c$  the SiO<sub>x</sub> network retains a sufficient concentration of connected Si-Si chains exceeding the minimum length of approximately ten atoms so that the VBM is determined by the Si-Si bonding states in these chains. Above  $x_c$  this requirement is not reached and the bandwidth is determined by the SiO<sub>2</sub> network. The Si-Si bonding states of isolated Si-Si bonds or short chain sequences are expected to form defect states lying in the lower half of the gap no more than 3 eV above the valence-band edge. These results are in keeping with the calculations of Zuther<sup>29</sup> and Hübner<sup>9</sup> which predict that the electronic properties of SiO<sub>2</sub> as measured by  $\epsilon_1$  and  $\epsilon_2$ are essentially defined at a concentration x = 1.3, which is also the predicted percolation threshold.9,17,29

In Fig. 4, it can be seen that the VBM measured by

XPS undergoes a small shift to higher binding energy in the range 0 < x < 1.5. This shift in the VBM is paralleled by similar shifts in the O-I peak of the valence band, the O 2s peak, and O 1s and Si 2p core levels. We have already explained the shift in the Si  $2p_0$  and part of the O 1s shift as a shift of the Fermi level toward the conduction band by roughly 0.7 eV. The similar shifts in the VBM, the O-I peak, and the O 2s peak are consistent with this interpretation.

Our inferred position of the Fermi level with respect to the core levels provides a means of obtaining the absolute position of the VBM relative to the [Si 2p]<sub>0</sub> core level. By comparing the position of the VBM at x = 0 with the position at x = 2 we obtain a measure of the natural band offset between a-Si and a-SiO<sub>2</sub>, which we determine to be 4.5±0.5 eV. This is within the range of estimates in the calculation of Herman *et al.*,<sup>55</sup> but somewhat higher than the experimental value of 3.75 eV for the Si/SiO<sub>2</sub> interface reported by Williams.<sup>56,57</sup> This latter value was obtained from the difference in the band gap of SiO<sub>2</sub> and the internal photoemission threshold at a Si/SiO<sub>2</sub> interface. Because this method measures the band offset between Si and SiO<sub>2</sub> in contact, it could, in principle, result in a value lower than our estimate. However, the difference might also be due to William's choice of 8 eV for the band gap of  $SiO_2$ .<sup>58</sup> A value of 8.5 eV (Ref. 59) for the band gap would increase William's estimate of the band offset to 4.25 eV, in better agreement with our value.

We have observed that the basic three-peaked structure (O-I, O-II, O-III) of SiO<sub>2</sub> is maintained over most of the concentration range in the  $SiO_x$  alloys. In Fig. 4, the positions of the O-I-O-III peaks indicate that the SiO<sub>2</sub> structure is retained down to about x = 0.2, where the peaks O-II and O-III merge to form the structureless broad feature mentioned earlier. This washing out of the basic structure at low x has not been observed in previous studies of  $\text{GeO}_x$  alloys.<sup>60</sup> Furthermore, the spectral shape around  $E_F - 12$  eV is at low x similar to the valence-band structure of slightly oxidized silicon.<sup>10,61</sup> The two-peaked structure is characteristic of the first stage of oxygen absorption on c-Si(111) where O<sub>2</sub> is believed to be bonded in a peroxyl configuration.<sup>12,62</sup> The shallow probe depth of He II together with the large photoemission cross section of O 2p at 40 eV makes this measurement particularly sensitive to surface oxidation. It is conceivable that a surface oxidation can occur as an inevitable result of the sputtering process, since activated oxygen is present after the discharge is stopped and before the sputter gas can be pumped from the chamber. Therefore, we cannot exclude a slight extra surface oxidation as a reason for the different character of the valence band at low concentrations. With this in mind it is safe to state that the three-peaked structure (O-I, O-II, O-III) is characteristic of the local bonding environment of O in a bridging position between two Si atoms. This structure apparently does not depend on the existence of longer chains since it persists through the critical oxygen concentration  $x_c = 1.5$ .

Martinez and Yndurain<sup>17</sup> have calculated the densities of states (DOS) in SiO<sub>x</sub> alloys using a cluster-Bethe-



FIG. 10. Bottom curve: XPS valence-band spectrum of SiO<sub>1</sub>. Center curve: normalized sum of our measured XPS and He II spectra of SiO<sub>1</sub>. Top curve: calculated density of states from Ref. 17 for SiO<sub>1</sub>.

lattice model and the tight-binding method. Because their results were presented in terms of total densities of states, it was not possible to compare our measurements with the calculations in the usual way by summing the calculated partial DOS corrected for cross-section effects. In order to compare our measured spectra with their calculated DOS quantitatively, we have partially separated the contribution from Si and O in our measurements on the basis of relative photoemission cross sections. The much greater sensitivity of the XPS measurements to Si 3p and Si 3s states together with the sensitivity of the He II measurements to the O 2p states allows us to regard the XPS and He II spectra as fair approximations to the Si- and oxygen-derived partial DOS, respectively. In Fig. 10 we have plotted the calculated DOS for  $SiO_{x=1}$  from Martinez and Yndurain along with our XPS spectrum (Si 3s, 3p partial DOS) and the normalized sum of the XPS and UPS spectra (total DOS). The individual UPS and XPS are normalized to the intensity of the pure Si 3pstates at the top of the valence bands. We have aligned the calculated spectrum with our measured spectra using the peak position of the states at the top of the valence band. Our "experimental" total DOS reproduces the essential features of the calculated spectrum: the Si 3p bonding states form the VBM, the O(2p)—Si(3p, 3s) bonding states produce the two peaks at 11.5 and 14.5 eV, and the O 2p lone-pair states give rise to the intense peak centered at 7.5 eV. In the calculated spectrum some structure is present in the gap between the Si 3p peak and the O 2p nonbonding peak and in the gap between the O 2p nonbonding peak and the bonding peak located at 11.5 eV. In the measured spectrum, these gaps are filled in due to disorder and the structure is lost. The positions of the bonding peaks are identical in the measured and calculated spectra, but the O 2p lone-pair state at 7.5 eV is shifted by about 1 eV to smaller binding energy in the calculated spectrum. Martinez and Yndurain have also noted a shift of about 0.6 eV of the lone-pair states in comparing their calculated spectrum at x = 1 with the available UPS data. They attributed this discrepancy to an overestimation of the Si-O-Si bond angle and find that a lower value of 125° reduces the shift of the O 2p lone-pair peak while introducing a discrepancy in the position of the bonding peak at 12 eV. A bond angle smaller than 144° would be in disagreement with our conclusions mentioned earlier regarding the variations in the chemical shift in this concentration range. Nonetheless, the calculated DOS at this concentration and also at the other concentrations studied by Martinez and Yndurain appear to be in good agreement with our measurements.

## **IV. SUMMARY AND CONCLUSIONS**

We have presented a comprehensive study of the electronic structure of SiO<sub>x</sub> alloys from x = 0 to x = 2 using XPS and UPS photoemission. Variations in line shape of the Si 2p core level were observed over the entire concentration range and they were interpreted in terms of a chemical shift of the Si 2p core level due to charge transfer from Si to O. We undertook an analysis of the Si 2p core-level spectra based on a superposition of five chemically shifted components corresponding to the basic bonding units in the RBM. The results indicate that our samples were composed essentially of randomly bonded fourfold-coordinated Si and twofold-coordinated O. Deviations in the suboxide concentrations and small differences in the O 1s and Si 2p,2s plasmon energies point towards a small amount of phase separation in the intermediate concentration range. It was not possible to determine from these measurements whether the phase separation is a natural tendency of SiO<sub>x</sub> alloys or whether it might be due to slight variations in the preparation conditions. From the uniform variation in the position of the Si  $2p_0$  component and the O 1s and O 2s core levels, we infer a movement of the Fermi level by about 0.7 eV toward the conduction band as x increases from 0 to 2.

Our measurements of the valence band show that the basic electronic structure of the bridging oxygen bond (O-I-O-III) is preserved over the whole concentration range, and that all of the SiO<sub>2</sub> structure is present at concentrations in excess of x = 1.5. This is consistent with the trends in the dielectric properties of SiO<sub>x</sub> alloys as calculated by Zuther. Our other observations are in essential agreement with the model calculations of Martinez and Yndurain on SiO<sub>x</sub> alloys. We find an abrupt transition in the VBM near  $x_c = 1.5$  which signals the transition from its definition by the Si 3p bonding states at low x to the onset of the O 2p lone-pair states above  $x_c = 1.5$ . This is in keeping with the concept of a percolation threshold for connected Si-Si chains as proposed by Martinez and Yndurain near the concentration  $x \approx 1.3$ .

For concentrations above  $x_c = 1.5$ , the network is essentially that of a-SiO<sub>2</sub> with Si as an impurity. In this concentration range, the Si—Si bonding states are expected to give rise to defect states just above the VBM. Below  $x_c = 1.5$ , the VBM is, in fact, determined by the Si 3p states of connected Si-Si chains.

The narrowing of 4.5 eV of the valence band over the entire concentration range accounts for about half of the increase in the optical gap as measured by Holzenkämpfer *et al.* In particular, the abrupt transition in the VBM from the Si 3p shoulder at low x to the onset of the O 2p lone-pair peak at large x can explain, in part, the nonlinear widening of the energy gap in the range x = 1.5 to x = 2.

A similar abrupt change was observed for energy of the

conduction-band edge in  $SiN_x$  (Refs. 27 and 63) for  $x_c \approx 1.3$  and for the VBM in  $GeO_x$  (Ref. 60) at  $x_c = 1.1$ . It appears, therefore, that a percolationlike threshold for the bandwidth is a common property of random-network alloy structures. Finally, the 4.5 eV difference in the VBM between x = 0 and x = 2 provides a measure of the natural band offset between a-Si and a-SiO<sub>2</sub>.

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