the plasma edge can be expected[9] to cause strong scattering of microwave radiation such as that incident upon the plasma during lower-hybrid heating experiments. Consequently the wave fronts of the radiation will be distorted and the intensity of the radiation will vary in the poloidal direction on the scale of the correlation length of the density fluctuations ($l \simeq 3$ mm).

In the interior of the low-density plasmas, the fluctuation amplitude is large enough to lead to appreciable transport; however questions remain about the spatial extent of the fluctuations and the appropriate diffusion coefficient (e.g., from strong- or weak-turbulence theory). Similar statements can be made about the transport to be expected in the interior of the high-density plasmas if the fluctuation amplitude is near the upper limit ($\tilde{n}/n \simeq 0.05$) set by our measurements. Using the techniques described above, the question of the spatial extent of the fluctuations could be resolved either in a larger plasma or in a plasma with greater angular access such as that which will be available in the alcator *C* tokamak.

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New Phenomenon in the Absorption of Oxygen on Silicon

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An O_2 adsorption state on the Si(111) 2×1 surface has been found which will remove surface states without producing a chemical shift of the Si $2p$ core level, suggesting a strongly covalent bond. This is accomplished by using an initial exposure pressure of 10^{-8} Torr. Exposures using an initial exposure pressure of 10^{-6} Torr also remove the surface states but produce a 2.0 eV Si $2p$ chemical shift indicating an ionic bond different from that of SiO_2 (shift of 3.8 eV).

Historically, surface states on Si have been associated with "dangling" bonds, i.e., bonds broken by formation of the surface. It followed that removal of these surface states by adsorption of a foreign gas—for example, oxygen—was associated with a strong chemical bond between the gas and the Si "dangling" bond.[1] Such a bond should lead to a chemical shift of the Si core levels. For example, a shift of 3.8 eV is found for the Si $2p$ levels in SiO_2,[2] and smaller shifts have been consistently reported previously for oxygen adsorbed on Si.[3]

Here, we report the surprising result of surface-state removal from the Si(111) surface without production of any measurable chemical shift (≤ 0.3 eV) of the Si $2p$ core levels even though the oxygen coverage is almost a monolayer. Thus, a new phenomenon in the adsorption of oxygen on Si has been found (similar adsorption appears[3] to occur on Ge), which should give new and important insight into the nature of surfaces and of the interaction of gases with them. Previously, Rowe *et al.*[4] reported on the adsorption of molecular O_2 on Si and interpreted the sorbed oxygen state as being O_2^-. However, the large electron transfer associated with this model can be excluded on the basis of our core level results as described below.

In these experiments, degenerate n-type silicon samples were cleaved [resulting in the 2×1

reconstruction of the Si(111) surface] *in situ* at a base pressure of ~ 5×10^{-11} Torr. All experiments were performed using a Redhead gauge (i.e., cold cathode) to measure the pressure to minimize the effects due to excited oxygen produced by an ionization gauge as reported by Ibach *et al.*[5] and Pianetta *et al.*[6] Monochromatized synchrotron radiation was used in the photoemission experiments at photon energies ($h\nu \approx 130$ eV) which would allow maximum surface sensitivity (~ 4 to 5 Å) in studies of the Si $2p$ core level.[7] The photoelectron spectra were measured with a double-pass cylindrical-mirror analyzer. The overall resolution of the monochromator and electron analyzer combination was ~ 0.3 eV. The Auger-electron-spectroscopy (AES) experiments were performed using the same experimental techniques as in the photoemission experiments in a high-resolution scanning Auger system.

In this study, two different exposure procedures were found to yield different states of adsorption, as will be described. The first, procedure 1, was to expose the freshly cleaved surface to 1 L (1 langmuir $=10^{-6}$ Torr sec) O_2 (10^{-8} Torr for 10^2 sec) followed by consecutive exposures of 9, 90, and 900 L O_2 (10^{-8}, 10^{-7}, and 10^{-6} Torr, respectively, for 900 sec each). The oxygen adsorbed after this procedure will be said to be in state 1. The second exposure procedure (procedure 2) was to expose the freshly cleaved surface to one exposure at 10^{-6} Torr for 10^3 sec to obtain 10^3 L O_2, producing state 2.

After cleaving, the Si was found to exhibit the well-established surface state in the gap as shown in curve *a*, Fig. 1. Upon being exposed to oxygen by either procedure 1 or 2, the surface states in the band gap disappeared, as has been reported consistently in the past and is shown in curve *b*, Fig. 1. (The data in Fig. 1, curve *b*, were taken after procedure 1.) Most strikingly, however, the Si $2p$ core level was found to exhibit no measurable shift when procedure 1 was used. This can be seen by comparing the Si $2p$ spectrum of the clean surface, curve *a*, Fig. 2, with curve *b* taken after the surface states disappeared, i.e., 10^3 L exposure.

The cleaved surface which was exposed to oxygen by procedure 2 was found to have a shoulder on the low-energy side of the $2p$ core level. By taking the difference between this curve and the clean-surface curve (Fig. 2, curve *a*), a peak shift by ~ 2.0 eV was revealed (Fig. 2, curve *c*). States 1 and 2 are the extremes which are obtained by a 10^3-L exposure, i.e., a 2.0-eV shifted peak could be produced with less strength[3] than in Fig. 2. This indicates that both types of adsorbed oxygen could be obtained simultaneously. The relative amounts may depend on, for instance, the exposure procedure.

Although no shift of the Si $2p$ level was observed in state 1 with the disappearance of the surface state, emission from the O $2s$ level was observed and with ~ 60% of the strength for state 2 indicating a corresponding oxygen coverage.[8]

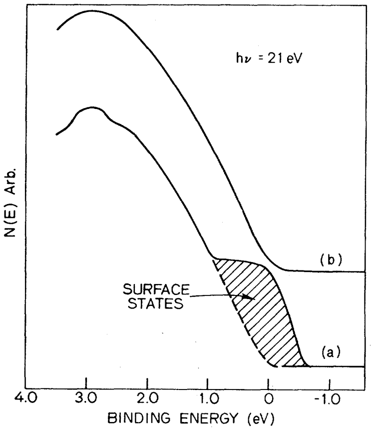

FIG. 1. Curve *a*, the emission from the clean surface; curve *b* shows the disappearance of the surface states after exposure to 1 + 9 + 90 + 900 L O_2 or to one 10^3 L O_2 exposure. Note: For comparison purposes, the zero of energy is the valence band maximum.

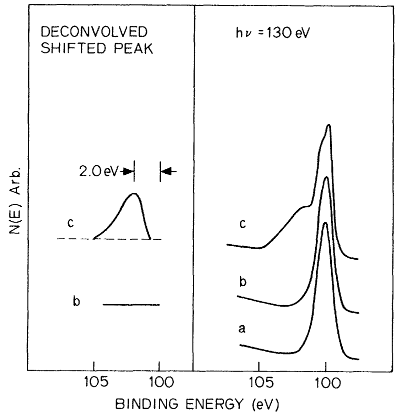

FIG. 2. Si $2p$ core levels plotted as a function of the exposures. Curve *a*, the clean Si surface. In curves *b* the surface exposed to 1 + 9 + 90 + 900 L O_2 by procedure 1 is shown to have no observable shifts, while in *c* the surface exposed to 10^3 L O_2 by procedure 2 is observed by the peak and deconvolved peak to exhibit a 2.0-eV shift of the Si $2p$ level.

This prompted additional AES studies to determine both oxygen coverage, using Si KLL and O KLL, and the shapes of the Si $L_{2,3}VV$ transitions of states 1 and 2. The oxygen coverages obtained from the AES studies were in agreement with those obtained from the O $2s$ emission.

In studies of the Si $L_{2,3}VV$ transition, one difference was observed between the spectra of states 1 and 2. The Si $L_{2,3}VV$ transition of state 2 was found to have additional structure at a kinetic energy ~ 71 eV, which state 1 did not have. Furthermore, the electron beam (4.5 keV with a current density of 20 mA cm^{-2}) was found to transform the Si $L_{2,3}VV$ spectrum of state 1 to that of state 2 within ~ 10 min, as seen in Fig. 3. This clearly shows that state 1 is transformed into state 2 via the electron beam, as indicated by AES. Ibach and Rowe[9] also reported that heating, electron bombardment, or very large oxygen exposures causes a conversion of the initially adsorbed state. This may be the same effect as discussed above. However, we favor the interpretation that the converted state seen by Ibach and Rowe is the same as we associate with the larger Si $2p$ core level shifts (≥ 2.6 eV) which we found at higher oxygen exposures,[3] also in agreement with Ibach and Rowe's own assignment.[9]

These results indicate the presence of an adsorbed state induced by procedure 1 which interacts strongly enough to cause the disappearance of the surface state but not strongly enough to cause a shift of the Si $2p$ level within the limits of the experiment (i.e., ~ 0.3 eV). The Auger results indicating that the electron beam is able to convert this state to state 2 (the 2.0-eV shifted Si $2p$) make clear that an activation energy is required to convert state 1 to state 2. Since the low-pressure exposure appears to be important in the formation of state 1 (i.e., no observable Si $2p$ level shift), it is possible that a surface relaxation, with a long time constant (i.e., $1<\tau<100$ sec), may occur, while at higher pressures (10^{-6} Torr), this relaxation may not have time to occur. At 10^{-8} Torr, oxygen molecules strike a given surface site roughly once every 100 sec, whereas at 10^{-6} Torr, the rate is 1/sec.

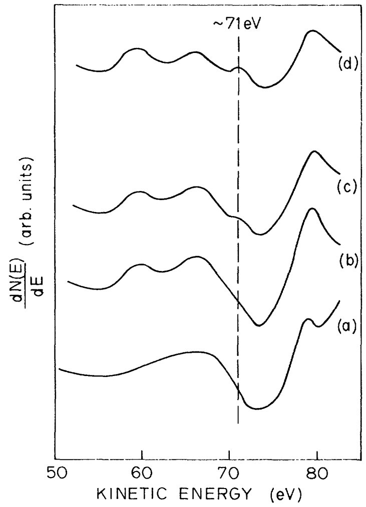

FIG. 3. Part of the Si $L_{2,3}$ VV Auger spectrum as a function of exposure to O_2 and to an electron beam. The curves are a, clean Si; b, Si exposed to $1+9+90+900$ L O_2 by procedure 1; c, the surface in b exposed to the electron beam for ~ 10 min; and d, the surface exposed to 10^3 L O_2 by procedure 2.

In order to understand this state and its relationship to state 2, it would be important to do studies of the dependence of these states on temperature to study the activation energy of the conversion of state 1 to state 2 if such conversion takes place or to study thermal desorption of O_2 from this state if desorption occurs. It is not known at this time if it is possible to produce this state (i.e., state 1) with a hot-filament ionization gauge present. Since electron beams have been found to convert this state to another, spectroscopies which utilize electron beams may easily destroy this state.

The prime purpose of this communication has been to report the existence of this new adsorption state of oxygen on silicon. Although no attempt will be made to give a definitive explanation, we will attempt to place these results in some perspective. The reader's attention is directed to the growing evidence[4,10] that (at least up to monolayer coverages) molecular oxygen may be an important adsorbed species. However, the adsorbed species has been discussed[8] as O_2^-, and our work suggests that this overemphasizes real charge transfer between the silicon and oxygen. The electron affinity of the O_2 molecule is smaller than that of the oxygen atom. In fact, there is reason to believe that the Si valence-band maximum and the upper filled O_2 levels lie at comparable energies.[11] Thus, an O_2-Si bond may form, which is basically covalent in nature, explaining the lack of a Si $2p$-level chemical shift.

One must also explain the disappearance of the surface states. We relate this to the recent recognition that large lattice rearrangements occur on the free surface of semiconductors. It should be noted that the 2×1 arrangement of the cleaved Si(111) is metastable. Harrison[12] has given arguments that the 2×1 rearrangement is driven by a strong electronic rearrangement due to termination of the lattice. This termination raises the energy of electrons in covalent bonds so that they move into the semiconductor band gap producing the observed surface states. This model helps explain the angularly resolved photoemission experiments of Rowe, Traum, and Smith.[13] If O_2 is "covalently" bonded to the surface silicon atoms, this may remove some of the driving force for the strong surface rearrangement, allowing the surface atoms and electronic states to relax toward their bulk configurations. In this way, the surface states might be removed from the band gap. The conversion of state 1 to state 2 by an electron beam, as well as the chemical shift of 2 eV associated with state 2, suggests that this state may be due to atomic oxygen (in an undetermined bonding configuration) attached by a surface bond involving considerable charge transfer. These identifications are for purposes of discussion; more work must be done before definitive identification can be made for the various adsorbed species.

In this context, we would also like to point out that chemical shifts have been used previously to distinguish between chemisorbed and oxidized states. Thus, it has been reported that a 3.8-eV Si $2p$-level shift is observed when SiO_2 forms in contrast to the 0- and 2.0-eV shifts discussed here. Flodstrom *et al.*[14] reported a 1.3-eV chemical shift for a chemisorbed phase of oxygen on Al, different from the 2.6-eV shift observed for the Al oxide. Hurych and Benbow[15] find in their work on Bi a precursory state of O_2 resulting in no measured $5d$ core-level shift before oxide formation.

The present work represents an important step in developing an understanding of the bonding of gases to solids on a molecular level. It suggests interesting new phenomena and the need for more theoretical and experimental work. For example, experiments involving oxygen core-level shifts, temperature effects, and low-energy electron diffraction should be pursued. Since the 2×1 reconstruction of the Si(111) surface was the subject of this study, more detailed studies of the other Si surfaces [i.e., different faces, (100) and (110), and different (111) reconstructions such as the 7×7] should be made to determine the effects of the surface silicon substrate bonding structure on the oxygen adsorption processes. Theoretically, for example, both the static charge distribution for various surface rearrangements and the dynamic distributions appropriate to core photoexcitation and surface vibrational excitation should be investigated.

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