Surface electronic structure of corundum transition-metal oxides: Ti_2O_3

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The surface electronic structure of Ti_2O_3 has been studied on single-crystal samples cleaved in ultrahigh vacuum. Ultraviolet photoelectron spectroscopy, electron-energy-loss spectroscopy, etc., have been used to study nearly perfect surfaces, surfaces containing defects, and O_2 chemisorption on both types of surfaces. Cleavage surfaces have a band structure essentially the same as the bulk, with a (1.4 ± 0.1) -eV-wide Ti 3d a_{1g} band separated from the (5.5-6)-eV-wide O2p valence band by a (2.5 ± 0.1) -eV band gap. No measurable band bending was seen on nearly perfect surfaces. Surface defects are associated with surface O vacancies and an accompanying transfer of charge to surface Ti 3d levels. The chemisorption of O_2 on nearly perfect Ti_2O_3 surfaces removes charge from the surface Ti ions, creating a negative adsorbed species (probably O^{2-}). The resulting surface dipole layer causes the surface O bands to shift in energy much more than either the filled or empty Ti 3d bands. Similar effects are seen for O_2 chemisorption on defect surfaces.

I. INTRODUCTION

Owing to the presence of partially filled *d*electron bands and a large variety of possible surface atomic arrangements, the 3*d* transitionmetal oxides form an extremely rich and interesting system from the standpoint of both their fundamental bulk and surface properties and their practical applications, particularly as catalysts and catalyst supports. The bulk properties of transition-metal oxides have received a fair amount of theoretical and experimental attention; that work has been reviewed by Goodenough.¹ Their surface properties, on the other hand, have only been investigated in any detail during the last few years.²⁻⁴

We have recently begun to study the surface electronic properties of transition-metal oxides having the trigonal corundum structure.⁵ The bulk electronic properties of these oxides are very interesting¹: Ti₂O₃ and V₂O₃ have strong semiconductor-to-metal transitions as a function of temperature; Ti₂O₃, Cr₂O₃, and α -Fe₂O₃ are antiferromagnetic, while V₂O₃ has complex para- and diamagnetic behavior. Fe₂O₃ and Cr₂O₃ are fairly active and selective catalysts for a number of heterogeneous catalytic reactions⁶; for example, Cr₂O₃ is the most important commercial catalyst for ethylene polymerization. Our initial studies, which are reported in this paper, have been performed on single-crystal Ti_2O_3 . Although it is not an exciting catalyst, Ti_2O_3 forms an important bridge between the insulating transition-metal oxides TiO_2 and $SrTiO_3$, both of which have been (and are being) rather thoroughly studied,² and the rest of the corundum oxides.

In Sec. II we will summarize the bulk structural and electronic properties of Ti_2O_3 . The experimental techniques employed will be described in Sec. III. Section IV will present the results of measurements of the electronic structure for both nearly perfect, atomically clean surfaces, and surfaces containing controlled numbers of defect sites. The interaction of adsorbed oxygen with both perfect and defect surfaces, which gives a great deal of information about the nature of the surface bands, is considered in Sec. V.

II. BULK STRUCTURAL AND ELECTRONIC PROPERTIES OF Ti₂O₃

The corundum lattice is built up of M_2O_3 molecular units, with the two M^{3+} cations occupying the threefold hollows on either side of a triangle of O^{2-} anions.^{1,7} There are two of these molecular units in the primitive trigonal unit cell.

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The M_2O_3 molecules are oriented with the cationcation direction along the trigonal axis and are packed in such a way that each M^{3+} ion is coordinated by six O^{2-} ions that form a distorted octahedron; only two-thirds of the available octahedrally coordinated cation sites are occupied. Oxides that crystallize in the corundum lattice include Al_2O_3 ("corundum"), Cr_2O_3 , Ti_2O_3 , V_2O_3 , α -Fe₂O₃, and Rh_2O_3 .⁷ A series of oxides exists with compositions between those of TiO₂ and Ti₂O₃, which are characterized by regions having the TiO₂ structure separated by stacking fault planes called Magnéli planes; the local atomic arrangement across Magnéli planes is just that of bulk Ti₂O₃.¹

The bulk electronic structure of the corundum transition-metal oxides varies widely depending upon the number of d electrons on the cation.^{1,8} For Ti₂O₃, the Ti³⁺ ions have a $3d^1$ configuration. There is a component of covalent bonding between the two 3d electrons on the pairs of Ti ions that share a common oxygen octahedral face; this bonding tends to localize the d levels into a_{1g} orbitals. However, a covalent component between cation and anion orbitals gives rise to cation-anion-cation interactions in the basal plane and delocalizes the delectrons, resulting in a collective a_{1g} band. (For a full discussion of the nuances of the electronic structure of Ti₂O₃, see Refs. 1 and 8.) For T < 200 °C, the a_{1g} band is filled and is separated from an empty e_g^{π} band by a gap of about 0.1 eV, making Ti_2O_3 a semiconductor. Both the a_{1g} and e_g^{π} bands are composed predominately of Ti 3d orbitals. Above 200 °C a broad semiconductor-tometal transition takes place, with the material being metallic for T > 400 °C; this behavior is believed to arise from overlap of the a_{1g} and e_g^{π} bands at high temperature.^{1,9} Optical measurements have placed the Fermi level (i.e., the a_{1g} - e_g^{π} band gap) about 3.8 eV above the top of a filled valence band comprised primarily of O 2p orbitals.¹ The width of the a_{1g} band is not precisely known, but it is separated from the valence band by a band gap of the order of 3 eV.^{1,8}

III. EXPERIMENTAL METHODS

The single-crystal Ti_2O_3 samples used in this work were grown by T. P. Reed at Lincoln Laboratory. Since a reasonable amount of material was available, it was possible to cleave samples in ultrahigh vacuum and hence obtain stoichiometric, atomically clean surfaces that could be studied *in situ*. Unlike TiO₂ and SrTiO₃, which do not cleave well along any atomic planes,^{2,4} Ti₂O₃ was found to have one cleavage plane that produced very well-ordered, defect-free surfaces; the geometry of that surface will be discussed in Sec. IV. Rods about $4 \times 4 \times 25$ mm³ were cut with the cleavage plane perpendicular to the rod axis, and shallow saw cuts were made along one face to facilitate cleaving. Samples cleaved in ultrahigh vacuum (UHV) were visually smooth and exhibited excellent (1×1) low-energy electron diffraction (LEED) patterns. No impurities were detected on cleaved surfaces by Auger spectroscopy.

Defects were produced on Ti_2O_3 surfaces by means of 500-eV Ar⁺-ion bombardment, as described previously.^{2,10,11} The density of surface defects was controlled by varying the ion-bombardment time.

Ultraviolet photoelectron (UPS) spectra were excited with the He I (21.2 eV) line from a microwave discharge lamp, and the photoelectrons were analyzed with a double-pass cylindrical mirror spectrometer having a resolution of 240 meV. Since the lamp also produces weak satellite lines at 23.1, 23.7, and 24.1 eV, the relative intensities of those lines were determined from UPS spectra of metal samples, and the experimental spectra were corrected to remove the contributions from those lines; all spectra presented here have been so corrected. The location of the Fermi level E_F was determined from UPS spectra of Au. The base pressure of the ultrahigh vacuum system was less than 2×10^{-10} Torr.

Auger and electron-energy-loss spectra were excited with an electron gun coaxial with the electron spectrometer. The energy resolution for energy-loss spectra was 0.55 eV. In order to obtain the greatest surface sensitivity, a primary electron energy of 100 eV was used. Low-energy electron diffraction (LEED) patterns were displayed on a four-grid, 96° LEED optics with a coaxial electron gun. The O_2 used for chemisorption studies was 99.99% pure and was admitted to the vacuum system through a copper-gasket-sealed, ultrahigh-vacuum variable leak valve.

IV. THE SURFACE OF ATOMICALLY CLEAN Ti_2O_3

A. Nearly perfect surfaces

From Laue x-ray measurements of the orientation of the smooth, flat facets present on many fractured Ti_2O_3 surfaces, the best cleavage face was found to have its surface normal 57° away from the trigonal axis in the trigonal-bisectrix plane. This surface indexes very nearly as an (047) plane in the binary-bisectrix-trigonal notation; its atomic geometry is shown in Fig. 1. The solid circles in Fig. 1 are Ti ions, the open circles are surface O ions that lie slightly above the Ti ion plane, and the shaded circles are surface O ions that lie slightly below the Ti ion plane. One surface O ion has been omitted in order to show the geometry of a surface O vacancy defect. All of the surface Ti ions have fivefold O coordination, four of their O ligands lying in the surface plane and one in the plane below (see defect site). The cation ligand environment on this surface is very similar to that of the fivefold Ti sites on either the (110) or (100) surfaces of TiO₂ (Ref. 4) and on the Ti-O₂ plane of SrTiO₃(100).^{11,12} Owing to the alternating inclination of the surface O octahedra relative to the macroscopic surface plane, adjacent surface cations are probably less well screened from each other than they are on the surfaces of either TiO_2 or SrTiO₃.⁴

A corrected 21.2-eV UPS spectrum for a vacuum-cleaved Ti₂O₃(047) surface is shown in Fig. 2; no inelastic background has been subtracted. The largest feature in the spectrum is emission from the O 2p valence band between 4 and 10 eV. The upper edge of the band lies 3.8-3.9 eV below E_F , in excellent agreement with the position determined from optical measurements.¹ The band is 5.5-6-eV wide, which is about 2 eV wider than the value indicated in Ref. 8. It exhibits the characteristic double-peaked structure seen in other transition-metal oxides.^{2,10,11} These peaks correspond to the nonbonding (lower binding energy) and the bonding (higher binding energy) orbitals of the O²⁻ 2p⁶ ions.¹² A shoulder is present on the



FIG. 1. Model of the $Ti_2O_3(047)$ surface. Solid circles are Ti ions, open circles are O ions lying slightly above the Ti-ion plane, and shaded circles are O ions lying slightly below the Ti-ion plane. Size of circles is proportional to Ti^{3+} and O^{2-} ionic radii. One surface O ion has been omitted to create a surface defect.



FIG. 2. UPS spectrum ($h\nu$ =21.2 eV) for vacuumcleaved Ti₂O₃(047) surface.

high-binding energy side of the O 2p band; this is the region of the valence band that contains an admixture of the Ti 3d orbitals.¹² The main emission feature due to the Ti 3d electrons is that from the a_{1g} band just below E_F . That band has a width of 1.4 ± 0.1 eV (based on the results from several cleaves) and is separated from the O 2p valence band by a (2.5 ± 0.1) -eV band gap. Because of the presence of the inelastic background associated with the a_{1g} band, it is difficult to determine whether or not there are any surface states in that band gap; we will return to that point in Sec. V below.

The small emission intensity at E_F indicates a small density of states in the Ti 3d bands there. This is consistent with the band model of Ti₂O₃ for T < 200 °C, which predicts a small band gap (about 0.1 eV) between the a_{1g} band and the empty e_g^{π} band.^{1,9} (We will see in Sec. IV B that the emission intensity at E_F increases when a metallic surface layer is formed due to the presence of surface defects.) The work function of the Ti₂O₃(047) surface, measured from the low-energy cutoff of the inelastic tail in the UPS spectra, varies slightly from cleave to cleave; the average value is 3.9 ± 0.1 eV.

It is difficult to interpret UPS intensities quantitatively since neither electron mean free paths nor photoemission matrix elements are accurately known. However, we can get some information from the ratio of the integrated intensities of the O 2p and Ti 3d bands by making a few assumptions. If we assume that the surface Ti ions have the same $3d^1$ configuration as those in the bulk, take electron mean free paths of 5 Å for the Ti 3d band and 8 Å for the O 2p band,¹³ assume that the

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matrix elements for emission from the two bands are equal, and assume that any angular emission effects average out, then the intensity of the a_{1g} band emission would be 0.07 times as large as that from the O2p band for stoichiometric Ti₂O₃. The measured value, averaged over several good cleaves, is 0.047±0.008, which is only about 40% smaller than the "ideal" value. This implies that the *d*electron and *p*-electron matrix elements are of comparable magnitude in Ti₂O₃ at this photon energy.

The first-derivative electron-energy-loss spectrum for a cleaved $Ti_2O_3(047)$ surface is shown as the solid curve in Fig. 3; the dotted curve is the spectrum after O adsorption and will be discussed in Sec. V. Peaks in the loss spectrum occur at 1.9, 6.2, and 13.2 eV (maximum negative slopes in the first derivative). There may be another weak peak at 3.5 eV but it could be an artifact of the differentiation.¹⁴ The very strong peak at 1.9 eV corresponds to an $a_{1g} \rightarrow e_g^{\pi}$ (Ti $d \rightarrow d$) transition; those transitions appear in the bulk optical spectra between 0.7 and 2 eV.^{1,15} The loss peak at 6.2 eV is an anion p to cation d transition, probably from the nonbonding states of the O 2p band to the e_{g}^{π} band. The origin of the transition responsible for the 13.2-eV loss peak is not completely clear, but it must originate in the O2p valence band. The final state is probably the empty O 3s band (see discussion in Sec. V).

In the above discussion we have assumed that the electronic structure of the $Ti_2O_3(047)$ surface is essentially the same as that of the bulk and that the bands are not bent at the surface.¹⁶ That this is



FIG. 3. Electron-energy-loss spectra for cleaved $Ti_2O_3(047)$ surface before (solid curve) and after (dotted curve) 10^6 -L O_2 exposure. Incident electron energy is 100 eV.

most likely the case is supported by the following pieces of information: (1) The top of the O 2pvalence band lies exactly the same energy below E_F as that determined from bulk optical measurements.¹ (2) If the top layer of Ti ions had fewer delectrons than those in the bulk, the bands would be bent up at the surface and the a_{1g} band would be partially depopulated.¹⁶ This effect is observed when O₂ is chemisorbed on the surface and will be described in Sec. V. (3) If the surface Ti ions had a larger d electron population than the $3d^{1}$ configuration of the bulk, the $a_{1g}-e_{g}^{\pi}$ band gap would most likely be removed and there would be significant emission intensity at E_{F} . This effect is seen when O vacancy defects are created on Ti₂O₃(047) (see Sec. IV B).

B. Surface defects

When defects are created on the $Ti_2O_3(047)$ surface by Ar⁺-ion bombardment, the UPS spectra shown in Fig. 4 are obtained. Figure 4(a) shows the development of the spectra as the surface is bombarded for the times shown. (An equilibrium state is reached after about 15 min of bombardment for our ion-beam parameters.) Figure 4(b) shows spectra for the cleaved surface (solid curve) and the equilibrium surface (dotted curve) aligned at E_F . Several changes occur in the spectra as the density of surface defect sites increases. The intensity of emission from the a_{1g} band increases and the band broadens; the O 2p valence band changes shape while its full width at half maximum (FWHM) narrows, and a broad spectrum of defect surface states appears in the O 2p- a_{1g} band gap. The work function decreases with increasing defect density, dropping by 0.2 eV when equilibrium is reached, and the intensity of emission at E_F increases by over a factor of 3. The ratio of the integrated intensity in the a_{1g} band to that in the O 2p band is more than three times larger for the high-defect-density surface than it is for the cleaved surface, indicating a significant loss of O from the surface. The loss of O is confirmed by Auger measurements, but diffraction effects for the nearly perfect surface have precluded an accurate quantitative determination. LEED patterns disappear after roughly a minute of ion bombardment.

Since the surface disorders on bombardment and a variety of surface defect sites no doubt exists, it is not possible to determine the detailed atomic arrangement on such surfaces. However, since the defects are associated with a loss of O, we can get

Ar^+ - Ion Bombardment of $Ti_2O_3(047)$



FIG. 4. (a) Series of UPS spectra for Ar^+ -ion bombardment of $Ti_2O_3(047)$ surface. (b) UPS spectra for cleaved $Ti_2O_3(047)$ surface (solid curve) and equilibrium ion-bombarded surface (dotted curve).

a good idea of the type of defect sites that will exist for small defect densities. Such a defect site is shown in Fig. 1, where one O ion has been removed from the surface plane. The resulting vacancy is bounded by three Ti ions, two having fourfold O coordination and one (in the second atomic plane) having fivefold O coordination. This type of defect site is similar to the defects that exist on TiO₂ surfaces that normally have fivefold coordinated surface cations.⁴ In that case, the O vacancy is bounded by two fourfold coordinated Ti ions. That site on TiO_2 is capable of trapping an electron, resulting in an increase in the population of the 3d orbitals of the cations; the electron is presumably shared by both Ti ions.4,10 We refer to those sites as "Ti³⁺-O-vacancy complexes" for want of a more precise description.^{2,4} The type of defect site shown in Fig. 1 for Ti₂O₂ can most likely trap an electron (or electrons) also, increasing the net charge on the adjacent Ti ions. However, because of the more complex atomic geometry of this type of defect and a lack of any real knowledge of its electronic structure, a name such as " $Ti^{2+} - O$ -vacancy complex" would be premature and perhaps misleading.

When the density of surface defects increases to

the point where they begin to interact with each other, the simple, isolated-defect picture described above breaks down. Many types of defects will exist, and gross rearrangements of the atomic structure will take place. The best that we can do is to rationalize the observed spectra in terms of plausible models of the surface composition.¹¹ If we assume that a layer on the Ti₂O₃ surface is reduced to a lower oxide, we can determine what layer thickness would yield the observed Ti-O UPS ratios. We will assume that some of the surface atomic layers have the composition TiO, with a $Ti^{2+} 3d^2$ electronic configuration on the cations.¹ There is no particular justification for this assumption, since the rocksalt (and sometimes monoclinic) oxide TiO_x , which has a bulk-defect structure, has a stoichiometry range of 0.6 < x < 1.28 (Ref. 1); we use it simply for illustration. If the top two atomic planes of the $Ti_2O_3(047)$ surface (each about 2.2-Å thick) were TiO, then the Ti a_{1g}-O 2p UPS ratio would be 3.0 times the value for a perfect surface, as observed. This surface-layer thickness is consistent with the depth of significant damage produced by 500-eV Ar⁺ ions. Such a model should not be taken too seriously, though, since the itinerant electron nature of Ti₂O₃ could give rise to an accumulation layer near the surface in the presence of surface defects.¹⁶ That layer would contribute to the a_{1g} UPS emission from a depth greater than just the top two atomic planes.

Even though the above model may be somewhat artificial, it is instructive to compare the spectra in Fig. 4(b) with the 21.2-eV UPS spectra for vacuum fractured $TiO_{0.93}$ and $TiO_{1.15}$ in Ref. 17. The photoemission intensity at E_F is much larger for TiO_{x} than it is for stoichiometric $Ti_{2}O_{3}$; for the latter surface it is about 0.08 times the intensity at the peak of the a_{1g} band. That ratio for TiO_x is about 0.4, and the values observed for ion-bombarded Ti_2O_3 are around 0.3. The large density of states at E_F indicates a more metallic nature for the nonstoichiometric damaged surface layer. On the other hand, the UPS spectra for fractured TiO_x samples do not show as large a density of states in the $O 2p - a_{1g}$ band gap as does the dotted curve in Fig. 4(b); those states arise from a variety of surface defects.

V. CHEMISORPTION OF O₂ ON Ti₂O₃

The UPS spectra that are obtained when a cleaved $Ti_2O_3(047)$ surface is exposed to O_2 are shown in Fig. 5. The same data are presented in



FIG. 5. Series of UPS spectra for $Ti_2O_3(047)$ surface exposed to O_2 . Same data are presented in (a) and (b).

Figs. 5(a) and 5(b), but viewed from a different angle. The changes that occur in the electronenergy-loss spectrum are shown in Fig. 3, where the dotted curve is the loss spectrum after 10^{6} -L O₂ exposure.

Figure 6 shows some of the parameters of the surface band structure that were determined from the UPS spectra in Fig. 5. The small solid circles in the lower half of Fig. 6 give the ratio of the integrated intensity in the a_{1g} band to that in the O 2p band, after a linear background subtraction under each band, normalized to the value for the cleaved surface. The larger solid circles in the upper part of Fig. 6 show the position of the top edge of the O 2p valence band relative to E_F , and the triangular points give the changes in the width of the $O 2p - a_{1g}$ band gap versus O_2 exposure. The change in the work function Φ with exposure is shown by the open circles.

The most striking change in the UPS spectra for $Ti_2O_3(047)$ upon O_2 exposure is the rapid reduction in the amplitude of emission from the a_{1g} band (Figs. 5 and 6). This emission drops to less than one-fifth of its initial value by 1-L exposure, indicating an initial O_2 sticking probability of essentially unity and a transfer of electrons from the



FIG. 6. Band-structure parameters for $Ti_2O_3(047)$ surface versus O_2 exposure. See discussion in text.

 Ti^{3+} ions to the adsorbed species. Although we have not been able to identify this specie from UPS difference spectra (see below), it probably consists of O^{2-} ions completing the sixfold coordination of the surface Ti ions.¹⁸ The surface dipole layer associated with the negative adsorbed species, together with possible changes in the polarization of the surface O ions, increased the work function as shown in Fig. 6. An additional change in the UPS spectra that can be seen in Fig. 5(b) is the complete disappearance of the shoulder on the high-binding energy side of the O 2p band by 1-L exposure, strongly suggesting that it arises from the Ti 3d admixture in the predominately O 2pvalence band. Above 1 L the emission from the a_{1g} band continues to decrease with O₂ exposure up to 10⁶ L, but at a much slower rate; the slope of the bottom curve in Fig. 6 above 1 L is forty times smaller than below 1 L.

We can attempt to determine whether or not any intrinsic surface states exist in the $O 2p - a_{1g}$ band gap on cleaved Ti₂O₃(047) from the change in amplitude of the UPS emission in the band-gap region with O₂ exposure. The apparent band-gap emission is the sum of emission from any intrinsic surface states in the gap and inelastically scattered electrons associated with the a_{1g} band. As the a_{1g} band intensity decreases, its inelastic tail should decrease proportionately, so one can plot the bandgap emission intensity versus the integrated intensity of the a_{1g} band and look for a nonzero intercept when the a_{1g} intensity is extrapolated to zero. Such a plot yields a rather good straight line whose intercept is about one-eighth of the value of the band-gap emission from the cleaved surface. If this number were to be taken seriously, it would correspond to less than 0.1 electrons per surface unit cell in the bulk band gap. However, this ignores any interactions between band-gap surface states and the adsorbed O_2 , which is probably a poor assumption. We must conclude that our angle-integrated UPS data are not sufficient to determine the presence or absence of intrinsic band-gap surface states. Angle-resolved photoelectron spectra should be able to locate such states if they exist.

A description of the motion of both the filled and empty surface energy bands with O_2 exposure can be obtained from the UPS data in Figs. 5 and 6 and the energy-loss data in Fig. 3. The width of the O2p valence band, measured from the band edges, remains constant to within +0.1 eV with O_2 exposure, but the band moves up toward the Fermi level by 0.8 eV. The position of the a_{1g} band, on the other hand, is relatively independent of O_2 exposure. The bottom edge of the band moves upward by only 0.2-0.3 eV as its emission intensity decreases by a factor of 10. This behavior of the a_{1g} band results in a decrease in the width of the $O 2p-a_{1g}$ band gap by about 0.5 eV. The location of the vacuum level, as determined from $\Delta \Phi$, follows the position of the O 2p band, remaining 7.7 ± 0.1 eV above the top of that band throughout the entire exposure range; its location does not correlate with the position of the a_{1g} band.

Some extremely interesting effects are seen in the electron-energy-loss spectra for Ti₂O₃(047) upon O₂ exposure (Fig. 3). The large loss peak at 1.9 eV in the cleaved surface spectrum, corresponding to an $a_{1g} \rightarrow e_g^{\pi}$ transition, is shifted to 1.7 eV. This shift is the same as the amount of narrowing observed for the a_{1g} band; thus, if we assume that the transition has the same initial and final states before and after O₂ exposure, the e_g^{π} band must remain very nearly fixed relative to E_F . The peak at 6.2 eV in the cleaved surface spectrum, attributed to transitions from the nonbonding O orbitals to the e_g^{π} band, is shifted to lower energy upon O_2 adsorption by 0.6 eV. Since the O2p band was seen to shift upward by about 0.8 eV, that also indicates that the empty e_g^{π} band does not move appreciably relative to E_F . The peak at 13.2 eV remains unchanged, suggesting an $O2p \rightarrow O3s$ transition, as mentioned earlier. If the final state for that transition were a Ti level, the loss peak would most likely shift with O_2 exposure.

Perhaps the most intriguing feature of the energy-loss spectrum after O₂ exposure is the appearance of a peak at 10.3 eV that was absent in the cleaved surface spectrum. Such a peak is present in the energy-loss spectrum of vacuum-fractured TiO_2 .^{10,19} The TiO_2 spectrum exhibits three peaks of roughly equal magnitude located at 5.6, 10.3, and 13.8 eV; there is no energy-loss peak in the vicinity of 2 eV for nearly perfect surfaces of TiO₂.¹⁰ Thus, with the exception of the peak arising from the $a_{1g} \rightarrow e_g^{\pi}$ transition, the energy-loss spectrum of Ti₂O₃ after O₂ exposure is very similar to that of TiO₂. The 10.3-eV loss peak almost certainly arises from an $O2p \rightarrow Ti 3d$ transition (if it were an $O2p \rightarrow O3s$ transition, it should behave in a manner similar to that of the 13.2-eV peak and be present on the cleaved surface), but the final dstate must be one characteristic of the octahedrally coordinated $Ti^{4+} 3d^0$ ions rather than $Ti^{3+} 3d^1$ ions. This is consistent with the removal of electrons from surface Ti ions, as shown by the large decrease in the intensity of emission from the a_{1g} band.

It is not correct, however, to refer to the removal of Ti 3d electrons from only the top plane of cations in Ti₂O₃. Owing to basal plane cationanion-cation interactions, the a_{1g} states form a delocalized band, and the removal of electrons from surface cations will give rise to a depletion layer extending a finite depth into the crystal.¹⁶ From the absence of any broadening of the O2pband in the UPS spectra, we can assume that the screening length is longer than the photoelectron escape depth and that we are only seeing the band locations at the surface. The observed decrease in the intensity of the a_{1g} band emission thus represents the creation of the depletion layer with O_2 exposure. It is apparent from Fig. 6 and the discussion above, however, that a simple model¹⁶ in which all of the bulk bands bend up equally at the surface is not a correct description for Ti₂O₃. There are large changes in the relative positions of the O and Ti bands as a result of the strong interaction between O_2 and the Ti_2O_3 surface.

The complex band-structure changes that occur

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when Ti₂O₃ is exposed to O₂ make it extremely difficult to apply UPS difference spectroscopy to the study of adsorbed species. In order to take meaningful differences between two UPS spectra, it is necessary to shift the spectra relative to each other by the difference in the band bending between the two.^{18,20} If all of the bands move rigidly, this is a simple matter. But it becomes almost impossible when band-structure changes of the type seen here occur. An example of the magnitude of the problem is shown in Fig. 7, where UPS difference spectra have been plotted for the same 10-L O₂ exposure (subtracting the clean surface spectrum) but with different band bending corrections. Any of the shifts shown in Fig. 7 might be justified based upon the measured spectra. We have thus not used difference spectra for studying O_2 chemisorption on Ti_2O_3 .

There is also a strong interaction between O₂ and surface defects on Ti₂O₃. Figure 8 shows a series of UPS spectra for an equilibrium Ar+-ion bombarded surface after various O2 exposures. The intensity of the a_{1g} band emission decreases relative to that from the O 2p band, but it does so more slowly than for the cleaved surface, dropping to 40% of its initial value by 2- to 5-L exposure. Above 5 L, the a_{1g} intensity continues to decrease with O_2 exposure, but at a much slower rate. (The slope of the data on a semilog plot similar to that in Fig. 6 is ten times smaller above 5 L than it is for lower exposures.) The work function increases during O_2 chemisorption, rising by about 0.4 eV by 10⁶-L exposure. As can be seen in Fig. 8, there are also significant changes in the O 2p band.



FIG. 7. UPS difference spectra for 10-L O_2 exposure on cleaved $Ti_2O_3(047)$ surface for various assumed values of the band bending.



FIG. 8. Series of UPS spectra for Ar^+ -ion bombarded Ti₂O₃ surface exposed to O₂.

Owing to the extreme complexity of both the geometric and electronic structure on high-defectdensity surfaces, we have not attempted any interpretation of data such as that in Fig. 8 in terms of surface band structure. There is clearly a transfer of charge from surface cations to a negative adsorbed species (again probably O^{2-} for low exposures), which is undoubtedly accompanied by an increase in the O ligand coordination of those cations, but any further attempts to explain bandstructure changes would be purely speculation. For the same reasons discussed in connection with O_2 adsorption on cleaved surfaces, we have not employed UPS difference spectra with this system.

We have ignored the possible role of hydrogen⁴ in modifying either the intrinsic surface electronic structure of Ti_2O_3 or the chemisorption of O_2 simply because nothing is known about the amount of H that could exist in the bulk of Ti_2O_3 . Our experiments were performed rapidly after cleaving in order to minimize such effects,⁴ but large amounts of interstitial H in the sample might possibly affect even cleaved surfaces.²¹ More work is needed before this possibility can be adequately addressed.

VI. SUMMARY

We have studied the surface electronic properties of Ti_2O_3 for both nearly perfect surfaces and surfaces containing defects. The cleavage face of Ti_2O_3 was found to be an (047) plane, whose surface geometry is similar to that for TiO_2 and $SrTiO_3$ surfaces whose surface cations are fivefold coordinated. The surface band structure of Ti₂O₃(047) is essentially the same as that of the bulk, and no intrinsic surface states could be identified in the UPS or energy-loss spectra. The O 2p valence band was found to be (5.5-6)-eV wide, with its upper edge lying 2.5 ± 0.1 eV below the Fermi level E_F . The Ti 3d electrons form an a_{1g} band that extends 1.4 ± 0.1 eV below E_F . The density of states at E_F is low, consistent with the semiconducting nature of the bulk band structure of Ti₂O₃. The work function of the nearly perfect surface is 3.9 ± 0.1 eV. Surface defects, produced by ion bombardment, are associated with surface O vacancies, as on most other oxides. Surface defects produce changes in the O 2p and a_{1g} bands, and surface states appear in the O 2p- a_{1g} band gap.

There is a strong interaction between the nearly perfect $Ti_2O_3(047)$ surface and adsorbed O_2 , with electrons being transferred from the a_{1g} band to the adsorbed species (probably O^{2-} at low expo-

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sures). The O and Ti surface bands move relative to E_F in different ways when the surface is exposed to O₂, the O bands being much more mobile than the Ti bands. Changes in the electronenergy-loss spectra with O₂ exposure helped to determine the location of the empty e_g^{π} band and its response to O₂ chemisorption. The surface band-structure changes are sufficiently complex that UPS difference spectroscopy cannot be applied to the study of adsorbed O₂. The photoemission matrix elements for p and d electrons at a photon energy of 21.2 eV are found to be roughly equal.

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