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Surface electronic structure of TiO_2: Atomic geometry, ligand coordination, and the effect of adsorbed hydrogen

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The intrinsic electronic surface-state structure in the region of the bulk band gap for the (110), (100), and (001) surfaces of TiO_2 (rutile) has been determined by fracturing single-crystal samples in ultrahigh vacuum and measuring their ultraviolet photoemission spectra. None of the faces exhibits an appreciable density of surface states in the bulk band gap, in disagreement with recent calculations for the TiO_2(001) surface by Kasowski and Tait. The atomic geometry of both perfect and defect surfaces is examined, and the incomplete screening of pairs of surface cations at defect sites is suggested to give rise to occupied band-gap surface states rather than the coordinative unsaturation of surface cations. Hydrogen-exposure experiments indicate that TiO_2 surfaces may not interact as strongly with hydrogen as has been suggested.

I. INTRODUCTION

The surfaces of insulating $3d$-transition-metal oxides [e.g., TiO_2 (rutile) and $SrTiO_3$] have been more thoroughly studied than those of any other oxide.[1] Theoretical calculations of surface electronic structure and experiments using surface-sensitive electron spectroscopic techniques have been performed for both perfect surfaces and for surfaces containing various amounts and types of defects. While progress has been made in understanding certain specific surfaces and defect and chemisorption systems,[1] a number of very fundamental conceptual problems remain unsolved.[2]

One of the most fundamental questions concerning the surfaces of transition-metal oxides, and one that has not yet been satisfactorily answered, is, "What properties of the surface (e.g., cation ligand coordination, atomic geometry, charge transfer between surface ions, reconstruction, or surface ionic polarization) are most important in determining its electronic structure, and how does that structure differ from that of the bulk?" That question was addressed recently by Kasowski and Tait,[3] who calculated the electronic states for the (110) and (001) crystal faces of TiO_2. They found strikingly different surface-state spectra for the two faces, resulting primarily from the different ligand coordination of the cations. In this paper we report ultraviolet-photoemission (UPS) measurements of the electronic structure of the (110), (001), and (100) faces of single-crystal TiO_2. The results are in basic agreement with the calculations of Kasowski and Tait[3] and others[4-9] for surfaces having high cation ligand coordination, but they are in significant disagreement for surfaces of low cation coordination number. We have also investigated the possible effects of hydrogen on intrinsic and defect surface states on TiO_2.

In Sec. II we present the historical background, both experimental and theoretical, upon which the present experiments are based. The experimental techniques and sample preparation are presented in Sec. III, and the experimental results are summarized in Sec. IV. In Sec. V the present results are discussed in light of the current theories, and some possible explanations for the observed discrepancies are suggested.

II. BACKGROUND

The theory of surface states on insulating transition-metal oxides was first addressed by Wolfram and co-workers[10-12] in a series of papers that examined the role of surface cation d orbitals on $SrTiO_3$(100) in both surface electronic structure and the ability of transition-metal oxides to chemisorb certain types of molecules. Since the most important region of the surface electronic energy spectrum for chemisorption is that near the Fermi level, E_F, both theoretical and experimental efforts have concentrated on the region of the bulk band gap, the O($2p$) valence band, and the Ti($3d$) conduction band. Initial UPS measurements were made by Powell and Spicer[13] and by Derbenwick[14] on both reduced and doped n-type $SrTiO_3$(100). Their results indicated a maximum density of surface states in the bulk band-gap region of no more than 10^{13} electrons/cm^2, a value consistent with density of surface defects resulting from fracture. Subsequent theoretical work[4-7] indicated that empty surface states, derived from the Ti($3d$) conduction band, should exist in the upper half of the bulk band gap for insulating $SrTiO_3$(100). However, attempts to fill those states by doping or reducing the crystal (and hence raising E_F up to the bottom of the conduction band) would push the surface states up into the bulk conduction band.[4] This "surface-enhanced covalency" results from the Coulomb repulsion among *d* electrons on the surface cations.

Experiments on vacuum-fractured $TiO_2(110)$ and $SrTiO_3(100)$ by Henrich *et al.*[15–19] confirmed the results of Powell and Spicer[13] on $SrTiO_3$ and showed the analogous behavior for TiO_2. The perfect $TiO_2(110)$ surface, shown in Fig. 1, contains two types of cations, one having full sixfold O coordination and the other having a fivefold O coordination essentially the same as that for $SrTiO_3(100)$. Since the Sr electronic levels in $SrTiO_3$ lie too far from E_F to have much of an effect on the electronic structure in the band-gap region,[19] the similarity of the results for $TiO_2(110)$ and $SrTiO_3(100)$ was not surprising. Henrich *et al.*[15–19] and Somorjai and co-workers[20–22] showed that filled band-gap surface states could be produced on TiO_2 and $SrTiO_3$ by creating surface defects (i.e., disorder and/or partial surface reduction produced by inert-gas-ion bombardment or by submonolayer cation desposition). Defect band-gap states appear to be associated with Ti^{3+}/O-vacancy complexes; they will be discussed in greater detail in Sec. V. Such complexes are associated with a reduction in cation ligand coordination number, and one would expect that reduced coordination to play a major role in determining the electronic surface-state spectra.

Recently Kasowski and Tait[3] used a linear combination of muffin-tin-orbitals method applied to thick slabs to calculate the surface electronic structure of the (110) and (001) surfaces of TiO_2. The perfect $TiO_2(001)$ surface, shown in Fig. 2, is significantly different from the (110) surface in that the surface cations, all of which are identical, have only fourfold O coordination. Low-energy-electron-diffraction (LEED) measurements on polished faces of $TiO_2(001)$ by Tait and Kasowski[23] showed it to be extremely unstable, forming facets on annealing that were large enough to produce sharp LEED spots with low background intensity. The surface electronic spectrum calculated by Kasowski and Tait[3] for $TiO_2(110)$ exhibited some surface states split off from the top of the O(2*p*) valence band into the bottom of the bulk band gap. The surface band gap was reduced to 1.78 eV, compared to their calculated value of 3.25 eV for bulk TiO_2. It was found, however, that a slight relaxation of the surface O ions brought those states back into the valence band, restoring the full 3.25-eV band gap at the surface, in agreement with the experiments described above.

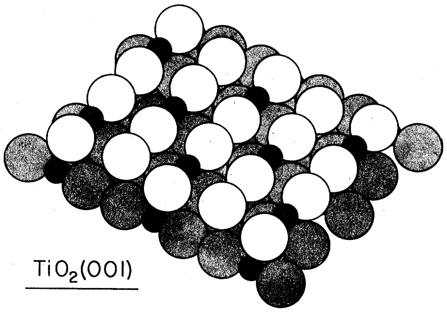

FIG. 2. Model of $TiO_2(001)$ surface.

The results of Kasowski and Tait[3] for the fourfold coordinated $TiO_2(001)$ surface were drastically different, however. For a perfect, unrelaxed surface, the bulk band gap contained states split off from both the O(2*p*) valence band and the Ti(3*d*) conduction band; the effective-surface band gap was reduced to only 0.95 eV. This was primarily a consequence of the reduced ligand coordination of the surface Ti ions. The authors remarked that simple relaxation of the surface atoms could not remove those states from the band gap.[3]

Since only the $TiO_2(110)$ surface had previously been prepared by fracturing in vacuum, we proposed to test the theory by preparing the $TiO_2(001)$ surface by fracturing in UHV ($\sim 2\times10^{-10}$ Torr) and measuring its surface electronic structure by UPS. At the same time we fractured the $TiO_2(110)$ surface for reference, and we also fractured the $TiO_2(100)$ surface. The last surface, which is shown in Fig. 3, contains all fivefold coordinated

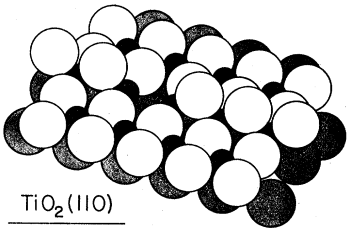

FIG. 1. Model of $TiO_2(110)$ surface, using ionic radii: $Ti^{4+} = 0.70$ Å and $O^{2-} = 1.40$ Å. Shaded O ions lie below the surface plane. One bridging O ion has been removed to create a surface defect (see discussion in text).

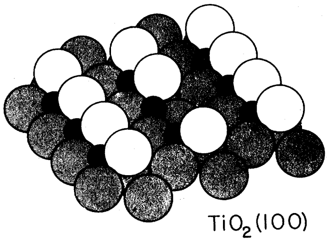

FIG. 3. Model of $TiO_2(100)$ surface. One O ion has been removed to create a surface defect.

Ti ions. Somorjai and co-workers,[20,21] working with polished samples, found the $TiO_2(100)$ surface to be slightly unstable in that it reconstructed on annealing to give (1×3), (1×5), and (1×7) LEED patterns. However, they did not observe faceting of that surface.

III. EXPERIMENTAL METHODS

The TiO_2 samples used were cut from a single-crystal rutile boule obtained from Commercial Crystals, Inc. Rods $4\times4\times{\sim}30$ mm^3 were cut with the rod axes parallel to within 1° to the $\langle110\rangle$, $\langle001\rangle$, and $\langle100\rangle$ directions, respectively. Shallow groves were cut in one side of the rods perpendicular to the rod axes to facilitate fracture. The samples were then reduced to a bluish-gray color (10^{18}–10^{19} O vacancies per cm^3 in the bulk)[24] by heating in UHV: such reduction pins E_F at the bottom of the bulk conduction band. Auger spectra of the fractured surfaces showed them to be atomically clean.

Since TiO_2 does not cleave well, different fractures result in surfaces having somewhat different topographies. Thus each rod was fractured at least three times and the UPS spectra were recorded after each fracture. All fractured surfaces were also examined by LEED. In all cases the LEED patterns were poor (see Fig. 1 of Ref. 1 for typical pattern quality), indicating a surface-defect density of a few percent or greater. But all of the patterns exhibited the spot symmetry and spacing characteristic of the face perpendicular to the rod axis; no evidence of reconstruction or faceting was found on any of the surfaces. (However, note that our samples were not annealed after fracturing.)

The 21.2-eV UPS spectra were recorded with a double-pass cylindrical mirror analyzer (CMA) at a resolution of 0.15 eV. The spectra were measured as soon as possible after fracture; they were completed within five to ten minutes after the surfaces were prepared. In order to determine the spectrum of states in the bulk band-gap region as accurately as possible, the UPS spectra were corrected for the presence of weak lines at 23.1, 23.7, and 24.0 eV in the output of the microwave discharge lamp. The relative intensities of those lines were determined from UPS spectra of clean Ta, which has a large density of states at the Fermi level. The strongest spurious line (23.1 eV) had an intensity 2.5% of that of the 21.2-eV line.

An electron-energy-loss (ELS) spectrum was also taken on each surface after the UPS spectra, using a low-current-density 100-eV electron beam to maximize surface sensitivity and minimize electron-beam damage of the oxide surface; such damage produces the same type of defect surface states discussed in Sec. II. The resolution for the ELS spectra was 0.5 eV. LEED patterns were taken after both the UPS and ELS spectra were completed.

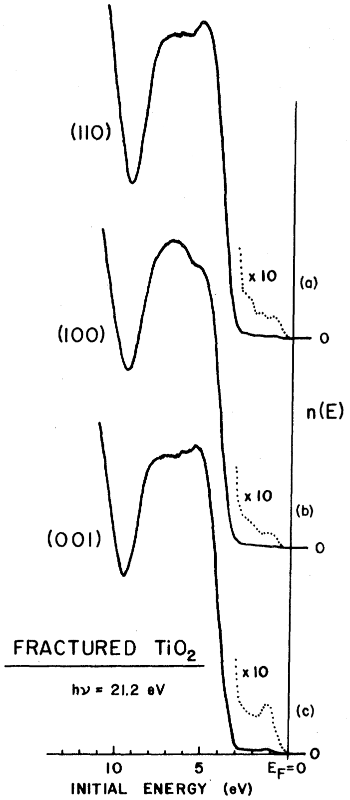

FIG. 4. He(I) UPS spectra for vacuum-fractured TiO_2, after correction for the presence of He(I) lines at 23.1, 23.7, and 24.0 eV: (a) $TiO_2(110)$, (b) $TiO_2(100)$, and (c) $TiO_2(001)$. Curves are aligned at E_F.

IV. EXPERIMENTAL RESULTS

The corrected UPS spectra for each of the surfaces investigated are shown in Fig. 4; no inelastic background has been subtracted. The spectra are qualitatively similar in that there is very little emission from the region of the bulk band gap for any of the faces. The differences in the $O(2p)$ valence-band emission for the three spectra are not significant; the details of the shape of that band vary somewhat from fracture to fracture even for the same crystal face.

Figure 5 shows, on an expanded vertical scale, the band-gap region of the spectrum for two fractures of each of the three faces in order to show the variability in the spectra obtained for different fractures. The energy scale for the spectra in Fig. 5 has been referenced to the upper edge of

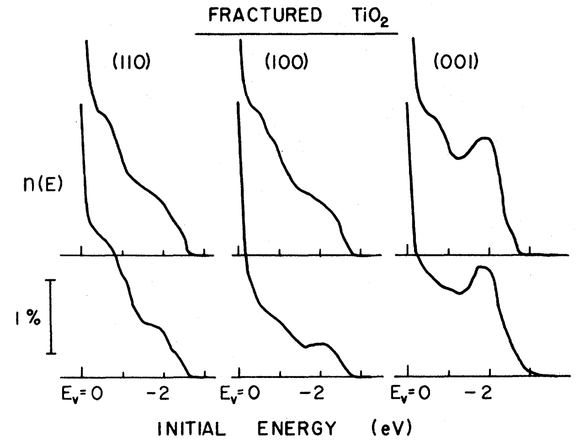

FIG. 5. He(I) UPS spectra (corrected) of the band-gap region for vacuum-fractured TiO$_2$. Spectra for two fractures of each face indicated are shown. Bar on $n(E)$ axis is 1% of the amplitude of the O($2p$) valence-band emission. Curves are aligned at E_v.

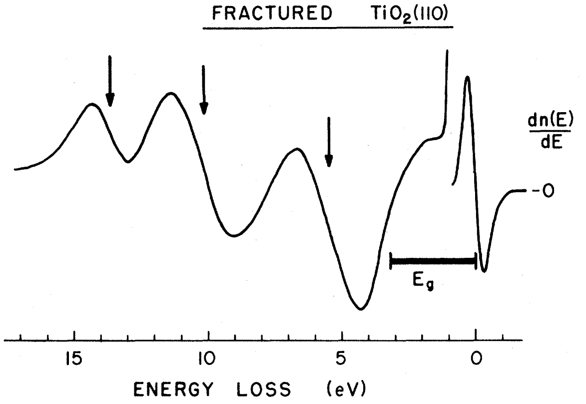

FIG. 6. Electron-energy-loss spectrum $dn(E)/dE$ vs E_L for vacuum-fractured TiO$_2$(110), taken with an incident-electron energy of 100 eV. Arrows indicate the location of peaks in $n(E)$. Heavy bar indicates width of bulk band gap.

the valence band, E_v. The bar on the $n(E)$ axis indicates 1% of the amplitude of the O($2p$) valence-band emission. The magnitude of the emission from the bulk band-gap region is roughly the same for different fractures of the same face, but the detailed features vary. The only feature in the band-gap emission that can be clearly identified is a peak at about 1.9 eV above E_v for the TiO$_2$ (001) surface. That peak is consistently two or three times more intense than the comparable emission for the (110) or (100) faces, but its amplitude still corresponds to only about one electron for every ten surface cations, an order of magnitude smaller than the density of intrinsic surface states predicted by the theory.[3]

We have also performed ELS measurements on all fractured surfaces; Fig. 6 shows such a spectrum for a (110) surface. The spectra are essentially the same for all of the faces, exhibiting no features at loss energies below the first bulk peak at 5.5 eV.[15] In particular, there is no evidence of the loss peak at 1.9 eV that is associated with Ti^{3+}/O-vacancy complexes on TiO$_2$.[15]

Since recent electron- and photon-stimulated desorption measurements[25-29] have indicated that hydrogen can be present in measurable quantities in the near-surface region of TiO$_2$, and since it has been suggested that such hydrogen might depopulate intrinsic surface states by forming hydride-type bonds with surface cations,[27,28] we have investigated the effect of hydrogen on TiO$_2$ surfaces by creating a small density of defect band-gap surface states on a fractured TiO$_2$(110) surface and then exposing that surface to hydrogen. (The reasons for performing the experiment in that manner will be discussed in Sec. V B.) The defects, which were produced by 500-eV Ar$^+$-ion bombardment, had a density about one-fifth of the saturation density for that surface, or about one defect for every three to five surface cations.[15] (In the notation of Ref. 15, the defect density was near the boundary between regions I and II.) Such defect states are associated with a reduction in the coordination number of the surface cations below the normal five or six; the details of these types of sites will be discussed in Sec. V A. The UPS spectrum for the clean surface immediately after defect creation is shown in Fig. 7(a). (Note that the vertical scale bar in Fig. 7 is 10% of the amplitude of the valence-band emission, as opposed to 1% in Fig. 5.) Exposure of the surface to 20 langmuir of H$_2$, with several electron-gun and ionization-gauge filaments in the system turned on, resulted in the spectrum shown in Fig. 7(b); there was no change in the amplitude of the band-gap emission peak following exposure. The surface was then bombarded with 500-eV hydrogen ions (predominately H$_2^+$ ions for the experimental conditions used here[30]) by using the ion-bombardment gun with an ambient H$_2$ pressure of 10^{-5} Torr for 1 min [Fig. 7(c)]. The focusing properties of the ion gun for hydrogen ions were not known, so the flux density striking the surface could not be determined. Since that dose produced no changes in the spectrum, the dose was increased by a factor of 40 (still using 500-eV ions). After the larger dose [Fig. 7(d)] the amplitude of the band-gap emission peak increased by about 10%, indicating that the hydrogen ions were beginning to create additional defects on the surface.

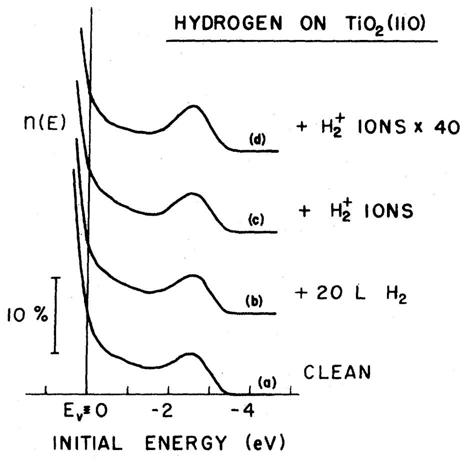

FIG. 7. He(I) UPS spectra (corrected) of the band-gap region for vacuum-fractured $TiO_2(110)$: (a) after bombardment with 500-eV Ar^+ ions, (b) surface in (a) after exposure to 20-L H_2, (c) surface in (b) after bombardment with 500-eV H_2^+ ions, and (d) surface in (c) after 40-times-larger dose of H_2^+ ions. Bar on $n(E)$ axis is 10% of the amplitude of the $O(2p)$ valence-band emission.

V. DISCUSSION

Because of the negative results obtained in the hydrogen-exposure experiments described above and the computations of hydrogen diffusion to be presented in Sec. V B, we believe that the surface electronic energy structure determined from our UPS measurements is characteristic of atomically clean TiO_2 surfaces without any complications from adsorbed hydrogen. We will therefore discuss the results first in the context of clean surfaces in Sec. V A; the possible effects of hydrogen will then be considered in Sec. V B.

A. Relation of electronic structure to surface geometry

The main conclusion that can be drawn from the spectra in Figs. 4 and 5 is that all three of the TiO_2 surfaces investigated have essentially no intrinsic surface states in the region of the bulk band gap. (Since the TiO_2 samples were reduced, pinning E_F at the botton of the conduction band, these results do not preclude the existence of empty band-gap surface states in insulating TiO_2, where E_F lies closer to midgap.) The small intensity of the band-gap emission and its variability from fracture to fracture, together with the quality of the LEED patterns for those faces, is consistent with that emission arising purely from defects resulting from fracture. This is the same result that was found for $SrTiO_3(100)$ (see Refs. 13 and 19). Even for the $TiO_2(001)$ face, whose total band-gap emission is $1\frac{1}{2}$ to 2 times as large as that for either of the other two faces, the band-gap surface-state emission is at least an order of magnitude smaller than that predicted by Kasowski and Tait.[3] The fourfold coordinated (001) surface is different than either of the more highly coordinated surfaces in that it exhibits a distinct peak in the band-gap emission at 1.9 eV above E_v. If that peak were in fact due to an intrinsic surface state (i.e., a state existing in each surface unit cell), then it would have a population of about 0.1 electron per unit cell. Although that is possible, it is not consistent with the much larger cation and anion contributions to the surface-state density in the band gap predicted by Kasowski and Tait.[3] Alternatively, if we assume that the band-gap emission arises from surface defects having a population of roughly 1 electron per defect site (as appears to be the case for defects purposely created on annealed TiO_2),[15] then the density of such defects inferred from the UPS spectra is consistent with the quality of the LEED patterns observed. We consider this to be the more probable explanation. The presence of a distinct peak in the band-gap emission from the (001) surface then suggests that there is some particular type of defect that forms preferentially on that face and not on the (110) or (100) faces.

In order to get a better idea of the nature of band-gap surface states on TiO_2 and the differences between perfect and defect surfaces, it is necessary to consider the atomic geometry of the various surfaces, which is shown in Figs. 1–3. The similarity in the electronic structure of the (110) and the (100) surfaces is reasonable in view of the equivalence of the ligand environment of the fivefold coordinated Ti ions on $TiO_2(110)$ and the surface Ti ions on $TiO_2(100)$. Both surface cations have the same O ligands; those on the (100) surface are merely rotated by 45° relative to the (110) surface because of the different macroscopic surface orientation. The fact that some of the O ions lie above the Ti-ion plane on the (100) surface probably accounts for its greater tendency toward reconstruction,[20,21] but the cation environment on the two surfaces is identical. The $TiO_2(001)$ surface differs from the (110) and (100) surfaces in that only four O ions coordinate each surface Ti ion, two in the surface plane and two in the plane below. Another difference between the (001) surface and the other two is the increased nearest-neighbor surface cation-cation separation, which is 4.59 Å for the (001) surface and 2.96 Å for the (110) and (100) surfaces.

Some of the types of defects that could be present on $TiO_2(110)$ and (100) surfaces are also shown shown in Figs. 1 and 3. From detailed studies of defect formation on TiO_2(110),[15] it is fairly well established that filled band-gap defect surface states correspond to Ti^{3+}/O-vacancy complexes, although the detailed geometry of those complexes is not precisely known. The most probable type of surface defect on TiO_2(110) is shown in Fig. 1 by the missing O ion that bridges two sixfold coordinated Ti ions. When a bridging O ion is removed, the two neighboring Ti ions become fivefold coordinated. But, based on the observations on nearly perfect TiO_2(110) and (100) surfaces above, fivefold coordination is not sufficient to populate band-gap surface states in n-type material. There is a difference, however, between the pair of fivefold Ti ions adjacent to the O vacancy in Fig. 1 and fivefold cations on perfect surfaces. On ideal (110) and (100) surfaces, the fivefold coordinated cations are shielded (or "screened") from neighboring cations by a pair of O ions lying midway between the cations. For the O-vacancy defect shown in Fig. 1, however, the two Ti ions are very poorly screened from each other; they can "see" each other, so to speak. This is somewhat analogous to the situation in bulk Ti_2O_3, where two Ti ions lie on opposite sides of the hollow between three adjacent O ions that constitute one face of an oxygen octahedron, and the paired Ti ions share two electrons across the O-ion plane.[31] The bonding and antibonding levels of that cation pair (a_1^T and e^T, respectively) give rise to the filled and empty conduction bands in Ti_2O_3. The poorly screened pair of Ti ions at the defect site in Fig. 1 may well share an electron in a similar manner, giving rise to a band-gap surface state. In fact, the defect site should exhibit less screening of the Ti ions from each other than in Ti_2O_3. This type of surface defect has been considered by Wolfram for the $SrTiO_3$(100) surface.[7]

A surface defect could also be formed on either the TiO_2(110) or (100) surface by removing one of the O ions from the fivefold coordinated cations; this is shown for the (100) surface in Fig. 3. Again the missing O ion greatly reduces the screening between cations, probably permitting a pair of them to trap an electron in a filled band-gap state.

The above observations concerning intrinsic and defect surface states on the (110) and (100) surfaces of TiO_2 may also carry over the (001) surface. Although the cations on the (001) surface have only four O ligands, they are still fairly well screened from neighboring surface cations, as can be seen in Fig. 2. Nearest-neighbor cations are separated by two staggered O ions in the surface plane, which should provide effective screening of one cation from another. In addition, the increased cation-cation separation will reduce pair interactions between Ti ions. The fourfold Ti ions on the TiO_2(001) surface are therefore more effectively screened from neighboring surface cations than are fivefold cations at surface-defect sites. The absence of any intrinsic band-gap surface states on TiO_2(001) suggests that cation pairing may be a more important factor in determining surface electronic structure than coordinative unsaturation.

Although the electronic structure of TiO_2 surfaces may depend more upon cation pairing than on ionic coordination, the stability of the surfaces is related to changes in the Madelung potential associated with coordinative unsaturation.[3] The (110) surface, which is the most stable of the three surfaces studied, has only one-half of its surface cations unsaturated; it has not been observed to either facet or reconstruct. (Nothing, however, is known about relaxation or rumpling on that surface; those cannot be determined from the symmetry of the LEED patterns, and no TiO_2 surface has yet been examined either theoretically or experimentally by means of LEED I-V curves.) The (100) surface, which has no coordinatively saturated cations, was found by Somorjai and co-workers[20,21] to exhibit three different reconstructions as a function of annealing. For the TiO_2(001) surface, the Madelung potential is very different from that of the bulk, owing to the large number of missing ligands.[3] There is thus a strong driving force for atomic rearrangement, which undoubtedly leads to the faceting of this surface that has been observed by Tait and Kasowski.[23]

B. Hydrogen and TiO_2 surfaces

The nature and extent of the interaction of hydrogen with transition-metal-oxide surfaces are still largely unknown. The diffusion of hydrogen into TiO_2 and its equilibrium bulk concentration have been studied by Johnson, DeFord, and co-workers,[32-36] but the thermodynamics are extremely complex and depend on defect type and concentration, Fermi-level position, etc.[32] The bulk hydrogen concentration in insulating (i.e., transparent) TiO_2 samples can be measured by means of infrared absorption,[33] but that method cannot be applied to reduced samples such as the ones used here. Electron- and photon-stimulated desorption experiments on TiO_2, $SrTiO_3$, etc., have detected the presence of hydrogen in the near-surface region,[25-28] even for single-crystal samples fractured in UHV,[29] but the amount of hydrogen present has not yet been determined. Knotek[27,28] has suggested that hydrogen may interact with intrinsic band-gap surface states on TiO_2, forming a hydride-type, $Ti^{4+}-H^{-}$ bond that would depopulate the states. However, no direct evidence for such a process has been found.

It is possible to get an idea of the amount of hydrogen that might be available to interact with surface states on a vacuum-fractured TiO_2 surface from the measured diffusion coefficients D of hydrogen in TiO_2 and the bulk H concentration. Johnson *et al.*[36] have measured D for hydrogen diffusing both parallel and perpendicular to the c axis; their results are $D = 1.8\times10^{-3}\exp[-0.59(\text{eV})/kT]$ cm^2/sec and $0.38\exp[-1.28(\text{eV})/kT]$ cm^2/sec, respectively. If we assume that $x \approx \sqrt{Dt}$, where x is the distance over which H can diffuse in time t, then we can compute the thickness of the near-surface region from which H could diffuse to the fractured surface during the time required to complete the UPS measurements. (This assumes that there is a strong driving force for the diffusion of bulk H to the fractured surface. If the driving force were in fact small, a much smaller surface H concentration would result than that calculated here.) For $T = 300$ K and $t = 500$ sec, the distances are 1100 and 0.03 Å for diffusion parallel and perpendicular to the c axis, respectively. Thus only diffusion along the c axis is important.

The bulk concentration of H in our reduced TiO_2 samples has not been determined directly. Johnson, DeFord, and co-workers[32,33] have shown that the equilibrium bulk H concentration for TiO_2 in an ambient where the partial pressure of H_2 is much greater than that of H_2O or O_2, as is the case for the UHV ambient in which our samples were reduced, is very small. The fact that E_F lies at the top of the bulk band gap in reduced material also favors a small H concentration.[32] A rough guess[37] of the bulk H concentration for our reduced undoped samples is less than 10^{18} cm^{-3}. The number of H atoms available to diffuse (parallel to the c axis) to the surface of TiO_2 during our measurements would then be less than 10^{13} cm^{-2}. This is too small a number to depopulate more than a few percent of the intrinsic surface states, even if all of that H did diffuse to the surface. An upper limit on the possible H concentration, based on a number of infrared measurements on insulating undoped TiO_2 by Johnson and co-workers,[37] is about 10^{19} cm^{-3}. With that bulk H concentration, the surface H density might possibly be as large as 10^{14} cm^{-2} before our experiments are completed. This is in the range where the type of interactions suggested by Knotek[27,28] might be observable, so the possible effect of hydrogen on the surface-state spectrum of TiO_2 cannot be excluded.

Since no intrinsic band-gap surface states are observed on any of the TiO_2 faces, even when the spectra are taken as soon as possible after fracturing, the interaction of hydrogen with band-gap states can only be studied via surface-defect states. We have thus created a small density of defect surface states as the closest approximation to possible intrinsic band-gap states. The absence of any interaction between hydrogen and those states suggests that hydrogen may not have a significant effect on TiO_2 surfaces.

There are two possible weaknesses in the adsorption experiments performed here. The hydrogen species used presumably contained only small amounts of atomic H,[30] while any interstitial hydrogen that might diffuse from the bulk would be atomic H.[32,38] Some H is produced at the hot filaments in the vacuum system, but the main component of the ambient is H_2. Even when an ion gun is used to bombard the sample, the ion mean-free paths are sufficiently long that the main species hitting the surface is H_2^+.[30] So the experiments do not directly test the interaction of H with the surfaces. However, bulk H diffusion measurements in rutile in H_2 ambients suggest that dissociation of H_2 on the TiO_2 surface is rapid compared to diffusion times,[37] so a significant amount of atomic H is probably present on the surfaces during exposure. The second argument that might be put forth is that hydrogen may interact more strongly with the perfect surface than with defect sites. That is not a particularly satisfying argument, however, since defect sites are known to interact more strongly with adsorbed molecules such as H_2O and O_2 than do nearly perfect surfaces.[17,18] The atomic sites on perfect surfaces are similar enough to those on defect surfaces that if hydrogen interacts strongly with intrinsic surface states, one would expect at least some observable interaction in the above experiments.

VI. SUMMARY

The TiO_2(110), (100), and (001) surfaces have been prepared by fracturing single-crystal samples in UHV, and the UPS spectra for those surfaces have been measured in order to determine the intrinsic surface-state structure in the region of the bulk band gap. All three faces exhibit only a small amount of emission in the band-gap region due to defects resulting from fracture. Specifically, the large density of surface states predicted by Kasowski and Tait[3] for the fourfold coordinated TiO_2(001) surface was not observed. The detailed atomic geometry of both perfect and defect surfaces has been examined, and it is suggested that incomplete screening of pairs of surface cations may play a larger role in the origin of band-gap surface states than the coordinative unsaturation of the surface cations. Surface-defect states in the band gap were found to be insensitive to both exposure to hydrogen molecules and bombardment by H_2^+ ions, indicating that the surfaces of TiO_2 may not be as reactive to hydrogen as has been suggested.[27,28]

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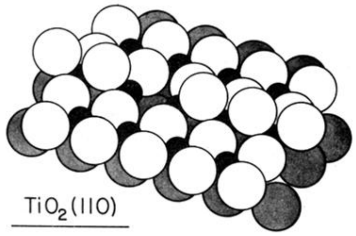

FIG. 1. Model of $TiO_2(110)$ surface, using ionic radii: $Ti^{4+} = 0.70$ Å and $O^{2-} = 1.40$ Å. Shaded O ions lie below the surface plane. One bridging O ion has been removed to create a surface defect (see discussion in text).

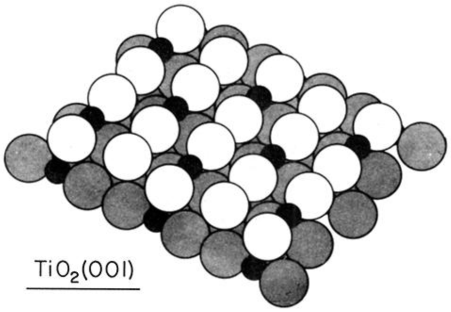

FIG. 2. Model of $TiO_2(001)$ surface.

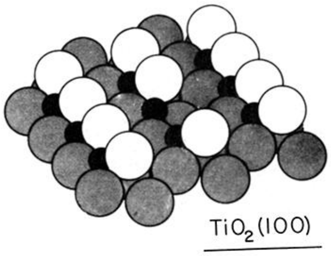

FIG. 3. Model of $TiO_2(100)$ surface. One O ion has been removed to create a surface defect.