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Electronic structure of ultrathin Fe films on $TiO_2(110)$ studied with soft-x-ray photoelectron spectroscopy and resonant photoemission

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We report on soft-x-ray photoelectron spectroscopy (SXPS) of a $TiO_2(110)$ surface during deposition of Fe in the monolayer regime. At low fractional monolayer coverages, the adsorbed Fe atoms are oxidized and Ti cations at the interface become reduced due to Fe adsorption. SXPS from shallow core levels and valence bands show that Fe starts to exhibit metallic character at a coverage of approximately 0.7 equivalent monolayers. Two well separated defect states appear in the band gap of TiO_2 at iron coverages well below one monolayer. We use resonant photoemission to obtain information on the partial density of states, and we assign these defect states as being Fe-derived and Ti-derived states, located at the Fe and Ti sites, respectively. We suggest that a position change of oxygen is involved in the bonding of Fe on the $TiO_2(110)$ surface.

I. INTRODUCTION

The surface electronic properties of transition-metal oxides can be significantly altered by the addition of dilute quantities of heterogeneous metal impurities or adsorbates. This quality enables metal-modified oxides to be used in a variety of important technologies including chemical sensors, photochemistry, and catalysis. Developing a predictive understanding of how metal adatoms, clusters, and films interact with an oxide substrate to produce electronic states may lead to the capability of synthesizing additional materials for specific applications. This approach requires electronic structure studies of well-characterized metal-oxide systems to elucidate the correlations between the surface atomic and electronic structures.

Resonant photoemission is a particularly useful technique for studying the electronic structure of transition-metal compounds. Several investigations have been performed on transition-metal oxide surfaces, in particular to examine the hybridization between metal cations and the surrounding oxygen.[1-8] An excellent review of this method is given by Davis;[9] only a brief description is given here. When the photon energy is swept through the binding energy of a core electron (e.g., a $3p$ level of a first-row transition metal), the core electron can be excited into an unoccupied state (e.g., a $3d$ state) of a partially filled valence band and decay in a subsequent autoionization process. This results in emission of an electron from the occupied part of the valence band. A photoelectron of the same kinetic energy can be excited by direct photoemission from the occupied valence band. Since these two processes represent two different pathways from the same initial state to the same final state, they interfere. This gives rise to a resonance, i.e., an enhanced photoelectron intensity where the emission intensity exhibits a characteristic (Fano) line shape when plotted against photon energy.

Because resonant photoemission involves the creation and decay of localized core holes, it is a site-specific process provided that only intra-atomic decay takes place during the autoionization process.[1] Hence the technique probes the partial density of electronic states on specific atomic sites. In the present study, we combine resonant photoemission and soft-x-ray photoelectron spectroscopy (SXPS) to characterize changes in the electronic structure of a metal-insulator system during the very initial stages of metal overlayer growth. Whereas resonant photoemission provides valence electronic information, SXPS provides the complementary core-level data used to assess the oxidation states of the substrate and overlayer metal atoms.

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The main goal of this work is to explore how chemical changes caused by adsorption of Fe on the TiO_2 surface are reflected in the electronic structure in the valence-band region of the substrate. Our interest in this system is also driven by technological aspects; Fe/TiO_2 is known to catalyze ammonia synthesis,[10] and ultrathin Fe films on oxide surfaces have been speculated to exhibit very strong two-dimensional magnetism.[11]

The surface of TiO_2 is an excellent candidate for such a study, since the resonant photoemission from TiO_2 has been studied extensively and is well understood.[12–15] The TiO_2(110) face is the most stable and hence most often investigated surface of this material. Moreover, several investigations of metal film deposition on TiO_2 surfaces have been performed and a general trend of metal overlayer oxidation and substrate cation reduction has been observed for reactive metal overlayers.[16–20] The growth of Fe films on TiO_2(110) surfaces also fits in this trend.[21,22] For deposition at room temperature, ultrathin Fe overlayers have been found to grow in flat islands,[21] exhibiting a bcc(100) structure at higher coverages.

The paper is organized as follows: after the experimental details, the results on soft-x-ray photoemission (SXPS) from core levels and the valence band region are shown for different Fe coverages. In short, we observe formation of an oxidized-Fe–reduced-TiO_2 interface followed by the formation of a metallic Fe overlayer. We then concentrate on photoemission from the valence band at coverages of a fraction of a monolayer, and show how two distinct valence-band features can be assigned unambiguously to being of Ti 3*d*- and Fe 3*d*-derived character.

II. EXPERIMENT

The experiments have been performed at the Sandia/Cornell beamline and at the Los Alamos/Sandia beamline on the UV ring at the National Synchrotron Light Source at Brookhaven National Laboratories.[23] Both beamlines are equipped with extended-range grasshopper (ERG) monochromators. Photoemission spectra are taken using a double-pass cylindrical mirror analyzer (CMA) in an ultrahigh vacuum end station with a base pressure of $\sim 1\times 10^{-10}$ torr. The combined analyzer and monochromator resolution for the spectra shown is ~0.3 eV. No attempt has been made to account for a change in analyzer transmission with kinetic energy. For the measurements with photon energies below 72 eV, a thin Al window in the beamline is used to filter out higher-order wavelengths of the light. This proves to be particularly useful for the resonant photoemission experiments of weak features. Without the filter, higher-order light from the ERG monochromator contributes substantially to the photoemission background in the band-gap region.

The CMA is mounted perpendicular to the photon beam and for most of the spectra shown the sample normal makes an angle of 24° with respect to the analyzer axis. The TiO_2(110) sample is mounted on an *xyz* manipulator with a rotational platform. The crystal is oriented with the surface normal and the [001] directions in the photon plane of incidence. The sample can be cooled with liquid nitrogen and heated by electron bombardment from the back side. All spectra are taken at 300 K.

Several TiO_2(110) crystals were used as samples. They were prepared following standard recipes for obtaining a clean, stoichiometric, and well-ordered surface.[24] The initial preparation step consists of heating in vacuum to a temperature of ~900 K for a few hours; this result in the formation of oxygen vacancies and *n*-type semiconducting properties of the bulk. Rare-gas ion sputtering is used to remove contaminants and Fe overlayers. Ar^+ sputtering results in an oxygen-deficient surface; heating a sputtered, oxygen-deficient surface in 10^{-6}-torr oxygen restores a stoichiometric, oxygen-rich surface with no photoemission states observable in the band gap. The sample and overlayer cleanliness are verified by Auger electron spectroscopy (AES).

Fe is deposited from a high-purity Fe foil spot welded to a W filament. The film deposition is controlled by the deposition time at constant heating power. The work-function change with Fe coverage proves to be a very reliable indicator of the film thickness, and allows us to cross calibrate the thickness with measurements from a separate experiment where a quartz-crystal monitor (QCM) was used.[21] The thickness reading from the QCM is based on the Fe bulk density and is an average value, hence it is useful to convert this thickness into coverages of equivalent monolayers (ML). Since we do not know the geometry of the Fe overlayers in the low coverage limit, we have to assume a certain surface density of Fe for this conversion. In accordance with the geometry observed for higher coverages,[21] we assume that the number density of a close-packed iron layer of the bcc(100) orientation, 1.2×10^{15} atoms/cm^2, corresponds to one equivalent monolayer.

III. RESULTS

A. Photoemission from core levels

The photoemission spectrum of the Ti 3*s* to 3*p* region shown in Fig. 1(a) is characteristic of a stoichiometric TiO_2(110) surface. The Ti 3*p* and 3*s* features with binding energies of 38 and 63 eV, respectively, are very sharp, indicating the presence of fully oxidized (Ti^{4+}) cations on the surface and in the near-surface region. Since the bulk of the TiO_2 crystal is *n*-type semiconducting, the Fermi level is pinned at the bottom of the conduction band. Binding energies in our spectra are referenced to the Fermi level as measured from a gold foil in contact with the sample. A satellite of the Ti 3*p* peak at ~14 eV higher binding energy is visible. This satellite is due to screening of the Ti core hole by the surrounding O ligands in the final state of the photoemission process. It has been suggested that screening by polarization of the O^{2-} anions results in a bound electron-hole pair, a so-called ligand exciton.[25] For fractional monolayer iron coverages, Fe 3*p* emission with a binding energy of 55.8 eV is observed [Figs. 1(b)–1(d)]. In agreement with photoemission data from bulk Fe oxides,[26] we assign this as emission from Fe^{2+}. Metallic Fe (binding energy of 53 eV) is observed at a coverage well below one equivalent monolayer [Fig.

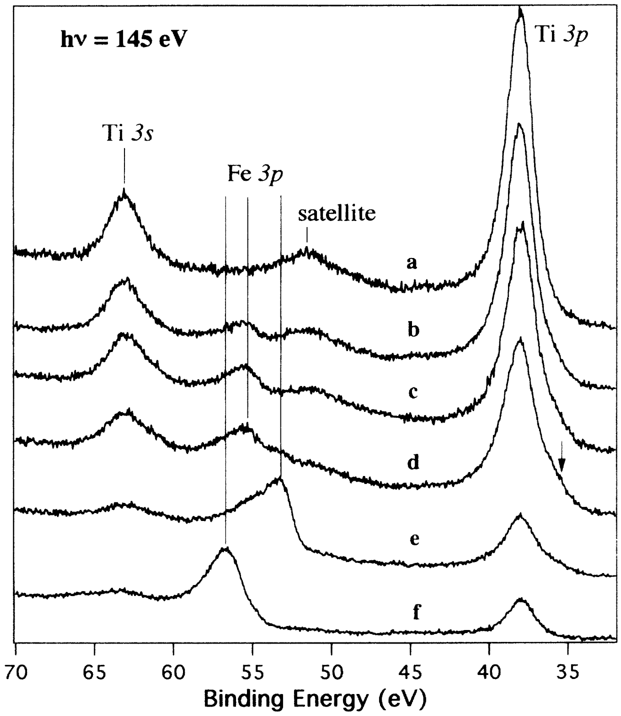

FIG. 1. Photoemission spectra from shallow core levels of (a) stoichiometric $TiO_2(110)$ and (b)–(f) after deposition of Fe at room temperature. Fe coverages (in equivalent monolayers, ML) are (b) 0.3, (c) 0.4, (d) 0.7, (e) 2.2, and (f) 2.2 ML after exposure to 160 L oxygen. The spectra have been recorded with a photon energy of 145 eV; the positions of the different oxidation states of Fe are indicated.

1(d)], and emission from the metallic state increases with higher coverages. When exposing the equivalent 2.2-monolayer-thick film [Fig. 1(e)] to 100 L oxygen ($1\ L=1\times10^{-6}$ torr sec), the metallic and oxidized contributions of the Fe 3*p* emission shift to higher binding energy [BE=56.8 eV (Ref. 26)]. We interpret this as formation of a fully oxidized overlayer [Fe^{3+}, Fig. 1(f)].

Ti 3*p* emission is suppressed by the Fe overlayer; the detected electrons have a kinetic energy of 70–100 eV and an inelastic mean free path length of a few Å. Note the broadening of the initially sharp Ti 3*p* peak with Fe deposition marked with an arrow in Fig. 1(d). This is assigned to the presence of reduced substrate cation states (Ti^{3+}), as has also been observed by core-level spectroscopy of the Ti 2*p* region using nonmonochromatized Al $K\alpha$ radiation.[21] Since surface oxygen atoms are in their closed-shell configuration (O^{2-}), additional electrons provided by the presence of oxidized Fe can populate empty states of the Ti cations. This picture will be established more clearly in the discussion of the resonant photoemission results given below.

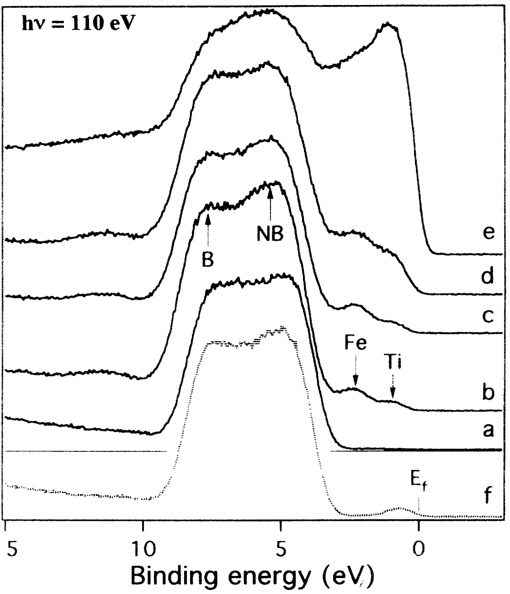

FIG. 2. Photoemission from the valence band of (a) stoichiometric $TiO_2(110)$ and (b)–(f) after deposition of Fe at room temperature onto a stoichiometric surface. Fe coverages (in equivalent monolayers, ML) are (b), 0.3, (c) 0.4, (d) 0.7, and (e) 2.2 ML. Spectrum (f) was taken after irradiation of an uncovered, stoichiometric surface with 3-keV electrons. All spectra are taken with a photon energy of 110 eV.

B. Photoemission from the valence band

The core-level spectra can be correlated with emission from the valence band. The data in Fig. 2 are taken with a photon energy of 110 eV, which is well above resonance energies connected with excitation of Ti 3*p* and Fe 3*p* levels.[5,27] Again we start with a clean, stoichiometric surface [Fig. 2(a); second curve from bottom], exhibiting emission from the mostly O 2*p*-derived valence band and no significant emission from the band-gap region. Incremental Fe coverages ultimately result in the formation of a sharp Fermi edge due to metallic Fe [Fig. 2(e), top curve]. At intermediate coverages [Figs. 2(b) and 2(c)], two distinct features appear in the band-gap region. Based on results discussed below, these peaks are labeled "Fe" and "Ti." The shape of the O 2*p* valence band changes with deposition of a small amount of Fe coverage, and a small broad peak at 12-eV binding energy evolves.

For comparison, a slightly oxygen-deficient surface is shown in Fig. 2(f) (bottom curve). This surface has been produced by irradiation of a stoichiometric surface with 3-keV electrons. Electron-stimulated desorption of O from TiO_2 is a well-known phenomenon,[28] and results in oxygen vacancies at the surface; oxygen vacancies can also be produced by annealing to high temperature *in vacuo*.[29] Since charge neutrality is preserved at the surface, a missing O^{2-} ion results in a negatively charged point defect, and the electrons occupy states in the band-gap region. Note that this band-gap state is at a binding energy similar to the feature labeled "Ti" in Fig. 2(b), which appears when depositing Fe onto a *stoichiometric* surface. This suggests that both of these band-gap states are asso-

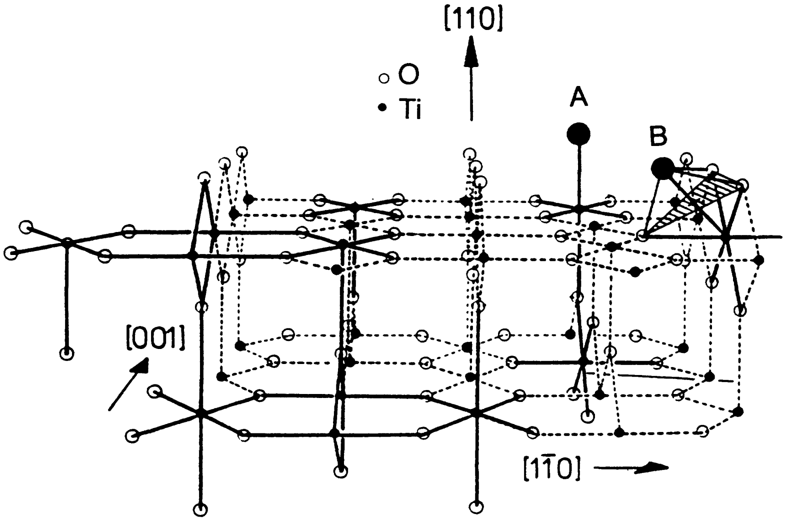

FIG. 3. Geometric structure of the rutile $TiO_2(110)$ structure. Full circles represent Ti, open circles O atoms. Two possible adsorption sites of metal atoms are indicated: (A) atop a Ti atom, and (B) tetrahedrally-bonded to bridging O atoms (from Ref. 35).

ciated with the surface Ti atoms.

The parallel between the band-gap state on a defective $TiO_2(110)$ surface and the Fe-induced "Ti" state on the stoichiometric surface is further supported by the response to oxygen exposure. On the defective, clean surface, oxygen reduces the band-gap state intensity, presumably because the number of oxygen vacancy sites is reduced.[29] For a stoichiometric surface with only a fractional ML iron coverage, a 10-L oxygen exposure suppresses the "Ti" band-gap state but leaves the "Fe" peak largely unaffected. This clearly indicates that although adsorbed iron induces two additional band-gap states, only the "Ti" labeled state is analogous to that seen on defective $TiO_2(110)$.

Electron irradiation also changes the shape of the mostly O $2p$-derived valence band; it increases the intensity of the lower binding-energy feature, similar to the case of low Fe coverage [Fig. 2(b)]. Using nomenclature from molecular-orbital theory and in accordance with the literature,[15] we refer to mainly O $2p$-derived states as "bonding" and "nonbonding" for the higher and lower binding-energy features, respectively. These are labeled in Fig. 2 as "B" and "NB." The rutile structure can be thought of as being composed of (slightly distorted) octahedra with Ti in the center and O on the vertices (see Fig. 3). The "bonding" orbitals refer to states of e_g and t_{2g} symmetry, and the "nonbonding" orbitals to states of t_{1g} and t_{2u} symmetry in an octahedral crystal field, respectively. Resonance photoemission of these states is discussed below.

C. Resonant photoemission

In order to examine resonant photoemission processes described in Sec. I, valence-band spectra from Fe/TiO_2 at a coverage of 0.4 equivalent monolayers are taken with different photon energies (Fig. 4). A set of four Gaussians is fitted to the spectra at binding energies of 0.7 ("Ti"), 2 ("Fe"), 5.6 ("nonbonding"), and 7.5 eV ("bonding"). Four Gaussians is the lowest number of curves that gives a satisfactory fit to the spectra. In a resonant photoemission experiment of stoichiometric and defective $TiO_2(110)$, Zhang, Jeng, and Henrich[15] used three Gaussians to fit the mainly O $2p$-derived states ("bonding,"

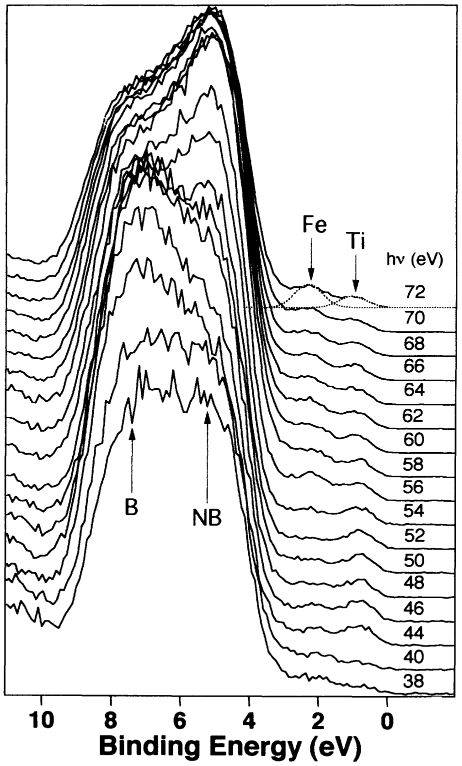

FIG. 4. Photoemission from the valence band of 0.4 equivalent ML Fe on stoichiometric $TiO_2(110)$ with different photon energies. Arrows correspond to 0.7-eV ("Ti"), 2-eV ("Fe"), 5.6-eV ("nonbonding"), and 7.5-eV ("bonding") binding energy.

"nonbonding," and "intermediate"); decomposing the spectra into a total of five curves does not change our conclusions. The intensity of the fitted peaks with photon energy is plotted in Figs. 5 and 6 to allow comparisons with constant initial state (CIS) data in the literature.

The intensity of the "Ti" and "Fe" states show distinctly different resonance behavior (Fig. 5). A maximum at $h\nu \cong 47$ eV is characteristic of Ti 3*d* states, as has been observed for polycrystalline Ti.[20] Ti_2O_3,[3] clean and oxidized Ti,[12,27] defective $TiO_2(110)$,[14,15] and $SiTiO_3(001)$.[8] For light transition metals, $3p \rightarrow 3d$ resonance occurs at a photon energy higher than the binding energy of the 3*p* core levels.[30] We take the similarity of our results with CIS spectra from all these materials as clear evidence that the peak labeled "Ti" in Fig. 2(b) is indeed of Ti 3*d*-derived character. This means that adsorption of Fe atoms on the TiO_2 surface induces defect states of Ti 3*d* character at the surface, and that these defect states are localized at the Ti atoms. A weaker and broader feature at 56 eV is seen in the "Ti" plot in Fig. 5. A similar double-peaked structure has been observed previously for metallic Ti and Ti_2O_3,[3,30] and it has been suggested that shake-up effects may be responsible for this second peak;[30] our own data for defective $TiO_2(110)$ surface also exhibit this line shape.

The "Fe" plot shows a Fano line shape with a very pronounced minimum near 53-eV photon energy and a maximum at 56 eV, in accordance with the expected energy of a Fe $3p \rightarrow 3d$ transition (see Fig. 1). The resonant photoemission results on Fe oxides by Lad and Henrich[5] show a very similar CIS line shape. The absence of any resonance of the "Fe" state with a Ti $3p \rightarrow 3d$ transition is quite striking. Again, this justifies our assignment of the valence-band feature with 2-eV binding energy as being Fe 3*d* derived.

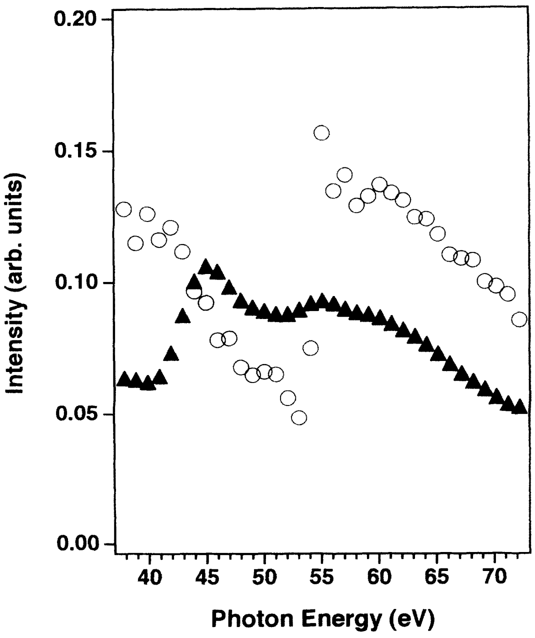

FIG. 5. Intensity of Fe 3*d*-derived (circles) and Ti 3*d*-derived (triangles) valence-band features from 0.4 equivalent ML Fe on stoichiometric $TiO_2(110)$.

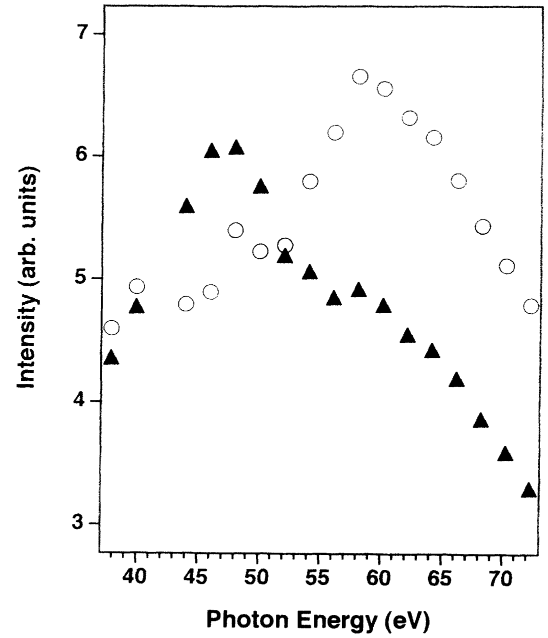

FIG. 6. Intensity of "bonding" (triangles) and "nonbonding" (circles) O 2*p* features from 0.4 equivalent ML Fe on stoichiometric $TiO_2(110)$.

Figure 6 shows the intensity change of the "bonding" and "nonbonding" states of the valence band of 0.4 equivalent ML $Fe/TiO_2(110)$ with photon energy. The "bonding" states of the mainly O 2*p*-derived valence band in Fig. 6 show pronounced resonance connected with transition from the Ti 3*p* core level, similar to the resonance observed for the band gap "Ti" state (Fig. 5). This is due to covalency effects between Ti and O;[12,15] calculations by Glassford and Chelikowsky indicate a considerable degree of covalent character present in the Ti-O bond.[31] The behavior of the "nonbonding" states is less clear. A broad maximum around 55 eV has been seen in CIS spectra of "nonbonding" features; this feature was found to be sensitive to the amount of reduction of the surface.[15] Results from a slightly O-deficient surface exhibit similar CIS line shapes to the ones shown in Fig. 6. This means that either adsorption of Fe does not affect the mainly O 2*p*-derived levels, or that our measurements are not sensitive enough to observe such a change.

IV. DISCUSSION

Before we elaborate on the details and consequences of the resonant photoemission results, let us establish a picture of the morphology and electronic structure of Fe films adsorbed at a TiO_2 surface as drawn from the deposition measurements in Figs. 1 and 2 and previous results.[21] One question we can address is: When are the Fe islands large enough to develop metallic structure? The appearance of a sharp Fermi edge in the valence-band spectra in Fig. 2 suggests the development of bands crossing the Fermi level at coverages of about 0.7 equivalent monolayers. This is also where the work function of the Fe/TiO_2(110) system has a minimum,[18] and where some emission from Fe^0 is observed in the core-level spectra [Fig. 1(d)].

At smaller coverages, we probably have a dilute overlayer of single oxidized Fe atoms and small clusters on the oxide surface. The atomic nature of the resonant photoemission effect allows us to probe the valence-band features of this system selectively. The band-gap states induced by Fe adsorption at these low coverages are well localized in energy and space, in close proximity to Fe and Ti sites, respectively. In a recent calculation,[11] Li and Freeman have shown that ultrathin Fe films on a MgO surface are extremely noninteractive with the substrate; this is very different from their behavior on TiO_2. The Fe 3*d*-derived states have a small bandwidth and show a strong splitting between majority- and minority-spin bands. Although we are not in a position to distinguish between positions of bands with different spin orientations, probing of magnetic properties of Fe/TiO_2(110) would be quite interesting.

Next we consider the geometry of the Fe-covered surface. The apparent lack of hybridization of the "Fe" and "Ti" states (Fig. 5) suggests that the bonding of Fe at very low coverages occurs predominantly via surface oxygen. Thus atop bonding above a Ti atom (site *A* in Fig. 3) appears unlikely. It has been conjectured that the Fe atoms interact with the "bridging oxygen" rows protuding from a TiO_2(110) surface[21] (site *B* in Fig. 3). A tetrahedral bonding involving the "bridging oxygen" atoms is indeed plausible since several structures of iron oxides exhibit tetrahedrally bonded cations.[32] Furthermore, preferred nucleation near these sites is in agreement with the fact that the [001] direction of thicker Fe films is commensurate with the [001] direction of rutile TiO_2 (i.e., the direction of the bridging oxygen rows).[19] This may mean that chainlike FeO_x islands are formed at low coverages. However, because we cannot show conclusive evidence about preferred adsorption sites of individual Fe atoms, the hypothetical position shown in Fig. 3 is simply consistent with our experimental results.

One interesting aspect of our results is the question of how the Ti 3*d*-derived states are formed. SXPS suggests that charge transfer from Fe atoms to surface oxygen atoms takes place, which results in a reduction of the Ti oxidation state. However, the "Ti" state due to Fe adsorption appears at exactly the same energy position as gap states induced by removal of surface oxygen via electron bombardment, and behaves very similarly upon oxygen exposure. A hypothesis is that physical removal or position change of bridging oxygen atoms occurs during adsorption of Fe. Extraction of oxygen from subsurface layers has been observed for adsorption of a highly reactive metal,[20] as well as "floating up" of interface oxygen on thick Fe layers.[21] The proposed surface displacement could be verified by direct structural probes such as scanning tunneling microscopy. The formation of reduced Ti states at the interface that is observed for Fe adsorption has also been seen for several metal overlayers.[18,20,33,34]

We draw the more general conclusion that the formation of this "reduced" interface between a reactive overlayer metal and the reducible TiO_2 surface involves a position change of oxygen at the interface.

V. SUMMARY AND CONCLUSION

SXPS and resonant photoemission have been combined to study the electronic structure changes associated with the deposition of iron on a stoichiometric TiO_2(110) surface. At low iron coverages, the iron is in an oxidized state which is assigned to (Fe^{2+}), and evidence for partially reduced titanium cations is seen. In this coverage regime, two additional states appear in the band gap of TiO_2(110). The state at 0.7-eV binding energy exhibits resonant behavior as the photon energy is swept through the Ti $3p \rightarrow 3d$ absorption threshold, indicating that it is of Ti 3*d* character and is localized on the titanium atoms. In contrast, the second state at 2-eV binding energy exhibits a Fano resonance at the Fe $3p \rightarrow 3d$ adsorption threshold, indicating an Fe 3*d*-derived origin for this state. The absence of cross resonant behavior argues against direct Fe-Ti bonding and supports an Fe adsorption site involving Fe-oxygen bonding. Consideration of the similarities between the "Ti" band-gap state on the Fe-decorated surface and oxygen vacancy band-gap states on defective surfaces suggests that oxygen removal or position change is associated with the formation of the "Ti" band-gap state.

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