PHYSICAL REVIEW B VOLUME 24, NUMBER 6 15 SEPTEMBER 1981

Defect states in WO_3 studied with photoelectron spectroscopy

R. D. Bringans, H. Höchst, and H. R. Shanks*

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany

(Received 16 March 1981)

The (001) surface of tungsten trioxide has been examined with ultraviolet photoemission spectroscopy. Results are presented for the defect-free surface using photon energies of 16.85, 21.22, and 40.82 eV and compared with x-ray photoemission spectra and a bulk density of states calculated for cubic WO_3 by Kopp *et al*. The experimental results show no evidence for the presence of intrinsic surface states in the energy of bulk WO_3. The calculated density of states can be seen to have both a valence-bandwidth and an energy gap which are too small. Electron irradiation and ion bombardment produced defects in the surface region of WO_3 which appeared as an increase in the density of states in the energy gap and a shift of the valence band away from the Fermi energy. The increase of the density of states in the band gap can be explained by the creation of oxygen vacancies and the valence-band shift by a band-bending effect. However, an alternative explanation that the shift is due to the creation of a layer of disordered WO_3 at the surface cannot be ruled out. Five distinct surfaces with different electronic structure were observed and are discussed.

I. INTRODUCTION

Both the bulk and surface electronic properties of transition-metal oxides have received attention recently owing to their suitability for various technological applications. WO_3 in particular is promising as a candidate for the efficient photolysis of water,[1] its electrocoloration[2] has been used for electric displays[3] and its catalytic properties have been known for some time.[4] It is probable that most of these properties are related to bulk and surface defects rather than to the intrinsic nature of WO_3. At room temperature WO_3 is monoclinic with lattice parameters $a = 7.30$ Å, $b = 7.53$ Å, $c = 3.85$ Å, $\beta = 90.88°$.[5] Each tungsten atom is surrounded by six oxygen atoms in an octahedral coordination, the four octahedra in the unit cell being slightly tilted with respect to one another. Langell and Bernasek[6] have observed LEED (low electron energy diffraction) patterns from the (001) surface of WO_3 single crystals and found evidence of slight distortions giving rise to a triclinic structure at the surface. The distortions were rather small and to a reasonably good approximation WO_3 can be regarded as having a cubic structure. This simplified structure is shown in Fig. 1. It has been known for some time that tungsten forms oxides with compositions slightly different from WO_3. Magnelli[7] described the compound $W_{20}O_{58}$ ($WO_{2.90}$) in 1950 and since then several compounds with other compositions have been found (see, for example, Sundberg and Tilley[8]). These materials do not require that oxygen vacancies be present, but are formed when some of the WO_6 octahedra, which are corner sharing in WO_3, become edge sharing. The electronic structure of the $W_{20}O_{58}$-type compounds has been characterized with x-ray photoelectron spectroscopy (XPS).[9,10]

Oxygen vacancies have been found on the surface of several other transition-metal oxides and drastically alter surface electronic properties. A recent review of photoemission studies of metal oxides by Henrich[11] summarizes the results for some of these oxides. The present work uses photoelectron spectroscopy to examine the "clean" (defect-free) and altered surfaces of WO_3. The effects of various surface treatments on the type and number of vacancies in WO_3 are examined and indicate that many of the techniques used today for the characterization of oxide surfaces drastically alter the surface being studied. The careful examination of these effects has allowed us to make reliable photoemission measurements on the defect-free $WO_3(001)$ surface.

II. EXPERIMENTAL DETAILS

Measurements were made on a WO_3 crystal grown by the sublimation method described by

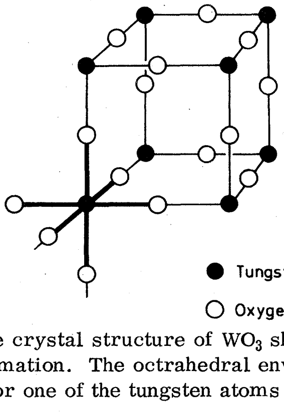

FIG. 1. The crystal structure of WO_3 shown in the cubic approximation. The octrahedral environment is emphasized for one of the tungsten atoms by the heavy lines.

Sawada and Danielson.[12] The crystal, a plate 3 × 5 mm^2 and 0.5-mm thick, was oriented with the c axis perpendicular to the face of the plate and had several large antiferroelectric domains visible in the plane of the crystal. A clean surface was obtained by argon-ion sputtering followed by exposure to ~10^5 L of atomic oxygen and then by annealing at 550 °C. Oxygen gas at 10^{-5} Torr was dissociated at a tungsten filament held at ~2000 °C near the crystal. Surfaces produced by sputtering and annealing without exposure to oxygen showed photoelectron spectra with a high density of states at the Fermi energy. It was not possible to make reliable LEED or Auger measurements on the surface because within a very short time the surface was drastically altered by the incident electron beam. The surface stoichiometry and its sensitivity to various experimental probes is discussed in more detail in Sec. III.

The experiments were carried out in the chamber of a Vacuum Generators ADES 400 angle-resolved photoelectron spectrometer which had a base pressure in the range $(1-3)\times 10^{-10}$ Torr. The photoemission spectra were taken using Ne I ($h\nu = 16.85$ eV), He I (21.22 eV), and He II (40.82 eV) photons from a differentially pumped discharge lamp. The spectrometer was operated with an energy resolution of 0.3 eV and an angular resolution of 3°.

III. DEFECT STATES IN THE SURFACE REGION OF WO_3 (100)

A. Defect-free WO_3

Clean tungsten trioxide surfaces, produced as described in the previous section, gave reproducible photoelectron spectra with a low density of states in the energy-gap region. While the absence of states in the gap is not proof that the surface is stoichiometric, this conclusion is the most reasonable because (i) WO_3 crystals with a known oxygen substoichiometry show a large DOS (density of states) in the gap region in XPS measurements,[9,10] and (ii) amorphous and polycrystalline films which we have prepared by evaporation of WO_3 in vacuum have a greater DOS in the gap region than films produced by evaporation in a high oxygen partial pressure. It can be seen from Fig. 1 that the composition of the surface layer of atoms on the (001) surface of WO_3 will have a composition of WO_2 or O (or domains of both). In the remainder of this paper we will refer to the WO_3 (001) surface, which has been prepared as described in Sec. II, as being stoichiometric and defect free but do not exclude the possibility that the surface layer is relaxed, or that the surface layer composition is one of those required by cleavage normal to the [001] direction. It has been shown for TiO_2 that reconstruction and facetting can be the cause of a low DOS in the energy-gap region,[13,14] however, the degree of rearrangement seen on the (001) surface of WO_3 by Langall and Bernasek[6] is rather small.

Results of the normal emission ultraviolet photoemission spectroscopy (UPS) measurements are shown in Fig. 2(a)–2(c) for three different photon energies. Conductivity and Hall-effect measurements have shown that high-quality WO_3 crystals normally have an activation energy at room temperature of ≃0.01 eV.[15] Consequently, it is not surprising that we found no charging effects which would have appeared as a sensitivity of the spectra to the photon flux and as a broadening of spectral features. The absence of charging allowed us to locate the Fermi energy unambiguously in each spectrum by comparison with a UPS spectrum of a clean molybdenum surface. X-ray photoemission spectra of WO_3 have been published by several authors[9,10,16,17] and the result in Fig. 2(d) has been taken from Hollinger.[10] The finite density of states at the Fermi energy in this spectrum is probably due to a small number of oxygen defects. This aspect will be discussed in more de-

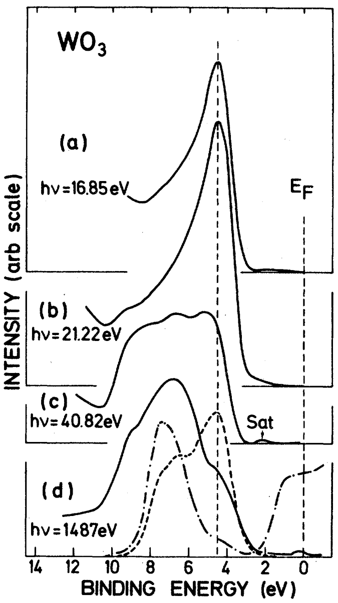

FIG. 2. (a)–(c): Normal emission UPS spectra for defect-free $WO_3(001)$ obtained with Ne I, He I, and He II photons. The small peak at a binding energy of 2.5 eV in (c) arises from He II satellite excitation. The XPS spectrum shown in (d) is taken from Ref. 10. The small peak near the Fermi energy indicates a small degree of nonstoichiometry. Partial densities of states from Ref. 18 are also shown in (d) where both the oxygen $2p$ (dashed line) and tungsten $5d$ (dashed and dotted line) have been broadened, as described in the text.

tail later in this section. A peak in the energy-gap region of the He II spectrum is due to satellite radiation at 48.4 eV and a contribution from the 23.1-eV satellite of He I is present in Fig. 2(b) at a binding energy of about 2.5 eV. This latter contribution has not been removed in any of the subsequently shown spectra but comparison of Figs. 2(a) and 2(b) shows it to be very small. Also shown in Fig. 2(d) are the tungsten 5*d* and oxygen 2*p* partial density of states (PDOS) from the work of Kopp *et al.*[18] These densities of states have been calculated for NaWO$_3$ but in the energy region of the valence band, band structures calculated by these authors for cubic WO$_3$ and NaWO$_3$ are identical to within 0.1 eV over the entire Brillouin zone.

The He I spectrum was taken for a series of electron emission angles and only slight angular dependence was observed. An absence of angular dependence of the photoelectron spectrum has been observed previously for SrTiO$_3$ for photon energies below 26 eV, despite the fact that the surface being examined exhibited a sharp LEED pattern.[19] Although this phenomenon is not yet understood, the similarity of the electronic structures of WO$_3$ and SrTiO$_3$ suggests that the same effect may occur for WO$_3$. Because the surface must have long-range order for angle dependence to be seen in the UPS spectrum, we cannot rule out the possibility that the surface is stepped or has domain structures. Experiments that we have carried out on evaporated films of WO$_3$ have shown that 550 °C is above the crystallization temperature and consequently, it is very unlikely that a disordered layer is present after annealing. The fact that we could not obtain a distinct LEED pattern of the surface is possibly related to loss of long-range order, but is most likely to be due to the electron-induced damage of the surface region. The most striking aspect of the UPS spectra in Figs. 2(a) and 2(b) is the sharp peak at a binding energy of 4.5 eV. The fact that this peak is in the same position for two different excitation energies is strong evidence that the indirect model of photoemission is applicable and thus the UPS spectra represent the DOS integrated over all wave vectors. The peak seen in the UPS spectra at 4.5 eV is also apparent at the same energy in the XPS spectrum. The absence in the Ne I and He I spectra of the strong peak seen at 6.75 eV in the XPS spectrum, may be due to the dependence of the photoelectron cross section on the photon energy. The energy bands within the valence band of WO$_3$ have almost entirely tungsten 5*d* or oxygen 2*p* character.[18] The partial densities of states plotted in Fig. 2(d) reveal that the low-photon-energy spectra 2(a) and 2(b) are dominated by the oxygen 2*p* density of states and the 1487-eV spectrum by that of tungsten 5*d*. This dependence on the photon energy has been seen previously by Pertosa *et al.*[20] The situation in the He*II* (40.82 eV) spectrum is intermediate between those in Figs. 2(a), 2(b), and that in 2(d).

There is reasonably good agreement between the calculated partial densities of states and the photoemission results. However, detailed examination reveals several discrepancies. The PDOS shown in Fig. 2(d) have been convoluted with the resolution function of the XPS spectrometer [Full width at half maximum (FWHM) 0.6 eV] and lifetime broadened by a Lorentzian of FWHM 0.6 eV. Comparison with the XPS results shows that (i) the calculated bandwidth is too narrow even after broadening, (ii) the calculated DOS does not reproduce the peak at 9.0 eV in the XPS and He*II* spectra, and (iii) the indirect and direct band gaps in the calculation are much smaller than the optical measured values of about 2.6 eV[15, 21, 22] and about 3.5 eV,[22] respectively.

B. Electron-induced defect states

When an attempt was made to investigate the LEED pattern of the defect-free surface using 100-eV electrons, it was discovered that the photoemission spectrum of the WO$_3$ surface was rapidly altered. This effect of the incident electrons on the WO$_3$ surface was examined in detail using a separate electron gun and the change in the UPS ($h\nu = 21.22$ eV) spectrum after irradiation with 3×10^{-5} amps cm^{-2} of 300-eV electrons can be seen in Fig. 3. This flux corresponds to approximately one incident electron per unit cell per second. Curves *B* and *C* show the UPS spectra after irradiation times of 2 and 60 min, respectively, and are compared with the spectrum of the clean surface shown as curve *A*. As was the case for the defect-free surface, no charging effects were seen either here or after any of the other surface treatments discussed in this section, and thus the Fermi energy could be reliably located in all cases. The three spectra in Fig. 3 have the same overall shape and to aid comparison, the curves *B* and *C* have been shifted so that the three curves are matched at the strong valence-band peak, which occurs at a binding energy of 4.5 eV for the clean surface. The amount by which the curves have been shifted is seen as the separation between the relevant Fermi energies. The difference between curves *B* and *A* and between curves *C* and *A* is also shown in Fig. 3 on an expanded scale.

The electron irradiation can be seen to increase the density of states in the energy-gap region, to broaden the strong peak in the valence-band density of states, and to increase the separation of this

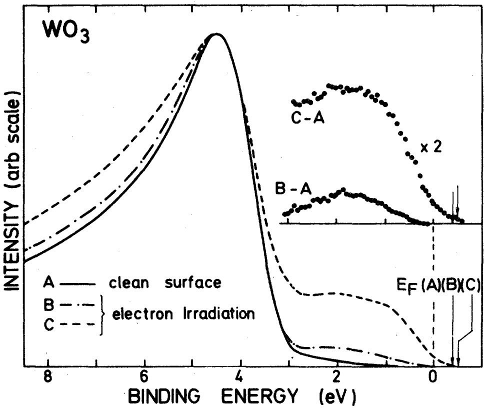

FIG. 3. Normal emission He I excited UPS spectra for the defect-free $WO_3(001)$ surface, curve *A*, and for the same surface after electron irradiation with two different electron doses, curves *B* and *C*. The three spectra have been matched so that they coincide at the top of the valence band. The Fermi energy is indicated for each spectrum, and the difference between the irradiated and defect-free curves is shown on an expanded scale. The energy scale is shown for the spectrum from the defect-free surface.

band from the Fermi energy. The DOS in the gap and the valence bandwidth increased with time of irradiation and did not begin saturating until well after 60 min (curve *C*). The shift of the valence band with respect to the Fermi energy on the other hand, occurred after very short irradiation times and saturated after 2 or 3 min with the electron beam energy and flux used. The UPS spectrum of the clean surface could be regained by annealing the sample at 500 °C for 30 min in an oxygen partial pressure of at most 10^{-10} Torr, the base pressure of the spectrometer's chamber.

The sensitivity of the electronic structure of oxide surfaces to electron irradiation has been observed for several different materials. For example, Thomas[23] found that when Auger measurements were carried out on SiO_2, the surface composition was altered by exposure to the primary electrons leaving it enriched in Si. The electron stimulated desorption of oxygen atoms appears to be the major process for many oxides (see the review by Henrich[11]) and has been observed for WO_3 single crystals,[24] WO_3 grown on metallic tungsten,[25,26] and for WO_3 powders.[26] Niehus[25] examined the angular distribution of O^+ ions which had been desorbed from WO_3 during electron irradiation and concluded that his results could be explained by desorption along the O–W bond direction. Lin and Lichtman[26] found that the O to W ratio determined from Auger measurements decreased from 3.0 to less than 1.0 for WO_3 powder after 5 h irradiation with 1.5×10^{-2} amps cm^{-2} of 3-keV electrons. Knotek and Feibelman's oxygen yield data for several metal oxides, and for electron energies below 50 eV, showed strong steps at the low binding energy metal level.[24] This step occurred near 45 eV for WO_3 and may explain why Langell and Bernasek[6] could obtain a LEED pattern at 40 and 45 eV, whereas we found the damage caused by 100-eV electrons too great to allow a well defined pattern to be obtained. Figure 2 shows how rapidly the electronic structure of the surface changes on electron irradiation: even after 2 min a significant number of states has appeared in the energy gap and the valence band has shifted dramatically.

These earlier results[24-26] for electron stimulated desorption imply that the changes in our UPS spectra with electron irradiation should be examined in terms of loss of oxygen from the surface region. In particular, the area under the UPS spectrum in the energy-gap region increased smoothly with time of electron irradiation and suggests that oxygen atoms were being systematically desorbed.

C. Argon-ion bombardment

The effect of argon-ion bombardment on the UPS spectrum of WO_3 is shown in Fig. 4. The spectrum of the clean surface, curve *A*, is compared with that following 2.5-min bombardment by Ar^+ ions with an energy of 1.5 keV using a Vacuum Generators AG2 ion gun at a pressure of 5×10^{-6}, curve *D*, and that following 5 min bombardment at the same flux, curve *E*. As was the case for electron irradiation, the valence-band peak at 4.5-eV binding energy remains largely unchanged and is shifted away from the Fermi energy, while there is an increase in the DOS in the energy-gap region.

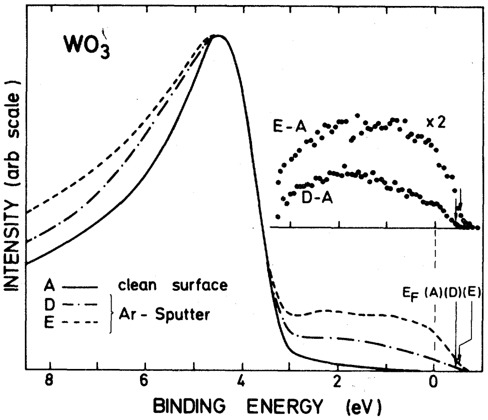

FIG. 4. Normal emission He I excited UPS spectra for the defect-free $WO_3(001)$ surface, curve *A*, and for the same surface after argon-ion bombardment with two different ion doses, curves *D* and *E*. The spectra have been matched as in Fig. 3.

The usual effect of ion bombardment of metal-oxide surfaces is the preferential removal of oxygen, leaving a reduced surface which is rich in the metal atoms.[11] Kim *et al.*[27] examined the chemical shifts of core lines with x-ray photoelectron spectroscopy for several metal oxides before and after Ar^+ bombardment. They found that many of these compounds were reduced to a lower oxide than the original material or even to the pure metal in some cases. For WO_3, Salje *et al.*[28] fitted the tungsten $4f$ lines from XPS measurements with four tungsten $4f$ doublets corresponding to W^{6+}, W^{5+}, W^{4+}, and W^0. These authors found (in agreement with Kim *et al.*[27]) that after Ar^+ bombardment the W^{6+} lines of pure WO_3 broadened to yield a mixture of all possible oxidation states, dominated by that of W^0 after long bombardment times. Auger measurements have also shown a reduction in the oxygen content of the surface region of several metal oxides following ion bombardment (see, for example, Thomas,[29] TiO_2). UPS studies of the effect of ion bombardment upon the valence band have been made on the materials TiO_2,[14,30,31] $SrTiO_3$,[32-36] and $BaTiO_3$,[36] which have similar electronic structure in the valence-band region to that of WO_3. All four materials are semiconductors with a band gap of about 3 eV, their valence bands consisting of a mixture of oxygen $2p$ and metal d states, and their empty conduction bands mainly of metal d states. The effect of ion bombardment on the UPS spectra of TiO_2, $SrTiO_3$, and $BaTiO_3$ was in general quite similar: The appearance of a peak near the Fermi energy and a shift of the valence band away from the Fermi energy. While the shift between the valence band and the Fermi energy is also similar to that found in WO_3, the shape of the DOS in the energy-gap region is quite different, a distinct peak at the Fermi energy compared with the broad DOS seen in WO_3.

The DOS in the energy-gap region does not have quite the same form after Ar^+ bombardment as it does after e^- irradiation. Comparison of Figs. 3 and 4 reveals that in the Ar^+ case the DOS just below the Fermi energy is relatively large, whereas following e^- irradiation, there is a very low DOS at the Fermi energy, particularly after short irradiation times. The difference curves in Figs. 3 and 4 otherwise appear quite similar, having a broad band of states with a maximum between 1.5 and 2.0 eV.

The relative movement between the Fermi energy and a peak in the valence band DOS, which retains much the same shape, suggests a band-bending process. Because (i) the Fermi energy is located very close to the bottom of the conduction band in the bulk,[15] and (ii) the valence band is seen in the experiment to move to higher binding energies, the only possibility is that the bands bend upwards at the defect-free surface and then become flattened after the defects are created. The validity of this interpretation which is illustrated in Fig. 5(a), can be tested by comparing the photoemission results which are surface sensitive with the measured optical energy gap. It has been shown by Koffyberg *et al.*[22] that WO_3 has an indirect optical gap of about 2.75 eV and a direct gap of about 3.5 eV. In the flat band case the difference in energy between the Fermi energy and the sharp edge seen in the photoemission spectra may represent either the direct or indirect gap, depending on the details of the band structure. A schematic arrangement of energy bands for which the photoemission measurement would reveal the direct gap is shown in Fig. 5(b), along with the three-dimensional density of states. The available volume of k space near Γ is small and so these states do not contribute much to the photoemission spectrum. If Γ and X are interchanged in Fig. 5(b) then the indirect gap would be seen as the strongest onset in the spectrum.

The measured energy differences between the Fermi energy and the photoemission onset extrapolated to zero intensity are 3.2 and 3.7 eV for the

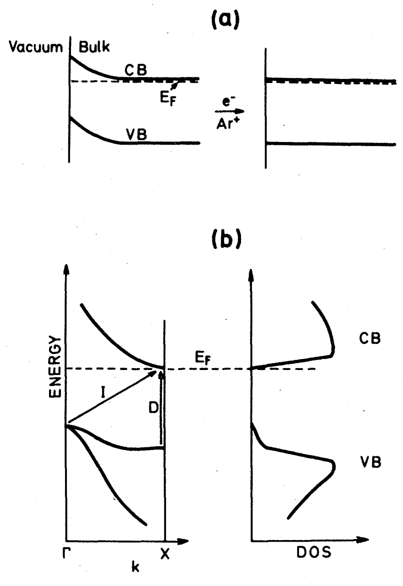

FIG. 5. (a) Simple behavior of valence and conduction bands in a band-bending model in which the valence band flattens after electron irradiation and argon bombardment. (b) Hypothetical band structure and the corresponding three-dimensional density of states. The direct (D) and indirect (I) transitions with the lowest energy are shown by arrows. The Fermi energy is held at the bottom of the conduction band and its separation from the strong onset in the photoemission spectrum will correspond to the direct optical gap.

defect-free and e^- or Ar^+ exposed surfaces, respectively. If the smallest gaps are as shown in Fig. 5(b) then the comparison with the optically measured direct gap of ~3.5 eV (Ref. 22) provides good evidence that the energy bands are bent upwards by up to 0.5 eV for the defect-free surface, and flatten after e^- or Ar^+ exposure. This arrangement of bands is in fact similar to that in the band structure of Kopp *et al.*,[18] although their values of 1.6 and 1.8 eV for the smallest indirect and direct gaps, respectively, are substantially different from the measured values.

Because of the apparent inaccuracy of the calculated band structure in the energy-gap region we cannot rule out the possibility that the smallest indirect gap is $X \rightarrow \Gamma$, for example. If this is the case then the photoemission results show the indirect gap rather than the direct one. The measured separation of the Fermi energy and the valence band would then imply that the Fermi energy was very close to the conduction-band minimum for the defect-free surface and hence, band bending could not explain the observed effects. An alternative explanation, which does not require band bending, is that a disordered layer is produced at the surface by the electron and ion damage. The indirect gap for amorphous WO_3 is about 0.5 eV greater than that for the crystalline material[2, 37] and so a movement of the valence band similar to that seen in the experiment would be expected.

D. Oxygen-ion bombardment and annealing

The clean surface was also bombarded with O^+ ions in order to examine the effects of this treatment on the surface stoichiometry. The results shown in Fig. 6 differ from the Ar^+ case in that there was no significant shift in the Fermi energy. The DOS in the energy-gap region increased, but comparison between the difference curve marked "*F-A*" in Fig. 6 with "*D-A*" or "*E-A*" in Fig. 4 indicates a different behavior. A peak occurs at a binding energy of 1.85 eV in the O^+ case and the occupied DOS near the Fermi energy is much smaller than it is for the Ar^+ bombarded surface.

It is tempting to conclude that these differences between the UPS spectra of the Ar^+ and O^+ bombarded surfaces imply that Ar^+ bombardment leaves the surface deficient in oxygen, whereas O^+ bombardment does not. The result of annealing both surfaces showed this conclusion to be incorrect. If O^+ bombardment damaged the surface region without removal of oxygen then one would expect that annealing the sample would simply reverse the process. It should be recalled that annealing the sample was sufficient to return the e^- irradiated, and thus oxygen deficient surface, to its stoichiometric state, so reversibility on annealing can only be regarded as a necessary and not a sufficient condition for oxygen stoichiometry. UPS spectra are presented in Fig. 7 for the surface which has been Ar^+ bombarded and annealed, curve *H*, and O^+ bombarded then annealed, curve *J*. These spectra are compared with that of the clean sample, all three being aligned at the Fermi energy. The bombarded surfaces had been annealed under similar conditions (500 °C for 30 min) as those which reversed the effects of e^- irradiation. It is clear from Fig. 7 that the spectra of curves *H* and *J* are similar and represent quite a different surface from either of the bombarded

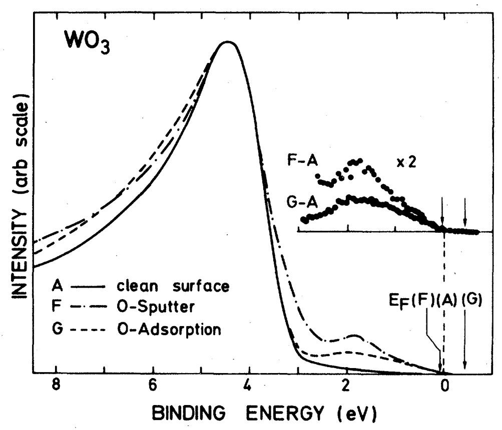

FIG. 6. Normal emission He I excited UPS spectra for the defect-free $WO_3(001)$ surface, curve *A*, and for the same surface after oxygen-ion bombardment, curve *F*, and oxygen adsorption, curve *G*. The spectra have been matched as in Fig. 3.

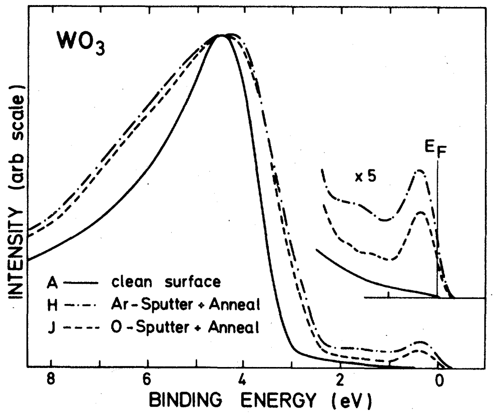

FIG. 7. Normal emission He I excited UPS spectra for the defect-free $WO_3(001)$ surface, curve *A*, for the same surface after argon-ion bombardment and annealing, curve *H*, and after oxygen-ion bombardment and annealing, curve *J*. The spectra which are aligned at the Fermi energy are shown on an expanded scale at low binding energies.

surfaces or of the clean one. The high DOS near the Fermi energy shows a metalliclike behavior and the form of the main valence-band peak is quite different from that of the clean surface. The Fermi energy has also moved nearer to the top of the main valence-band peak. Using a band-bending description, one could interpret these spectra as showing the appearance of a high density of states within the WO_3 band gap which pins the Fermi energy nearer the center of the gap than it was in the clean sample. It seems likely, however, that the surface has been drastically altered and the spectra *H* and *J* are not merely slightly perturbed versions of spectrum *A*.

E. Oxygen adsorption

The surface treatment method, which reproducibly yielded the clean spectrum *A*, required that the surface be exposed to ~10^5 L of oxygen atoms at room temperature between the sputtering and the annealing stages. The spectrum of the defect-free surface with adsorbed oxygen atoms is shown as curve *G* in Fig. 6. Oxygen adsorbed on the Ar^+ or O^+ bombarded surfaces yielded a very similar UPS spectrum to curve *G* but with a smaller DOS in the energy-gap region. There is in all cases a great similarity with the clean spectrum labeled *A* with the exception of the small DOS in the energy-gap region and a shift of the valence band away from the Fermi energy by about 0.5 eV. The fact that the number of energy-gap states created by Ar^+ or O^+ bombardment decreased after oxygen exposure is further evidence that both of these bombarded surfaces have a reduced oxygen content. Schiavello *et al.*[38] measured the oxygen uptake of powders of stoichiometric and reduced WO_3 and found that oxygen was taken into the bulk of the reduced material only at temperatures above about 400 °C. At lower temperatures only one monolayer was taken up. We found that oxygen exposure at room temperature of ion bombarded WO_3 followed by annealing at 500 °C returned the surface to its stoichiometric state. Hence, the results of Schiavello *et al.* imply that the total oxygen deficit in the bombarded surface must be small (less than the equivalent of one monolayer). We used atomic rather than molecular oxygen, however, and this may penetrate the surface more easily at room temperature.

IV. CONCLUSIONS

Our investigation of the (001) surface of WO_3 has shown its electronic structure to be very sensitive to many of the standard ultrahigh-vacuum surface-measurement techniques. Its electronic structure, as revealed by UPS measurements, behaves similarly on ion bombardment to that of TiO_2, $SrTiO_3$, and $BaTiO_3$,[14, 30-36] for example, but is much more sensitive to electron irradiation. In addition to the defect-free WO_3 surface, we have seen several other distinct surfaces derived from it after various surface treatments. These other surfaces are seen as the result of the following:

(i) electron irradiation,
(ii) argon-ion bombardment,
(iii) oxygen-ion bombardment,
(iv) argon- or oxygen-ion bombardment followed by high-temperature annealing, and
(v) oxygen atom adsorption.

We have also examined the effect of hydrogen-ion bombardment on WO_3 in the light of previous claims[28] that this treatment produces hydrogen tungsten bronze H_xWO_3, $x<1$. This study, which will be described in detail in a later publication,[39] revealed no evidence for the formation of the hydrogen tungsten bronze.

Unlike the defect-free surface which has a very low DOS in the energy gap, the other five surfaces listed above all have a large number of states in this region. It is known from previous work that electron irradiation[24-26] and argon-ion bombardment[27] definitely lead to a loss of oxygen from the surface region of WO_3. Consequently, it is reasonable to examine the appearance of states in the gap for surfaces (i)–(iv) with this in mind. The form of this DOS differs but comparison with the XPS results of de Angelis and Schiavello[9] and Hollinger[10] indicates that for surfaces (i)–(iv), these states are associated with a lower oxidation state than the W^{6+} state present in defect-free WO_3. These authors measured the XPS spectra for several substoichiometric tungsten oxides WO_{3-x} and found a peak in the DOS near the Fermi energy for x less than 0.3 and a strong double peak in the energy-gap region for WO_2. This conclusion is also reinforced by the work of Kasowski and Tait[13] who found good agreement between their calculated DOS for Ti_2O_3 and experimental UPS spectra for ion bombarded TiO_2.

The second major difference between the defect-free surface and the others involves the separation between the strong valence-band peak and the Fermi energy. The separation is greater than that for the defect-free surface by about 0.5 eV for surfaces (i), (ii), and (v), the same for (iii) and smaller for (iv). An explanation of these shifts can be made in terms of a band-bending model in which the bands are bent upwards by about 0.5 eV for the defect-free surface and then flattened following electron irradiation, argon-ion bombardment and oxygen adsorption. Small alterations of the surface region must thus be enough to remove the charge imbalance which gives rise to the bending. It is not clear, however, why oxygen-ion bombardment does not cause the bands to flatten when the annealing experiments strongly indicate that bombardment with both O^+ and Ar^+ ions leads to a loss of oxygen from the surface region. The ion bombarded and then annealed surface has a high DOS at the Fermi energy and this suggests that a large density of states is created near the center of the optical gap which then pins the Fermi energy. In a constant Fermi energy diagram this represents a downward band bending because in the bulk the Fermi energy is within 0.01 eV of the bottom of the conduction band.

Band-bending models, however, are too simplified when the alterations to the surface region are large. In the case of the heavily ion bombarded and then annealed surface it is more likely that the surface region has a different composition or structure than the bulk. This interpretation is suggested by the presence of a peak at the Fermi energy similar to that seen in XPS studies[9,10] of the Magnelli phases of WO_{3-x}. In this interpretation the ion sputtering removes oxygen atoms from the surface region creating some disorder in the process and then the annealing recrystallizes the region but with a substoichiometric oxygen content. The structure in the surface region would then be similar to that of the bulk (Fig. 1) but with a small proportion of the WO_6 octahedra becoming edge sharing rather than corner sharing. Some degree of disorder must also be present at the other oxygen deficient surfaces and, as was noted in the previous section, the shift between the valence band and the Fermi energy may be due to a disordering of the surface region rather than to a band-bending effect. The band-bending model does seem to be justified at least for small alterations to the surface region by the constancy in shape of the valence band and may be less applicable after high electron or ion doses. The band-bending model also appears to be consistent with the comparison between the optically measured band gaps and the photoemission onset. This latter argument, however, depends on detailed knowledge of the band structure near the energy gap, and as there has not been a calculation with sufficient accuracy in this energy range, disorder in the surface region cannot be ruled out as the cause for the valence-band shift.

R.D.B. would like to thank the Alexander von Humboldt Foundation for the award of a fellowship.

---

[*] On leave from Ames Laboratory, USDOE, Ames, Iowa 50011.

[1] M. A. Butler, R. D. Nasby, and R. K. Quinn, Solid State Commun. 19, 1011 (1976).

[2] S. K. Deb, Philos. Mag. 27, 801 (1973).

[3] B. W. Faughnan, R. S. Crandall, and P. M. Heyman, RCA Rev. 36, 177 (1975).

[4] A. M. Alquié-Redon, A. Aldaz, and C. Lamy, Surf. Sci. 49, 627 (1975).

[5] E. Salje and K. Viswanathan, Acta. Crystallogr. Sec. A 31, 356 (1975).

[6] M. A. Langell and S. L. Bernasek, J. Vac. Sci. Technol. 17, 1296 (1980).

[7] A. Magnelli, Ark. Kemi 1, 513 (1950).

[8] M. Sundberg and R. J. D. Tilley, J. Solid State Chem. 11, 150 (1974).

[9] B. A. de Angelis and M. Schiavello, J. Solid State Chem. 21, 67 (1977).

[10] G. Hollinger, thesis, Université Claude Bernard Lyon-1, France, 1979 (unpublished).

[11] V. E. Henrich, Prog. Surf. Sci. 9, 143 (1979).

[12] S. Sawada and G. C. Danielson, Phys. Rev. 113, 1005 (1959).

[13] R. V. Kasowski and R. H. Tait, Phys. Rev. B 20, 5168 (1979).

[14] R. H. Tait and R. V. Kasowski, Phys. Rev. B 20, 5178 (1979).

[15] J. M. Berak and M. J. Sienko, J. Solid State Chem. 2, 109 (1970).

[16] G. K. Wertheim, M. Campagna, J.-N. Chazalviel, D. N. E. Buchanan, and H. R. Shanks, Appl. Phys. Lett. 13, 225 (1977).

[17] R. J. Colton, A. M. Guzman, and A. J. Rabalais, J. Appl. Phys. 49, 409 (1978).

[18] L. Kopp, B. N. Harmon, and S. H. Liu, Solid State Commun. 22, 677 (1977).

[19] R. Courths (private communication).

[20] P. Pertosa, G. Hollinger, and F. M. Michel-Calendini, Phys. Rev. B 18, 5177 (1978).

[21] M. A. Butler, J. Appl. Phys. 48, 1914 (1977).

[22] F. P. Koffyberg, K. Dwight, and A. Wold, Solid State Commun. 30, 433 (1979).

[23] S. Thomas, J. Appl. Phys. 45, 161 (1974).

[24] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. 40, 964 (1978).

[25] H. Niehus, Surf. Sci. 78, 667 (1978).

[26] T. T. Lin and D. Lichtman, J. Appl. Phys. 50, 1298 (1979).

[27] K. S. Kim, W. K. Baitinger, J. W. Amy, and N. Winograd, J. Electron Spectrosc. Relat. Phenom. 5, 351 (1974).

[28] E. Salje, A. F. Carley, and M. W. Roberts, J. Solid State Chem. 29, 237 (1979).

[29] S. Thomas, Surf. Sci. 55, 754 (1976).

[30] V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. Lett. 36, 1335 (1976).

[31] Y. W. Chung, W. J. Lo, and G. A. Samorjai, Surf. Sci. 64, 588 (1977).

[32] R. A. Powell and W. E. Spicer, Phys. Rev. B 13, 2601 (1976).

[33] V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. B 17, 4908 (1978).

[34] W. J. Lo and G. A. Samorjai, Phys. Rev. B 17, 4942 (1978).

[35] Y. W. Chung and W. B. Weissbard, Phys. Rev. B 20, 3456 (1979).

[36] R. Courths, Phys. Status Solidi B 100, 135 (1980).

[37] A. Nakamura and S. Yamada, Appl. Phys. 24, 55 (1981).

[38] M. Schiavello, F. Pepe, M. Cannizzaro, S. de Rossi, and R. J. D. Tilley, Z. Phys. Chem. (Leipzig) 106, 45 (1977).

[39] R. D. Bringans, H. Höchst, and H. R. Shanks, Surf. Sci. (unpublished).