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Photon-stimulated desorption and other spectroscopic studies of the interaction of oxygen with a titanium (001) surface

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Synchrotron radiation at the Synchrotron Ultraviolet Radiation Facility at the National Bureau of Standards has been employed to study the adsorption of oxygen on a Ti(001) surface using photon-stimulated desorption (PSD), electron-stimulated desorption (ESD), and ultraviolet photoemission spectroscopy (UPS). The dominant ESD and PSD products observed for oxygen exposures greater than one langmuir are O^+ ions having a most probable kinetic energy of about 3 eV. The photon energy dependence of the PSD ion yield is similar to the major features of the constant final-state secondary-electron yield although there are some differences in detail. This similarity is consistent with the O^+ desorption being initiated by the production of a Ti 3*p* core hole as suggested by the Knotek-Feibelman Auger decay mechanism. The dependence of the O^+ ion yield on oxygen exposure and surface temperature is compared with UPS and work-function measurements. These data indicate that surface oxidation occurs at temperatures as low as 90 K and that at least a fraction of the surface oxide is electronically similar to the maximal valency compound TiO_2.

INTRODUCTION

A variety of spectroscopic techniques (AES, UPS, ESD, PSD, TFMS, ESDIAD, and LEED, *vide infra)* have been employed to gain information about the interaction of oxygen with a stepped titanium (001) surface. [Three indices are used to specify the basal plane of titanium rather than the redundant (0001) notation.] A major motivation for this work was to obtain evidence for the mechanism of photon-stimulated desorption (PSD) of ions from a metallic system for which a maximal valency oxide exists. Several recent PSD experiments[1–6] have been understood in terms of the core hole Auger decay mechanism originally proposed by Knotek and Feibelman[7] to explain electron-stimulated desorption (ESD). While results of ESD and PSD experiments have been reported for bulk TiO_2,[1,8] in the present work the oxide is grown on the surface of a single crystal of the metal. This study of the oxidation of Ti(001) is the first to be done using synchrotron radiation, as well as the first at low temperatures, about 90 K. Where possible, our results are compared with other studies done on titanium films, on polycrystalline titanium, and on the (001) surface.

It is found that for low oxygen exposures little ion desorption occurs. At higher exposures, O^+ desorption is seen with an ion yield spectrum that appears to be dominated by titanium substrate excitations. This primary excitation process suggests that the Knotek-Feibelman mechanism is operative.[7] The O^+ ions desorb perpendicular to the surface, which implies that the Ti—O bonds ruptured in PSD and ESD are perpendicular to the (001) surface.

TECHNIQUES

Measurements were performed in a stainless-steel ultrahigh vacuum (UHV) chamber containing, as shown in Fig. 1, a double-pass electrostatic cylindrical mirror analyzer (CMA) with a concentric electron gun, a second electron gun combined with two microchannel plates and a fluorescent screen assembly[9] to observe low-energy electron diffraction (LEED) and electron-stimulated desorption ion angular distributions (ESDIAD), and a calibrated aluminum-oxide photodiode to determine the photon flux from the monochromator. The CMA, normally used as the electron energy analyzer in ultraviolet photoemission spectroscopy (UPS) and in Auger electron spectroscopy (AES), also was used to measure both ion yield spectra and ion kinetic energy distributions in ESD and PSD.

Measurements of the work function and changes

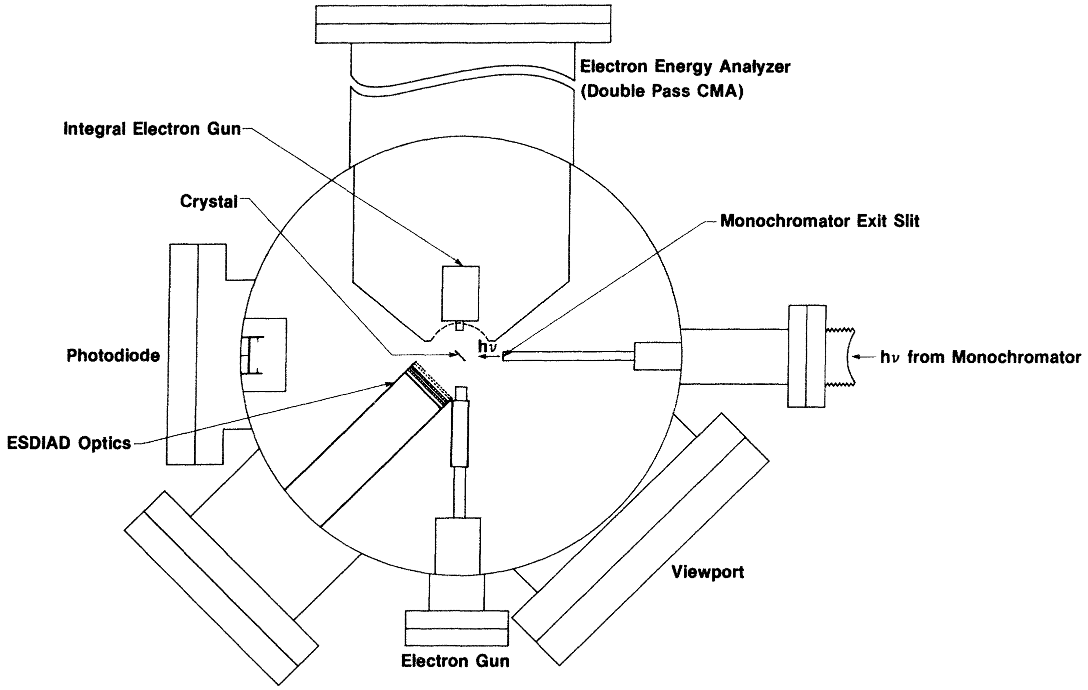

FIG. 1. Diagram of the UHV chamber used for surface science studies at NBS-SURF II.

in the work function were accomplished by UPS. The work function is given by the photon energy minus the width of the electron kinetic energy distribution. Changes in the work function are observed more precisely (± 25 mV) by monitoring the change in the onset for low-energy photoelectrons with a -5.00-V bias potential on the sample.

The desorbed ions were identified with time-of-flight mass spectroscopy (TFMS) by measuring the transit times of the ions through the CMA[10] following pulsed electron beam stimulated desorption. These time measurements were accomplished in a pulse counting mode with a time to pulse height converter and a pulse height analyzer. The ion counting rates in PSD were too low to use TFMS.

Radiation from the Synchrotron Ultraviolet Radiation Facility at the National Bureau of Standards (NBS-SURF II) was monochromatized with a toroidal grating monochromator having a useful photon energy range from 25—75 eV and a spectral bandpass of about 0.1 eV at 25 eV, 0.8 eV at 50 eV, and 2.5 eV at 75 eV. UPS cross sections and PSD ion yields were measured over this range. A spot about 1×2 mm^2 on the sample was illuminated.

The titanium crystal, about $4 \times 7 \times 0.25$ mm^3 in size, had been cut and polished at approximately 4° to the (001) face for other experiments. The sample, mounted on an UHV manipulator equipped with liquid-nitrogen feedthroughs for cooling, was cleaned by repeated argon-ion bombardment and annealing and flash heating to about 500 °C by radiation from a tungsten filament mounted behind the sample. After a number of cleaning cycles, three tests for surface cleanliness were fulfilled: the absence of impurity peaks in AES, the absence of a sharp hydrogen induced state with a binding energy of about -1.3 eV in UPS,[11,12] and the suppression or elimination of impurity ions, mostly F^+ and H^+, in ESD and PSD. The problem with impurity ions was particularly vexing. Even when AES and UPS showed no contamination, hydrogen and fluorine ions were still produced by ESD and PSD, and were eliminated only after many cleaning cycles under UHV conditions.

RESULTS AND DISCUSSION

The change in the oxygen intensity in the Auger electron spectra, the change in the work function, and the change in the photon-stimulated ion desorption rate as a function of exposure of the Ti(001) surface to oxygen at room temperature are shown in Fig. 2. The preservation of crystalline order on the clean surface and after low oxygen exposures was demonstrated by observation of the LEED pattern. The oxygen Auger intensity is seen to rise monotonically with oxygen exposure. Al-

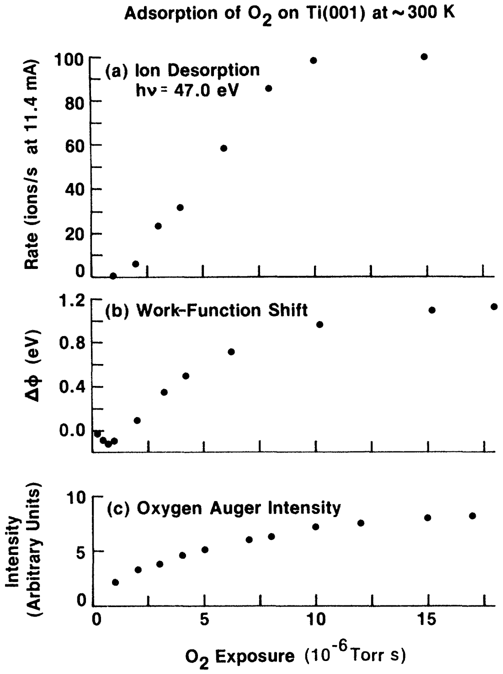

FIG. 2. Changes in (a) the PSD ion yield, (b) the work function, and (c) the oxygen *KLL* Auger intensity caused by exposure of the Ti(001) surface to increasing amounts of oxygen. The data for the PSD yield are normalized to a storage ring current of 11.4 mA which produces a photon flux onto the sample of 2.83×10^9/s at 47 eV. The measured yield is for detected ions and is better than 20% of the total yield.

though the adsorption rate is low above 15 L, the surface is not saturated at 15 L. (Exposures are measured in langmuirs: $1\ \text{L}=10^{-6}$ Torr s $= 1.33\times10^{-4}$ Pa s.) This observation is consistent with oxygen adsorption on films[13] and on polycrystalline titanium.[14] The UPS data for the films show "saturation" at about 100 L, implying[13] an oxide layer thickness of less than 6 Å, which corresponds to one or two layers of TiO_2. The x-ray photoelectron spectroscopy XPS data for polycrystalline titanium demonstrate[14] that oxide films as thick as 45 Å can be grown at 300 K with 760-Torr oxygen pressure. In the present case, the identification of the first monolayer is ambiguous because there is no sharp "knee" in either the work function or Auger intensity data to mark completion of the monolayer.

A work function of 4.6 ± 0.2 eV was measured for the clean surface, in agreement with other recent results.[12,15] Changes in the work function with exposure to oxygen resemble those found by Fukuda, Elam, and Park[16] for oxygen on polycrystalline titanium. They reported a decrease of -0.25 eV at 1-L exposure and a net increase of 1.3 eV at higher exposures with saturation occurring around 1000 L. In contrast Jonker, Morar, and Park[15] report that the work function is constant for low doses of oxygen on Ti(001) at 300 K and rises to a saturation value about 0.7 eV above the clean surface value. Ours is not the only observation of a decrease in the work function following oxygen adsorption on close packed surfaces. Engel, Niehus, and Bauer[17] reported a decrease of -0.050 eV for W(110) at 300 K and suggested a reconstruction of the surface as the cause. A recent proposal indicates that an electronegative adsorbate on the surface of a metal may decrease the work function by a polarization effect that is expected to be most significant for dense surfaces.[18] A decrease in the work function also has been interpreted as being due to a penetration of the oxygen into the surface plane creating a dipole layer with the positive end outward.[19] We also have observed an initial decrease in the work function following exposure of the (100) surface of niobium to oxygen,[20] and others have observed similar behavior for the niobium (110) and (111) faces as well.[21]

The photon-stimulated ion desorption rate shown in Fig. 2(a) exhibits an onset at oxygen exposures between 1 and 2 L, corresponding approximately to the point at which the work function change crosses zero. Similar "delayed onsets" in the electron-stimulated desorption of ions from oxygen on transition metals are well known[17,22] and also have been observed in PSD for oxygen on niobium.[20] The first oxygen to adsorb has a low cross section for ion desorption presumably because it is chemisorbed with a high coordination number, which results in rapid neutralization from the surrounding metal atoms following ion formation, or because the initial sites are somewhat below the surface, which is consistent with the decrease in the work function. As the exposure to oxygen increases, lower coordination sites and defect sites with higher energy can be populated, and oxidized regions of TiO_2 also can be formed, all resulting in an increase in the cross sections for electron- and photon-stimulated ion desorption.

Measurements with the sample at about 90 K reveal no qualitative but some quantitative differences between adsorption at this temperature and at room temperature. The work function decreases initially by about -0.10 eV and then rises for exposures up to 10 L for a net increase of 1.5 eV, which is higher than at 300 K. The onset for photon-stimulated ion desorption still is delayed

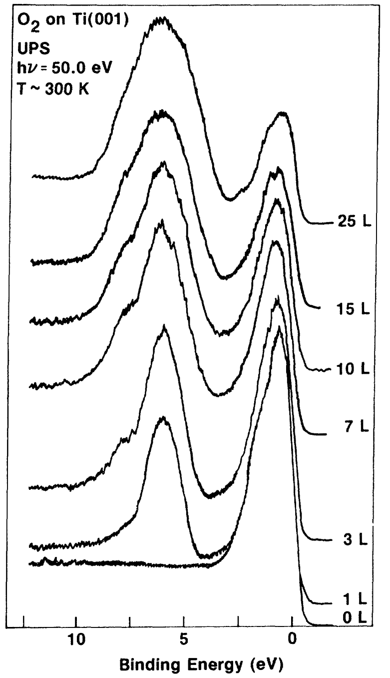

FIG. 3. Changes in UPS caused by exposure of the Ti(001) surface (~300 K) to increasing amounts of oxygen. Note that the Ti *d*-band peak at 1-L exposure overlaps that of the clean surface even though the base line is offset.

with respect to oxygen exposure, but the ion yield is about 5 times higher. Similar changes with temperature in the work-function shift and in electron-stimulated desorption have been observed[23,24] for oxygen on W(111). While condensation of impurities on the surface at low temperatures is a concern, none were detected in the UPS and ESD experiments. Two common impurities in UHV systems are water and carbon monoxide, and neither of these can contribute to the high PSD yield since an ice layer was observed to inhibit PSD from oxygen on titanium, and carbon monoxide on titanium did not result in a detectable PSD yield.

From electron-stimulated desorption ion angular distribution measurements (ESDIAD),[9] it was observed that the O^+ ions desorb perpendicular to the surface. Only the ion beam normal to the surface was seen as the position of the sample and its angle relative to the electron beam were scanned. In the PSD experiments it appears that the ions desorb normal to the surface as well because the maximum number of ions were observed by aligning the surface normal with the collection aperture of the CMA. Based on previous work,[22,24] these observations imply that the oxygen observed in PSD and ESD originates from sites with Ti—O bonds perpendicular to the (001) surface.

A series of ultraviolet photoemission spectra obtained using a photon energy of 50.0 eV after increasing exposures of Ti(001) at room temperature to oxygen is shown in Fig. 3. The photoemission from the *d* band yields a narrow distribution about 2 eV in width, in agreement with previous measurements.[11–13,25] A peak at 1.3 eV binding energy that has been identified[11,12] as due to impurity hydrogen is absent. This feature also is absent in spectra taken with lower photon energies where the instrumental resolution and the photoemission cross section are higher.

Upon exposure to oxygen, a peak in the UPS spectrum appears at 5.9 eV. Starting about 1 L, a second feature appears as a shoulder on the high binding energy side of the initial peak. This shoulder grows in intensity with increasing exposure while the 5.9-eV feature appears to saturate. These data are in qualitative agreement with UPS studies of oxygen on titanium films,[13,25] where two peaks were observed to develop in a similar manner. Those studies were done with a photon energy of 21.2 eV. It is of interest that the photon-stimulated ion desorption rate grows in parallel with this shoulder. After high oxygen exposures, photoemission from the titanium *d* bands is suppressed more dramatically than was observed for titanium films.[13] In fact, the spectrum following 25 L of oxygen exposure is similar to that seen for the cleaved nonstoichiometric compound $TiO_{1.15}$ obtained with $h\nu = 21.2$ eV. (See Ref. 26, Fig. 28.)

A series of UPS spectra obtained using a photon energy of 50.0 eV after increasing exposures to oxygen with the titanium crystal cooled to about 90 K are shown in Fig. 4. At low levels of exposure the spectra are similar to those obtained at room temperature (Fig. 3). At higher exposures, starting about 3 L, a difference is seen; shoulders grow on *both* the low and high binding energy sides of the peak at 5.9 eV with increasing exposure to oxygen. The low binding energy feature develops at room temperature at exposures > 50 L and appears to saturate at about 70 L. All three of the features apparently result from adsorbed atomic oxygen or surface oxides on titanium since additional features at higher binding energies that are expected for species of molecular oxygen[27] are not seen in our experiments. The photoelectron spectrum of molecular oxygen in the gas phase has features around 13, 17, 18.5, and 20.5 eV with respect to the vacuum level. (See Ref. 28, Fig. 9).

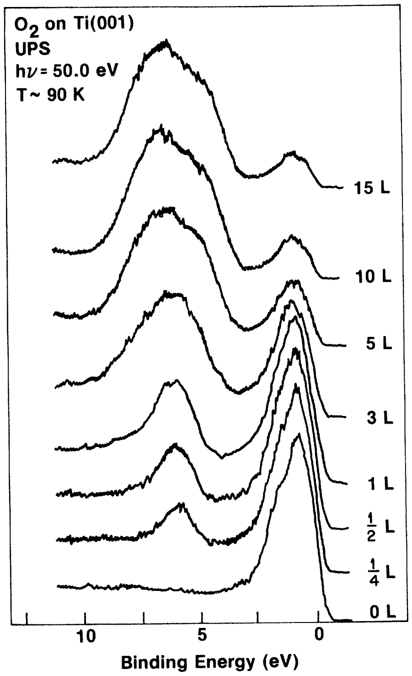

FIG. 4. Changes in UPS caused by exposure of the Ti(001) surface (~ 90 K) to increasing amounts of oxygen.

Similar multiple-peak structure has been seen in the ultraviolet photoemission spectra of cleaved TiO_2 crystals,[29] and the intensity of the corresponding low binding energy feature in sputtered (reduced) TiO_2 and in $TiO_{1.15}$ increases upon exposure to oxygen.[26] Also noteworthy is the fact that the attenuation of the *d*-band photoemission is more pronounced at 90 K than at 300 K (compare Figs. 3 and 4) for comparable oxygen exposures. Attenuated *d*-band emission also is characteristic[29] of TiO_2 and the oxygenated (Ref. 26) $TiO_{1.15}$. The development of the low binding energy feature in the photoelectron spectra and the suppression of the *d*-band photoemission, therefore seem to correlate with the formation of the maximal valency compound TiO_2, and these differences in UPS appear to correlate with the increased PSD yield at 90 K. Although ion desorption is understood in terms of a local electronic configuration, the photoelectron spectra may reflect the development of a delocalized adsorbate energy band.[30] The "energy band structure," however, will depend upon the varying local electronic configurations in a disordered system. It is of interest that for an ordered layer of O on Al(111), the three peaks in the photoelectron energy distribution have been shown to stem from oxygen p_z and oxygen p_x, p_y derived bands.[30(a)]

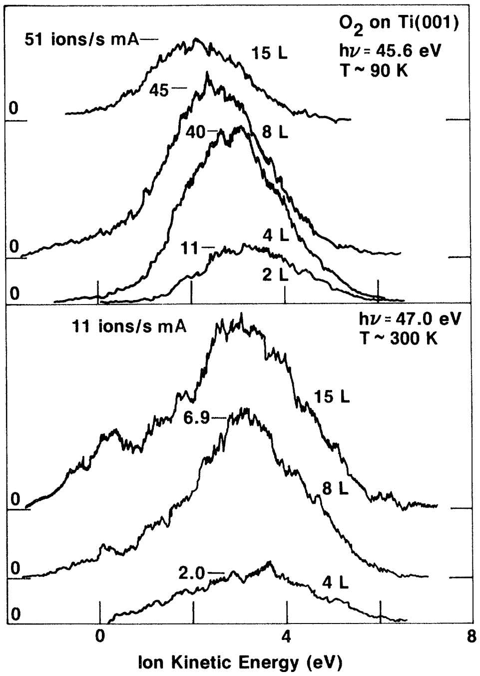

FIG. 5. PSD ion kinetic energy distributions following increasing oxygen exposure of the Ti(001) surface at about 90 and 300 K. The ordinate scale for each curve differs due to the decreasing storage ring current and light flux during the course of the experiment. The zero point and maximum, normalized to a 1-mA current, is indicated for each. A 1-mA current produces a photon flux onto the sample of 2.40×10^8/s and 2.48×10^8/s at 45.6 and 47.0 eV, respectively. Data were collected with beams in the range 5–25 mA and with a kinetic energy resolution of about 1 eV.

The kinetic energy distributions of ions produced by photon-stimulated desorption at 300 and 90 K are shown in Fig. 5 as a function of oxygen exposure. At 300 K these distributions are dominated by a peak at about 3 eV over the entire range of exposure. The same 3-eV peak in the ion kinetic energy distribution is seen by electron-stimulated desorption, thus implicating the same electronic transition in both processes and allowing ESD to be used for the mass analysis. From the time-of-flight spectrum shown in Fig. 6, it is clear that the dominant contribution at this kinetic energy is from O^+ ions. In the TFMS experiment we were not able to eliminate contributions to the wings of the 3-eV kinetic energy peak from F^+ ions, which were dominantly at lower kinetic energies, $\lesssim 1$ eV, or H^+ ions, at higher kinetic energies, $\gtrsim 5$ eV.

At the lower temperature, 90 K, the same kinetic energy peak is seen at low oxygen exposures, but the distribution shifts noticeably to lower kinetic

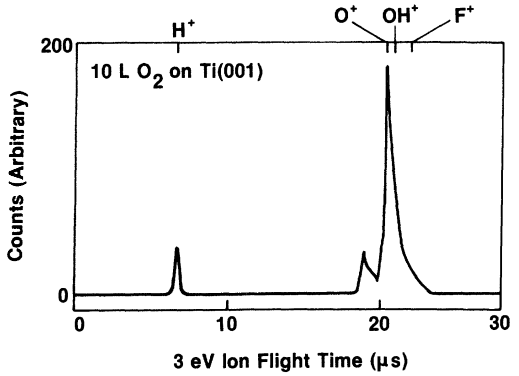

FIG. 6. Time-of-flight spectrum of ions leaving the surface with 3-eV kinetic energy. The clean Ti(001) surface (~300 K) first was exposed to 10-L oxygen. The small peak preceding O^+ lies in the mass range 12—14.

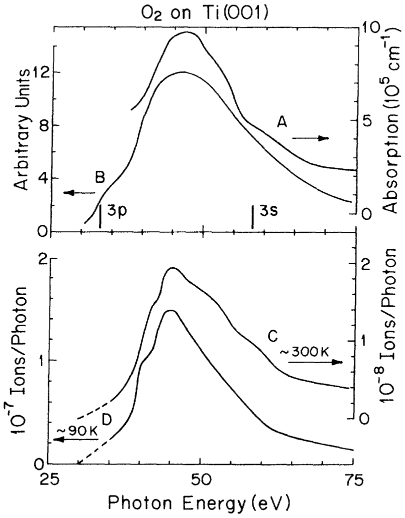

FIG. 7. Ion yield spectra (*C* and *D*) obtained by monitoring the transmission of ions with the most probable kinetic energy through the analyzer in each case: 2 eV at 90 K following 15-L oxygen exposure and 3 eV at 300 K following 8-L exposure. For comparison, the absorption spectrum (*A*) for an evaporated titanium film (Ref. 31) and the CFS secondary electron yield spectrum (*B*) for the clean titanium crystal are shown. The CFS electron spectrum was obtained with the energy analyzer set for 0-eV kinetic energy and 2-eV resolution. The binding energies (Ref. 33) for the titanium 3*p* and 3*s* electrons are marked. The expected and observed increase of the 3*p* binding energy of about 5 eV following exposure to oxygen (see text) matches the sharp rise in the PSD spectra at about 38 eV. The second-order correction (Ref. 32) is a significant factor in determining the dashed portions of the PSD curves.

energies as the exposure increases, which is different from the behavior at room temperature. This shift in the ion kinetic energy distribution may be another manifestation of the state of adsorbed oxygen that causes the low binding energy shoulder in UPS and the enhanced PSD ion yield. The observed peak positions do not correlate with changes in the work function, see Fig. 2, but rather seem to correlate with features in UPS. The zero of ion kinetic energy is referenced to the zero of electron kinetic energy observed in photoemission from Ti(001) at room temperature following exposure to 30 L oxygen.

Ion kinetic energy distributions for O^+ from W(111) has a peak energy about 8 eV,[4] and O^+ from Nb(100) about 5 eV.[20] The widths of the distributions observed here are comparable to those found in other ESD and PSD measurements. It is interesting to note that the higher ion kinetic energies correlate with the higher formal charges on the cations: W^{+6}, Nb^{+5}, and Ti^{+4}.

Figure 7 compares the O^+ PSD ion yield spectra for oxygen on titanium at 300 and 90 K with the constant final-state (CFS) secondary electron yield spectrum and with the absorption spectrum of titanium films.[31] The spectra are corrected for the monochromator transmission and the second-order contribution.[32] The second-order correction assumes the cross sections to decrease monotonically above 75 eV. The ion yield spectra were obtained by monitoring transmission of ions with the most probable kinetic energies through the analyzer in each case: 2 eV at 90 K following 15-L exposure and 3 eV at 300 K following 8-L exposure. It has been shown in certain cases that the CFS secondary electron yield spectrum is proportional to the soft x-ray absorption coefficient for the substrate. (See Ref. 4 and references cited therein.) Since the photon penetration depth is many atomic layers, about 100 Å, and the secondary electrons result from many scattering processes that occur following ionization beneath the surface, the secondary yield spectrum is largely insensitive to the nature of the surface and mostly represents the probability for titanium excitation. The absorption spectrum of the thin titanium film in Fig. 7 may be affected by the nature of the film and differ from the secondary electron yield spectrum for the single crystal. In the energy range covered here, 25—75 eV, thresholds are reached for excitation of titanium 3*p* with a binding energy of 32.6 eV and 3*s* with a binding energy of 58.4 eV.[33] A 3*p* binding energy of 32.7±0.1 eV was observed in the present work. The dominant features of the CFS spectrum, the threshold at about 32 eV and the maximum at about 46 eV, appear to be due primarily to 3*p* excitation, although variations of the valence-band excitation cross sections with photon energy may contribute as well. The energy dependence of the cross section is similar to that for other transition metal *p* levels. The step onset at about 33 eV may be a manifestation of a high density of states just above the Fermi edge or a resonance effect involving 3*d* electrons. Evidence for surface states of Ti(001) has been seen recently by Jonker *et al.*[15] The sharpness of this step onset is lost in the secondary yield from an oxidized surface as would be expected for surface states being involved.

The general agreement of the PSD ion yield with the CFS electron spectrum and the absorption spectrum of titanium is consistent with the Knotek-Feibelman mechanism of the desorption proceeding via excitation of a 3*p* core hole and an interatomic Auger process resulting in an O^+ ion.[7] Some substantial differences in detail exist, however. First, the maximum in each of the ion yield spectra is at a lower photon energy than the maxima of the absorption and secondary electron spectra. If the O^+ ions are originating from surface TiO_2-like maximal valency species, then the 3*p* binding energy for these ions, involving Ti^{+4}, is expected to be about 5 eV larger than for metallic Ti.[13,14] In the present work, a shift 4.7 eV to higher binding energy was observed for the 3*p* peak in the photoelectron energy distribution from Ti following exposure to 65 L of oxygen. One then expects the PSD ion yield curve to be displaced to higher photon energies relative to the absorption and secondary electron spectra if these spectra are determined primarily by the 3*p* ionization and if the proton energy dependence of the cross section for 3*p* ionization of Ti^{+4} is similar in shape to that for Ti. Quite to the contrary, a shift to lower photon energies is observed. This difference contrasts with results for the desorption of O^+ from molybdenum[6] and tungsten[4] where the above logic explains the observed shift of the PSD yield to higher photon energies. Second, the PSD ion yield spectra are much more sharply peaked than the other spectra. Third, corresponding fine features do not appear in all spectra. The shoulder at about 40 eV in the PSD spectra is barely, if at all, discernible in the secondary yield curve, and the sharp onset at 33 eV in the secondary yield curve is absent, or at best becomes more diffuse, in the PSD spectra. The shoulders at about 53 and 60 eV in the 300-K PSD spectrum were just discernible above the noise level and were not unambiguously seen in the 90-K PSD spectra or secondary electron yield spectra. They do, however, seem to have analogs in the absorption spectrum of the thin film.

It would appear that these differences are due to the fact that the secondary yield spectrum does not measure only the probability for 3*p* core hole formation and that other excitations may be contributing to the photon-stimulated ion desorption spectrum. It has been documented in some cases that excitations other than from the core *p* level contribute to the secondary yield spectrum.[34] In chromium the secondary electron yield is substantially different from the partial photoyield from the chromium 3*p* level.[35] Data for niobium show a doublet structure for the absorption coefficient,[34] whereas the photon-stimulated ion desorption spectrum only has a single peak.[20] Clearly, additional information is needed from both theory and experiment pertaining to the photon energy dependence of the 3*p* and 3*d* ionization cross sections in both Ti and Ti^{+4} for comparison with the PSD spectra and the CFS secondary electron yield spectrum. Such measurements are now underway. These partial photoionization yield measurements may provide insight into the origin of the shoulder at 40 eV in the PSD spectrum, but we also cannot rule out the possibility of small amounts of adsorbed molecular oxygen species that are sufficiently low in concentration that they do not appear in UPS but have sufficiently high cross sections to contribute to PSD. Recently, molecular oxygen adsorbed on metal surfaces has been documented.[27,36] It is suggestive that in the photoionization of gaseous oxygen, the probability for the formation of O^+ increases at about 40 eV.[37]

A series of PSD ion kinetic energy distributions are shown in Fig. 8 as a function of photon energy to examine whether there may be "many-body effects" in ion desorption as one moves from the regime of the "sudden" approximation, with the excitation energy far above threshold, to the regime of the "adiabatic" approximation near threshold. This effect, as proposed by Weng,[38] should appear as a shift in the ion kinetic energy distribution as the photon energy is changed. Second-order light may be contributing at the lower energies,[32] but it appears clear that these data reveal no marked shift in the peak position as the threshold for 3*p* photoionization is approached. Thus, these data do not substantiate this proposal.

SUMMARY

In these studies of the interaction of oxygen with the (001) surface of a titanium crystal, the concen-

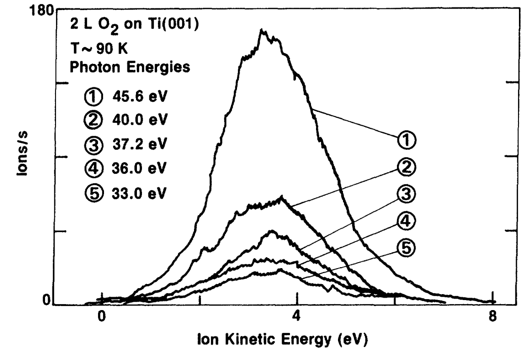

FIG. 8. PSD ion kinetic energy distributions at photon energies approaching threshold for Ti 3*p* photoionization. The decreasing yield with photon energy stems from the decreasing cross section and the decreasing photon flux.

tration of oxygen on the surface was monitored by AES, and the preservation of crystalline order on the clean surface and at low oxygen exposures was demonstrated by observation of the LEED pattern. The ions produced by ESD were identified by TFMS as being predominantly O^+. The O^+ ion kinetic energy distribution served to identify these ions as the ones produced by PSD as well. The ESDIAD technique demonstrated that the O^+ ions desorb in a beam normal to the surface.

The photon-stimulated desorption of O^+ ions from the titanium (001) surface occurs upon exposure to oxygen after a small threshold exposure is reached. The ion yield spectrum is similar to the major features of the absorption spectrum of a titanium film and the CFS secondary electron yield spectrum of the titanium crystal. This similarity is consistent with the O^+ desorption being initiated by the production of a Ti 3*p* core hole as suggested by the Knotek-Feibelman Auger decay mechanism. This mechanism requires a low density of valence electrons on the titanium atom in order to allow interatomic Auger decay, resulting in the formation of an O^+ ion, to compete effectively with the intra-atomic Auger decay. Sufficiently low valence-electron densities are expected in maximal valency compounds.[7] Changes in the structure of the oxygen peak in UPS as a function of oxygen exposure appear to correlate with the PSD ion yield, and the features that develop appear similar to those found in UPS of crystals of TiO_2 and UPS of crystals of $TiO_{1.15}$ after exposure to oxygen.[26] Since the exposure levels investigated here result in coverages less than and up to about one monolayer of oxygen, it does not seem reasonable to attribute the observed PSD *only* to the maximal valency compound TiO_2. The surface studied here was stepped, and the valence-electron density of a surface titanium atom can be diminished by having a low coordination at a step or defect as well as by bonding to oxygen. Defects may also serve to decouple the surface atom from the bulk so the probability of a neutralizing transition, once the Ti is photoionized or the O^+ is formed, is greatly reduced.

The experimental observations can be summarized in a way that indicates the presence of at least two distinct forms of oxygen on the titanium (001) surface. Form 1 develops at low oxygen exposures and is characterized by a low work function, very low ESD and PSD yields, and a binding energy feature at 5.9 eV in UPS. Form 2 grows at high oxygen exposures, and the growth is enhanced at 90 K relative to 300 K. This form is characterized by a high work function, a high PSD yield, additional binding energy features in UPS, and a 3-eV peak in the ion kinetic energy distribution at room temperature that shifts to 2 eV during oxygen exposure at 90 K. Form 1 may correspond to oxygen atoms below the surface plane, thereby giving rise to the lower work function, or in high coordination sites, possibly the threefold hollows, from which the cross section for ion desorption is low because of the high neutralization rate. Form 2 may correspond to low coordination sites, possibly at steps or defects, or to TiO_2, all with a low valence-electron density at the titanium atom so the cross section for ion desorption will be higher. Evidence for "two distinct binding states of oxygen on the basal plane of titanium" also has been found by Jonker, Morar, and Park.[15]

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