

Electron-stimulated desorption of neutrals from ionic surfaces: OH from TiO₂

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Electron-stimulated desorption of neutral hydroxyl radicals ($\cdot\text{OH}$) from TiO₂ has been studied by observing the near-ultraviolet emission of $\cdot\text{OH}$ leaving the surface. In contrast to ^+OH , the $\cdot\text{OH}$ yield versus the incident electron energy shows a sharp onset at 11.5 eV, a peak at 17.5 eV, no pronounced increase at the O 2s threshold, and only a weak effect at the Ti 3p edge. The results are analyzed in terms of the different mechanisms for transferring one or two holes to ^-OH .

Electron-stimulated (ESD) and photon-stimulated (PSD) desorption of positive ions from the surfaces of "maximal valency" ionic materials (those in which the formal oxidation state of the cation is isoelectronic with a rare gas) are well understood¹ in terms of the Auger decay process described by Knotek and Feibelman.² In this mechanism, interatomic Auger decay of a hole in the uppermost cation core level, created by photon or electron excitation, yields a final state in which the two holes are localized on a surface anion which is then ejected from the substrate in a "Coulomb explosion." In spite of the considerable amount of attention given to ion desorption, there has been no investigation of the desorption of neutral species from such materials.

Recent work by Feulner and co-workers^{3,4}—for molecular adsorbates on metal surfaces—indicates fundamentally different mechanisms for ion and neutral desorption in these systems. For the latter, reneutralization of desorbing ions, formation of an excited repulsive state or electronically induced vibrational predissociation can occur, depending on the nature of the adsorbate-substrate interaction. It is yet to be determined whether any of the processes occurring in desorption from an adsorbate overlayer on a metal are applicable to the ejection of neutrals from the surface of an ionic material.⁵ In addition to basic questions concerning mechanisms, desorption phenomena are also important in understanding radiation damage in technologically useful oxide materials, as discussed by Knotek and Feibelman.⁶ In this work, we describe the first detailed study of the ESD of anionic neutrals from an ionic substrate, using photoluminescence of the desorbed electronically excited species⁷ to measure the neutral yield versus incident electron energy.

We have chosen to study neutral hydroxyl radicals ($\cdot\text{OH}$), desorbed from ion-damaged TiO₂ by electron impact, following dissociative chemisorption of H₂O. Ar⁺-ion bombardment of TiO₂ preferentially removes oxygen, producing chemically active surface defects which may be formally described⁸⁻¹⁰ as Ti⁺ ions adjacent to oxide-ion vacancies. The initial sticking coefficient of H₂O on such a surface is high¹¹ ($\sim 0.2-0.5$), leading to dissociative adsorption, which saturates at an exposure of a few langmuirs^{11,12} [1 langmuir (L) = 10⁻⁶ Torr sec = 4.78 × 10¹⁴ molecule-surface collisions/cm² for H₂O at 300 K]. Higher exposure might lead to physisorption of molecular water.¹¹⁻¹³ Knotek and co-workers have reported extensively^{2,6,14-17} on the electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD) of ^+OH (and also H⁺ and O⁺) from TiO₂ and found a strong desorption threshold at the O

2s core-level excitation energy (21 eV) and another at the Ti 3p edge (32 eV), indicating desorption from surface Ti-OH sites.

The sample was a (001)-oriented rutile single crystal reduced by vacuum annealing (2 h, 950°C, 3 × 10⁻⁵ Torr). The resulting material contains oxygen vacancies and is thus *n*-type semiconducting (64 Ω cm, 1 × 10¹⁸/cm³ carrier density¹⁸). The crystal was etched in NaOH/H₂O [2.5 h, 70°C, 5M (Ref. 13)] and in H₂O₂ [5.5 h, 25°C, 30% (Ref. 15)] and rinsed ultrasonically in isopropanol. The gases were research-purity argon and distilled H₂O outgassed by repeated freeze-pump-thaw cycles (dry-ice/acetone bath). The vacuum system (base pressure < 3 × 10⁻¹⁰ Torr) was an improvement of that described previously,¹⁹ with a quadrupole mass spectrometer and a water-cooled Ti sublimator added. Initially, the system, as described in Ref. 19, was used in an unsuccessful attempt to detect desorbed $\cdot\text{OH}$ in the ground electronic state by laser-induced fluorescence. Following Ar⁺-ion bombardment (1 keV $\sim 25-100$ μA/cm²) for 30 min or more, the surface was exposed to H₂O. Subsequent Auger electron spectroscopy experiments (in a different vacuum chamber) verified that samples treated in this way were atomically clean except for a trace amount of carbon. After reevacuation of the chamber to $\leq 1 \times 10^{-9}$ Torr, the electron beam was turned on (normal to the sample surface) and the luminescence collected at a right angle to the beam (see Ref. 19), focused onto the entrance slit of an *f*/3.5 $\frac{1}{4}$ -m monochromator (14-nm spectral slit width) and detected by a cooled photomultiplier (GaAs photocathode, RCA 31034) with subsequent signal processing via photon-counting electronics. Previously, Tolk *et al.*²⁰ have used a similar method to observe ESD of $\cdot\text{OH}$ from contaminated alkali halide surfaces during electron irradiation in an H₂ ambient. To obtain a reasonable gun current (~ 5 μA) at very low incident energies (< 50 eV), two modes of operation were employed. In the first, the sample was maintained at a fixed bias (typically $V_s = -95$ V) and the gun voltage swept in the V_s to $V_s - 50$ -V range. For this mode, it was verified that the data were independent of large ($\pm 50\%$) changes in V_s . In the second, the gun voltage (and, therefore, the gun current) was held constant at $V_G = -145$ V and the sample bias swept in the V_G to $V_G + 50$ -V range. Both modes gave essentially the same results. It was also verified that the luminescence intensity varied linearly with incident current (in the 0-7-μA range). Yield data were taken using a microcomputer to control the voltage sweep while averaging the ratemeter output. Typically, the data were averaged over 16 sweeps.

Figure 1 shows the electron-induced emission spectrum. The only features observed in the 200–850-nm (6.2–1.5-eV) range are at 306 and 281 nm, which correspond closely to the desorbed neutral $\text{OH } 2\Sigma^+ \rightarrow 2\Pi$ 0-0 and 1-0 emissions, respectively, seen during electron bombardment of ice.²¹ Intersystem crossing of $2\Sigma^+$ with the dissociative $4\Sigma^-$ state²² eliminates emission from excited vibrational states with $v'' > 1$. From the relative intensity of the two peaks a “vibrational” temperature of $T_{\text{vib}} \sim 2000$ K is estimated for the desorbed OH , suggesting that the dissociative excited state leading to desorption is distorted relative to the ground state of the surface complex.

Figure 2 shows the $\lambda = 306$ nm emission intensity versus E_p , the incident (primary) electron energy relative to the Fermi level, defined by $E_p = eV + \phi_f + kT_f$ where V is the bias voltage of the gun filament relative to the sample, ϕ_f the work function of the filament (clean polycrystalline tungsten, 4.5 eV) and $T_f \sim 1700$ K the filament temperature. The OH yield shows a sharp onset at $E_p = 11.5$ eV, with a peak at 17.5 eV, and increases steadily to higher E_p , reaching a broad maximum between 90 and 140 eV. Similar results are obtained by monitoring the 281-nm emission. In particular, we note the absence of a pronounced increase in yield at the O 2s edge and the indication of a weak threshold effect at Ti 3p. By “weak” we mean that the OH yield doubles in going 10 eV above the Ti 3p edge,^{15,16} whereas, the OH emission increases by only 25% over the same range.

Several observations preclude gas-phase or physisorbed molecular H_2O as the OH source. First, the signal disap-

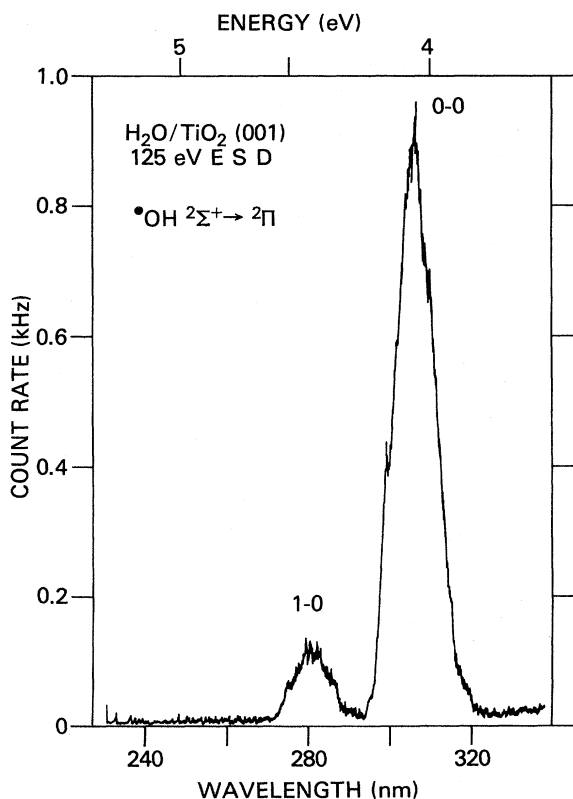


FIG. 1. Emission spectrum obtained during electron irradiation ($E_p = 125$ eV, $i_p = 6 \mu\text{A}$) of Ar^+ -ion bombarded TiO_2 (001) following a 300-L H_2O exposure.

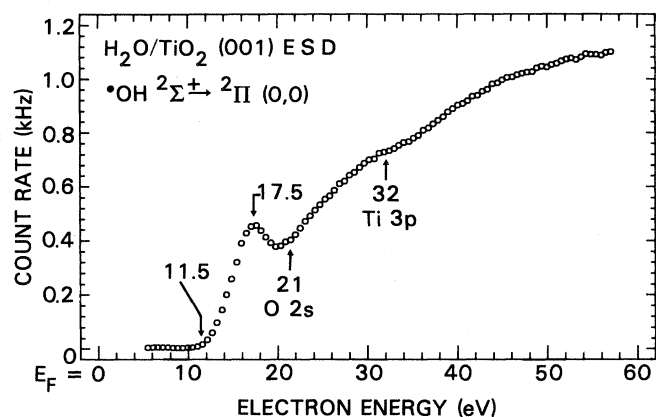


FIG. 2. Emission intensity at $\lambda = 306$ nm vs electron energy, E_p (relative to the Fermi level), at constant primary beam current ($i_p = 3 \mu\text{A}$).

pears when the electron beam is deflected off the sample or when the exposed stainless-steel parts of the sample holder are irradiated. Second, the data in Fig. 2 are very different from the results for molecular (solid²¹ or gas-phase²³) H_2O . Ice exhibits²¹ an OH onset at $E_p = 10$ eV but no peak below 25 eV. Water vapor²³ shows a maximum in the OH yield at $E_p = 20$ eV (relative to vacuum). Taking $\phi_s \sim 4.7$ eV as the sample work function¹¹ [Ar^+ -ion bombarded TiO_2 (110) after H_2O exposure], we estimate that such a peak would appear at ~ 24.7 eV in Fig. 2. Furthermore, the atomic hydrogen Balmer emission lines, seen²³ during electron impact dissociation of H_2O vapor, were not observed here, nor was the broad, intense visible emission of irradiated ice.²¹ Finally, previous¹⁵⁻¹⁷ ESD studies of $\text{H}_2\text{O}/\text{TiO}_2$ —under conditions similar to those of the present work—gave no indication of physisorbed molecular H_2O .

Based on an assessment of the efficiency of the optical and detection systems, we estimate a yield on the order of 10^{-8} OH (in the $v'' = 0$ level of $2\Sigma^+$) per incident electron at $E_p = 50$ eV. From the observed decrease in OH signal during prolonged irradiation at energies well above threshold, we estimate that the net yield for removal of surface Ti-OH is in the range $1-5 \times 10^{-6}$ per incident electron. This represents the combined effects of all ESD processes that break Ti-OH or Ti-O-H bonds. Weak OH emission (10% of that shown in Fig. 1) was observed ~ 1 h after Ar^+ -ion bombardment but before H_2O exposure, consistent with the H_2O partial pressure in the UHV chamber and the high initial sticking coefficient.^{11,12} The OH emission intensity differed by less than a factor of 2 for 30 L and 5×10^4 -L H_2O exposures, also consistent with the high reactivity of surface defects.

Two other experiments were carried out to verify the role of surface defects in H_2O dissociation and to assess the importance of sample preparation. First, the Ar^+ -ion bombarded sample was annealed at $\sim 600^\circ\text{C}$ to reduce the surface defect density²⁴ (by out-diffusion of bulk oxygen) and then exposed to H_2O (300 L). The resulting OH yield was reduced, relative to that in Fig. 2, by a factor of 20, verifying the observation of Knotek^{15,16} and of others that defect-free TiO_2 does not dissociate H_2O . Second, the annealed sample was given a light Ar^+ -ion dose ($\sim 5 \times 10^{14}/\text{cm}^2$ at 1 keV) and exposed to H_2O (300 L), after

which the $\cdot\text{OH}$ yield returned to within a factor of 2 of that in Fig. 2.

The results in Fig. 2 are distinctly different from those for ^+OH desorption,^{2,14-17} for which negligible ion yield is detected below $E_p = 21$ eV (O $2s$), with a very sharp increase above this threshold and another increase above $E_p = 32$ eV (Ti $3p$). These differences between $\cdot\text{OH}$ and ^+OH desorption can be understood in terms of various mechanisms for transferring one (and only one) hole to $\cdot\text{OH}$ to form $\cdot\text{OH}$, versus two holes to form ^+OH . To begin, we assume that reneutralization of desorbed ^+OH is not significant in n -type TiO_2 because of the small free-electron density, so that only processes that create $\cdot\text{OH}$ directly are important. Furthermore, if ^+OH reneutralization were a source of $\cdot\text{OH}$, the data in Fig. 2 would show the core-level threshold effects seen in ^+OH ESD.

For ionic oxides, in which the valence-band charge density at the site of the initial cation core hole arises mainly from nearest-neighbor oxide ions, two types of interatomic Auger final states can be distinguished:²⁵ those for which both holes are on the same oxygen site and those for which the holes are on different sites. For those cases studied in some detail²⁵— MgO and Al_2O_3 —both types appear to have comparable intensities. The energies are given by²⁵

$$E(X) - E(YZ) = E(X) - E(Y) - E(Z) - U_{\text{eff}}.$$

$E(YZ)$ is the energy of the final two-hole state and $E(X)$, etc., are empirical one-electron binding energies for the three levels involved in the Auger transition. U_{eff} is the "effective hole-hole interaction energy" and is a sum of a Coulomb repulsion energy and a polarization term arising from the response of the medium to the doubly ionized final state. For both holes on the same site, U_{eff} is dominated by the intra-atomic Coulomb energy and $U_{\text{eff}} \approx 10$ eV; whereas, U_{eff} is much smaller (≤ 3 eV) for holes on nearest-neighbor oxygen sites.

To convert $\cdot\text{OH}$ to ^+OH , only those transitions of the first type (both holes on the same site) are effective; whereas, to obtain $\cdot\text{OH}$ from $\cdot\text{OH}$, only those of the second kind (holes on different sites, one or both of which is $\cdot\text{OH}$) are significant. Hence, the weak Ti $3p$ threshold in $\cdot\text{OH}$ yield, as compared to that for ^+OH , can be understood in terms of U_{eff} using localization arguments²⁶ advanced by Ramaker, White, and Murday and by Feibelman. For $U_{\text{eff}} > 2\Delta$, where Δ (~ 4 eV in TiO_2 , Ref. 11) is the half-width of the valence-band density of states, the two-hole final state is effectively localized on a time scale (one vibrational period) appropriate to desorption. The localization arises from the absence of an energy-conserving channel for "hopping" of one of the holes off the site of localization. Feibelman has noted a second contribution, termed "orbital shrinkage," which gives rise to a reduced overlap between orbitals on the two-hole site and those on neighboring sites as a result of the diminished intra-atomic screening on the two-hole site. Localization thus favors desorption, in the form of ^+OH , when the Auger final state places both holes on the same site (initially $\cdot\text{OH}$). On the other hand, for holes on different sites, U_{eff} is significantly less than 2Δ , so delocalization can compete with $\cdot\text{OH}$ desorption.

For the case of O $2s$ excitation, direct ejection of $\cdot\text{OH}$ through an Auger process is unlikely since intra-atomic decay, involving O $2p$ orbitals on the hole site, should be more probable than an interatomic mechanism.²⁷ Intra-

atomic decay leads, again, to a localized two-hole final state, giving the observed ^+OH desorption threshold. Furthermore, even if a fraction of the O $2s$ holes decay through an interatomic process, the resulting final state will be delocalized, as discussed above, with the net result that an $\cdot\text{OH}$ ESD threshold at the O $2s$ edge should be much weaker than at the Ti $3p$ edge.

To interpret the ESD yield curve, we must estimate the available energy,²⁸ $E_a = E_p - \delta E$, where δE is the energy relative to E_F of the lowest unfilled level which can be occupied by the incident electron after inelastic scattering. Photoemission data^{11,13,24} for Ar^+ -ion bombarded semiconducting TiO_2 indicate that E_F is a few tenths of an electron volt below the conduction band edge at the surface, and there appears to be no significant change in band bending with H_2O exposure. Hence, $\delta E \sim 0.5$ eV, and the threshold at $E_p = 11.5$ eV corresponds to a transition energy of ~ 11 eV. Kawai *et al.*⁹ have calculated the energy levels of $\cdot\text{OH}$ adsorbed on a TiO_2 surface defect site. The lowest-energy excitation of the $\cdot\text{OH}$, from the O $2p$ nonbonding level to an antibonding Ti-OH molecular orbital at 5.7 eV above the conduction-band edge, occurs at about 10.7 eV, in reasonable agreement with the observed threshold. Hence, the threshold desorption process may be described as a valence excitation²⁹ involving charge transfer (i.e., $\text{Ti}^{+4} - \cdot\text{OH} \rightarrow \text{Ti}^{+3} + \cdot\text{OH}$), with the electron transferred into the $3d\sigma^*$ antibonding orbital lying well up in the conduction band.⁹

The appearance of a peak near the ESD threshold is not straightforward to explain; however, Knotek²⁸ has shown that such an effect may be expected if the threshold excitation is dipole forbidden. Since the initial and final states of the transition both have O $2p$ character, and the $\cdot\text{OH}$ is essentially a localized surface impurity, it seems reasonable that the threshold process should have some dipole-forbidden character. A second explanation involves a resonant enhancement, based on consideration of the state of the inelastically scattered incident electron. If the incident energy were such that the electron, after losing 11 eV, had an energy corresponding to a maximum in the conduction-band (CB) density of states (DOS), a peak should occur in the $\cdot\text{OH}$ yield. Hence, the peak at 17.5 eV would require a CB maximum at 6.5 eV above E_F . Recently, Grunes *et al.*³⁰ have reported high-resolution transmission electron energy loss data for O $1s$ and Ti $2p$ near-edge structure in TiO_2 showing a CB DOS consisting of several overlapping peaks centered about 5–6 eV above the CB edge. The fact that a similar peak is not seen^{15,16} in the ^+OH ESD may result from the very sharp rise in yield above the O $2s$ threshold; however, PSD data¹⁴ for TiO_2 do exhibit some structure near threshold.

In summary, we have carried out the first study of ESD of neutral species from adsorbate overlayers on an ionic oxide substrate. The results emphasize the importance of the number of holes transferred to the adsorbate in determining the desorption mechanism. For a process requiring transfer of two or more holes (ESD of ^+OH , O^+ , or H^+ from TiO_2) the Auger-induced mechanism has already been shown² to be the dominant effect. For transfer of only one hole (ESD of $\cdot\text{OH}$) the Auger process could, in principle, still be effective if the two final-state holes are on different anion sites. However, we have argued that the presence of only a weak Ti $3p$ threshold in the $\cdot\text{OH}$ yield indicates that—as a result of final state delocalization—the Auger process is less effective than the valence excitation mechan-

ism²⁹ in this case. Furthermore, by comparing our data with theoretical results of Kawai *et al.*,⁹ we have been able to identify the desorption threshold with a particular valence excitation. Such a specific assignment, for ion desorption from adsorbates on metals, has been achieved only recently.³¹ This work suggests interesting further investigations. A very useful test of the conclusions of this work would be the measurement (as in Refs. 3 and 4) of the ESD yield of neutral atomic oxygen from TiO₂. This is an example of neutral desorption requiring transfer of two holes and would be expected to show the same threshold behavior as the ⁺OH ESD. It would also be instructive to consider neutral ESD from covalent oxides, e.g., ⁺OH from SiO₂. Here, the

localized two-hole final states^{31,32} are molecular orbitals (rather than atomic orbitals as in the highly ionic limit), and Auger-induced ⁺OH desorption may be more significant than for TiO₂.

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