Electron-stimulated positive-ion desorption caused by charge transfer from adsorbate to substrate: Oxygen adsorbed on TiO$_2$(110)

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(Received 13 January 2009; published 27 February 2009; corrected 4 March 2009)

The electron-stimulated desorption of O$^+$ from atomic oxygen (O$_t$) species on the TiO$_2$(110) surface has been investigated. Adsorbed O$_t$ species, produced by O$_2$ dissociation, desorb as O$^+$ ions by hole production in the Ti(3p) level of lattice Ti^{4+} ions. A factor of 600 increase in the O$^+$ desorption cross section for the O$_t$ species is observed compared to lattice O. Very efficient charge transfer from the O$_t$ species to the Ti(3d) level, accompanied by a low reneutralization rate for the O$^+$ ions at the Ti sites, is postulated to be responsible for the greatly enhanced O$^+$ ion yield.

Metal oxides are widely used in heterogeneous catalysis, photocatalysis, gas sensors, and photovoltaic devices.[1,2] The rutile TiO$_2$(110) surface has been thoroughly studied and is considered to be a prototypical metal oxide.[3] In many of the applications of TiO$_2$, the interaction of molecular oxygen with the TiO$_2$ surface plays a significant role.[3] The electron-stimulated desorption (ESD) phenomenon is particularly well suited for studying metal oxides and adsorbates on metal oxides due to its high surface sensitivity. We employ mass analysis of desorbing ions produced by ESD of isotopically labeled oxygen adsorbate species to provide chemically important information for discriminating adsorbate-derived isotopomer O$^+$ ions from O$^+$ species originating from the TiO$_2$ lattice.

The Knotek-Feibelman (KF) mechanism for the ionization of atoms on surfaces was proposed to explain the ESD of O$^+$ ions originating from the TiO$_2$(110) surface.[4] These ions originate from the surface atoms of the TiO$_2$ crystal lattice when it is excited by electron impact. In the original KF mechanism the production of O$^+$ is ascribed to the ionization of the Ti(3p) electron in the TiO$_2$ lattice followed by an *interatomic* Auger transition between O^{2-} (formal charge) ions in the lattice and the partially vacant Ti(3p) level. In the KF mechanism, this interatomic Auger transition is followed by the ejection of two other electrons from the lattice O valence level to produce O$^+$ and leads to electron-stimulated O$^+$ desorption via a Coulomb repulsion between a Ti^{4+} lattice ion and the adjacent surface O$^+$ ion. The electron energy threshold for the ejection of O$^+$ is at ~34 eV which is the core-hole excitation energy of the Ti(3p) level.[4] Normally the hole produced in the Ti(3p) level would be filled by higher-lying Ti valence electrons. The interatomic Auger process occurs within the framework of the KF mechanism because it was postulated that in a maximal valency oxide there are no Ti valence electrons available for filling the Ti(3p) hole. There have been numerous electron-stimulated ion desorption studies that showed the general validity of the KF model on metal oxide surfaces insofar as the involvement of the ionization of the metal core hole for the first step.[5,6] In addition, there are ESD results for the adsorbed species such as H and OH species on metal oxide where site specificity and threshold electron energies for desorption have been discussed.[7,8] The KF mechanism has been modified to explain the ion desorption phenomena from nonmaximum va-

lency metal oxides and we will discuss this later. In this Rapid Communication we demonstrate that an *adsorbed* oxygen species on the TiO$_2$(110) surface is also excited by hole production in the *lattice* Ti(3p) state, producing O$^+$ ions which desorb with very high efficiency compared to lattice O$^+$ desorption.

The experiments were performed in an ultrahigh vacuum chamber (base pressure: 2×10^{-11} mbar) equipped with time-of-flight electron-stimulated desorption ion angular distribution (TOF-ESDIAD) capability using a pulsed electron gun operating at 40 kHz with 75 ns pulse width at 180 eV.[9] In addition, in a separate ESD measurement capability involving mass spectrometric detection of ESD-produced ions, we employed a second continuous-beam electron gun. The TiO$_2$(110) single crystal (Princeton Scientific, $7 \times 7 \times 1$ mm^3) was mounted on a tantalum support plate using a high-temperature alumina-based inorganic adhesive (Aremco 503). Two tungsten wires were spot welded at the back of the Ta plate for resistive heating. The temperature of the crystal was measured and electronically controlled using a K-type thermocouple contacting the TiO$_2$ crystal through a hole in the tantalum support. The O$^+$ ion desorption threshold energy measurements were performed using the separate electron gun (Kimball Physics ELG-2) and a quadrupole mass spectrometer (QMS) (UTI-100C). The filament in the QMS was turned off to eliminate ionization of the residual gas in the UHV chamber. Thus all the ions detected were only from the electron-impact ionization processes on the TiO$_2$ surface. Electron beam damage was minimized by using low electron current to the TiO$_2$ surface (400 nA) and by using high gain in the QMS. The TiO$_2$(110) crystal was cleaned by Ar$^+$ sputtering followed by annealing at 900 K in vacuum. Within the sensitivity limits of Auger spectroscopy, the surface was free of contamination. Low-energy electron-diffraction (LEED) measurements on the cleaned surface showed a sharp (1 $\times$ 1) pattern. Adsorption of ^{18}O$_2$ (99% isotopically pure) was carried out using a calibrated capillary array doser.[10]

Figure 1 shows a mass spectrometric analysis of O$^+$ ions ejected from TiO$_2$(110)-(1 $\times$ 1) surface which has been prepared to contain surface oxygen-vacancy defect sites. The density of the defect sites is estimated to be about 8%–10% of a monolayer (ML).[11] Desorbed ions from the TiO$_2$(110) surface, produced by electron-stimulated desorption, were detected using the QMS. Upon electron irradiation, as shown
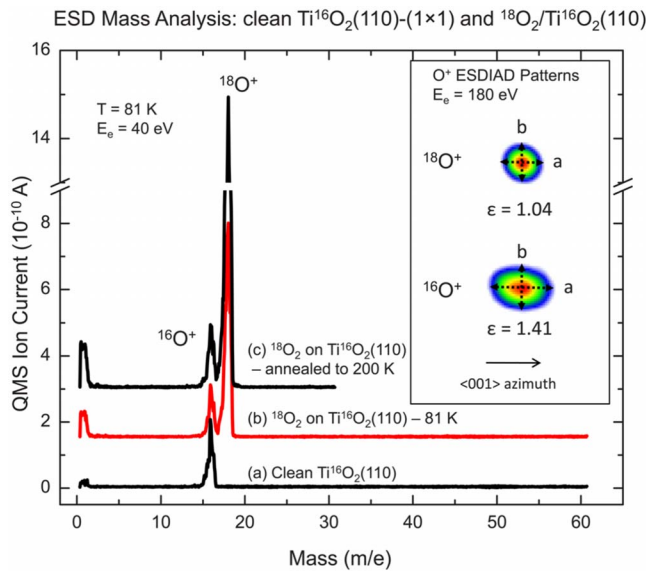
FIG. 1. (Color online) Mass spectrometric analysis of positive ions desorbing from (a) clean TiO$_2$(110)-(1×1), (b) the surface covered with a small amount of ^{18}O$_2$ adsorbed at 81 K, and (c) the ^{18}O$_2$ dosed surface after annealing to 200 K. All the measurements were conducted at 81 K. The incident electron energy is 40 eV. The O$^+$ ESDIAD patterns from the lattice ^{16}O and the adsorbed ^{18}O$_2$ are also shown in the inset. In the TOF-ESDIAD measurement the excitation electron energy was 180 eV and the crystal bias was at +30 V to compress the ion trajectories. The ESDIAD pattern for ^{18}O$^+$ ions was obtained after annealing to 200 K to dissociate all adsorbed O$_2$ molecules. The ellipticity ε is the ratio of the widths along the two axes (a and b) obtained through fitting the data to Gaussian curves.

in trace (a) in Fig. 1, the surface ejects ^{16}O$^+$ ions from the clean TiO$_2$(110) lattice as well as H$^+$ ions from a small coverage of adsorbed impurity H$_2$O or OH species produced by residual water in the background gas. There were no other masses desorbing. By using TOF-ESDIAD, an angular distribution pattern for the ^{16}O$^+$ ions from the bridging oxygen rows on the clean surface has been obtained as shown in the inset to Fig. 1. This O$^+$ angular distribution pattern shows that the ion ejection direction is perpendicular to the surface plane and is slightly elliptical with the long axis parallel to the $\langle 001 \rangle$ crystal azimuth, i.e., parallel to the bridging oxygen row direction on the TiO$_2$(110)-(1×1) surface. Trace (b) in Fig. 1 shows the mass spectrometric analysis when a small coverage of ^{18}O$_2$ (exposure=9.6×10^{12} molecules/cm^2) has been adsorbed at 81 K. The ^{18}O$^+$ ion signal from the adsorbed oxygen species is observed with much higher intensity than ^{16}O$^+$ from the lattice oxygen, and the ^{16}O$^+$ ion signal from the lattice is still present with a slight decrease in intensity. Trace (c) represents the mass spectrum after annealing the adsorbed ^{18}O$_2$ on the TiO$_2$(110) surface from 81 to 200 K. The intensity of the ^{18}O$^+$ ion signal from adsorbed oxygen species increases while the intensity of the ^{16}O$^+$ ion signal from the lattice shows no change from trace (b) after annealing. The ^{18}O$^+$ ESDIAD pattern from the adsorbed oxygen species is also shown in the inset to Fig. 1. One sees that the adsorbed
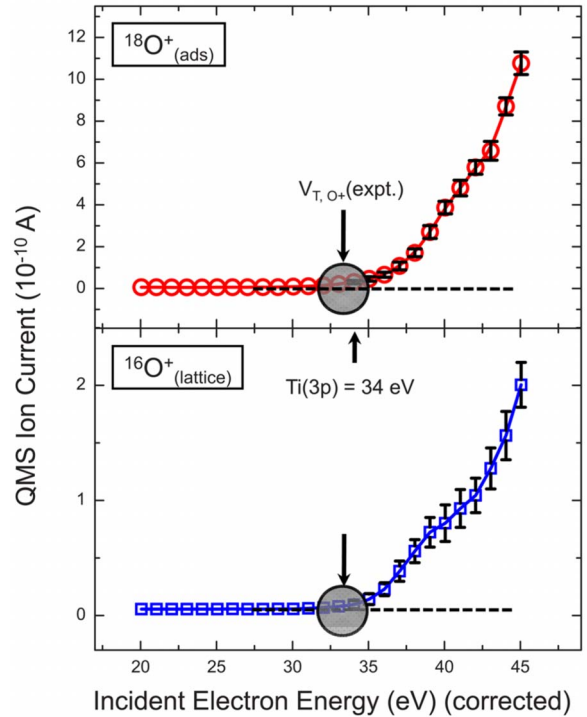

FIG. 2. (Color online) O$^+$ ion yield from clean TiO$_2$(110) and from ^{18}O$_2$ adsorbed on the surface upon annealing to 200 K versus the incident electron energy. The adsorption temperature for ^{18}O$_2$ was 81 K. Measurements are made with a quadrupole mass spectrometer. Corrections have been made to the energy scale for the work function of the Ta electron emitter filament in the electron gun. The positions of the experimental threshold for ^{18}O$^+$ desorption and the Ti(3p) excitation energy are indicated by arrows. The shaded circle represents the estimated experimental uncertainty including the thermal spread of electron energy.

oxygen species also produces a normally oriented and almost circular O$^+$ ESDIAD pattern with a significantly lower ellipticity of the ion angular distribution compared to the ESDIAD pattern from the lattice O species. The results in Fig. 1 indicate the desorption of the O$^+$ ions from the adsorbed oxygen species is much more efficient and that the ion trajectories are less perturbed from the normal direction compared to the lattice O$^+$ ions. The desorbing lattice O$^+$ ions are influenced by a more highly corrugated repulsive potential compared to O$^+$ from adsorbed oxygen.

Figure 2 shows the ion yield of ^{16}O$^+$ from the clean TiO$_2$(110) surface versus the incident electron energy compared to the ^{18}O$^+$ yield from the surface species produced after adsorption of ^{18}O$_2$ at 200 K. Here the QMS allowed measurements of the isotopic positive ions originating from the TiO$_2$ lattice and from adsorbed oxygen. Each data point in the ion yield measurements in this work represents an average of 3500 acquisitions, which was necessary due to the low electron current used to minimize significant adsorbate damage. *It is clearly seen that the adsorbed oxygen species exhibits a threshold electron energy for ^{18}O$^+$ production which is almost identical to that seen for the lattice ^{16}O$^+$.* The incident electron energy scale shown involves a 4.25 eV

(Ref. 12) work-function correction for the Ta electron emitter in the electron gun.[13] The threshold electron energy for $^{18}O^+$ production from adsorbed oxygen is 33 ± 0.5 eV, corresponding closely to the excitation energy of the Ti(3p) level (34 eV) in the underlying TiO$_2$ surface.[4] The errors in determining threshold energy include the thermal spread of electron energy which is in the range of 0.5 eV.[13] This observation of the electron-stimulated desorption of an *adsorbed species* on TiO$_2$ via Ti(3p) ionization is of note, particularly when contrasted with the status of our current knowledge.[14]

The electron energy threshold for the $^{18}O^+$ desorption from adsorbed oxygen at 81 K is virtually the same at 32.5 ± 0.5 eV, in close agreement with the threshold measured for $^{18}O^+$ at 200 K. At 81 K, there is a mixture of surface species including O$_2$ molecules adsorbed on the oxygen-vacancy defect sites.[3,15] Recent studies suggest that O$_2$ molecules chemisorbed at low temperature convert to a multiatom complex upon annealing between 200 and 400 K but this occurs at relatively high coverages compared to the coverage in this work.[16,17] However, it is observed by scanning tunneling microscopy (STM) that, even at a low temperature near 120 K, O$_2$ has dissociated, healing the vacancy defects and forming oxygen atoms (O$_t$ species) adsorbed on the fivefold coordinated Ti (Ti$_{5c}$) sites on the TiO$_2$(110) surface.[18] The increase in the O$^+$ desorption intensity upon annealing to 200 K, where all adsorbed O$_2$ molecules are dissociated,[11] indicates that the produced O$_t$ species undergo a high cross-section ESD ionization process to yield O$^+$.

The yield of O$^+$ from the oxygen species at 81 K is observed to be a factor of 1.2 larger than that from the lattice oxygen in angle-integrated intensity ESDIAD measurements at an electron energy of 180 eV. The data were taken for an exposure to $^{18}O_2$ of 9.6×10^{12} molecules/cm^2 which corresponds to only about 0.9% of a monolayer considering 1 ML=5.2×10^{14} Ti$_{5c}$ sites/cm^2 on the TiO$_2$(110)-(1$\times$1) surface and an initial O$_2$ sticking coefficient of 0.5.[11] The $^{18}O^+$ ion yield further increases to 5.4 times that of the lattice $^{16}O^+$ upon annealing to 200 K, where all adsorbed O$_2$ molecules have dissociated.[11] Comparing the ESD ion yield for an adsorbed O$_t$ atom to the ion yield per lattice oxygen atom, a factor of $\sim$600 increase in ESD ionic cross section is observed. For the lattice oxygen species of the clean TiO$_2$(110)-(1$\times$1) surface, the ESD ionic cross section $Q^+_{(\text{lattice O})}$ is measured to be $(5 \pm 2) \times 10^{-19}$ cm^2 in our experiment. The ESD ionic cross section for the O$_t$ species $Q^+_{(\text{adsorbed O})}$ corresponds to $\sim 3 \times 10^{-16}$ cm^2, which is an extremely high value for the ionic cross section for a surface species. For comparison, the electron-impact ionization cross section for the atomic oxygen species at 190 eV in the gas phase is 1.3×10^{-16} cm^2.[19] Thus the ESD cross section of O$^+$ ions from the O$_t$ species generated by hole formation in the Ti(3p) level is comparable or even higher than the gas phase ionization cross section for an oxygen atom.

The interatomic Auger process leading to O$^+$ desorption invoked in the KF mechanism should have a low cross section compared to an *intra-atomic* Auger transition.[20–22] The KF mechanism has been revised [Kotani-Toyozawa (KT) mechanism] to involve the electron transfer from lattice O to an intermediate Ti(3d) hybridized (and partially filled) state which is lowered in energy as a result of the core potential
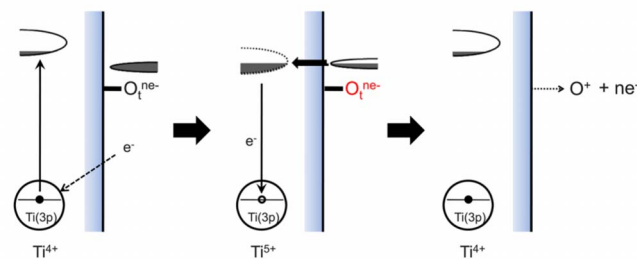

Schematic Excitation and Charge Transfer Process for O$_t$ Species – TiO$_2$(110)

FIG. 3. (Color online) Schematic of the O$^+$ desorption process involving Ti(3p) electron excitation followed by a charge-transfer process from adsorbed oxygen (O$_t$) species (KT mechanism). In this mechanism, the charge transfer occurs by a resonance process through a partially filled Ti(3d) level whose energy is lowered by a core-potential change due to the hole in the Ti(3p) level produced by electron impact. For O$_t^0$ species, $n=0$. For O^{2-} lattice oxygen, $n=2$.

change due to the hole produced in the Ti(3p) orbital, causing the Ti(3d) level to align with the O(2p) level.[21] The resonant charge-transfer process invoked in the KT mechanism is much more efficient for O$^+$ ion production than would be expected for the interatomic Auger transition of the KF mechanism. Despite the difference in the charge-transfer process in the two mechanisms, both the KF and the KT mechanisms will exhibit the same threshold energy corresponding to excitation of the Ti(3p) electron at 34 eV. For the O$^+$ desorption from the O$_t$ species, charge transfer is envisioned to occur from adsorbed O$_t$ atoms to a hole in the Ti(3d) level of a surface Ti atom. The large enhancement of the cross section for O$^+$ production from O$_t$ species, compared to the production of O$^+$ from lattice oxygen ions, may arise from the fact that an efficient resonant charge-transfer process occurs from the O$_t$ species to the Ti(3d) level (conduction band) following Ti(3p) core-hole generation. It is also likely that the differences in the reneutralization rate for the O$^+$ ions from the two types of surface species (lattice O and O$_t$ species) contribute to the observed enhancement in the cross section for O$^+$ production from adsorbed O$_t$ species.

An alternative model to explain the high ionic cross section for O$_t$ species involves assigning a charge state of zero to O$_t$. If the O$_t$ species is neutral, then only one electron needs to be transferred to the Ti^{5+} leading to a high ESD cross section. In comparison lattice O^{2-} has to lose three electrons to form O$^+$, which would be a very low probability process. Both bridging O and O$_t$ species share the same threshold energy for excitation, which is the energy needed to ionize the Ti(3p) level in the Ti^{4+} ion bonded to either lattice oxygen or to the adsorbed O$_t$ species. A schematic of the excitation process, followed by charge transfer (KT mechanism) is shown in Fig. 3. The charge transfer between the surface oxygen anion and the Ti^{5+} ion produced by electron-impact ionization will be facilitated by the presence of the lowered Ti(3d) resonance level in the KT mechanism.

One might ask whether the excitation of the Ti(3p) level in TiO$_2$ is responsible for the ESD of other adsorbed molecules. The answer to this question is no for the surface
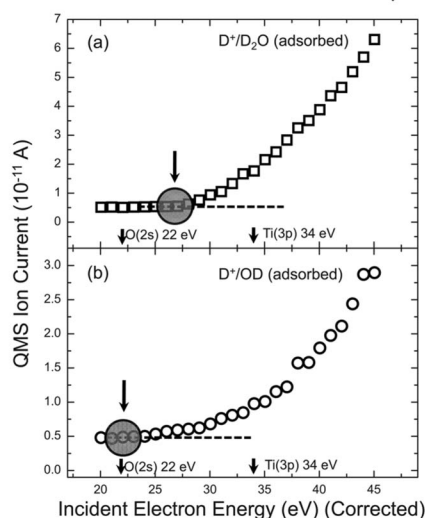
Ion Yield Threshold Measurements from Adsorbed Species on $TiO_2(110)$

FIG. 4. D^+ ion yield measurement from (a) D_2O and (b) OD adsorbed on $TiO_2(110)$ at 81 K versus the incident electron energy. The estimated uncertainty in electron energy is represented by the shaded circles. The arrows indicate the positions of the D^+ threshold and the $Ti(3p)$ excitation energy, which is unrelated to the D^+ ion desorption.

species investigated in this work. For example, the excitation of adsorbed D_2O on the reduced clean $TiO_2(110)$ surface at 81 K produces D^+ ions with an electron-impact threshold energy of 27 ± 0.5 eV, as shown in Fig. 4(a). This energy threshold for D^+ production is likely related to the $O(2s)$ excitation in the adsorbed D_2O molecule.[23] We also observed

that the D^+ threshold energy (22 eV) from the hydroxylated (OD)/$TiO_2(110)$ surface in Fig. 4(b) is also near to the $O(2s)$ excitation energy in agreement with previous work.[23] In both cases, one can clearly see that the excitation of the $Ti(3p)$ state is not responsible for the electron-stimulated D^+ desorption.

From these studies, we can conclude the following: (1) Adsorbed O_t species on the Ti_{5c} site on $TiO_2(110)$ are preferentially ionized by a very high cross-section process to produce O^+ ions initiated by the ionization of the $3p$ level of Ti^{4+} ions in the TiO_2 lattice. This finding has not been reported for adsorbed oxygen species or any other adsorbed species on TiO_2. (2) Water molecules (D_2O) adsorbed on TiO_2 at 81 K are not strongly associated with the lattice Ti^{4+} ions but instead undergo electron-induced ionization to produce positive D^+ ions due to the $2s$ excitation of their own O atoms. Similar D^+ ionization occurs also for adsorbed OD species. (3). O_t species adsorbed on Ti_{5c} sites exhibit an unprecedented high ionic cross section for an adsorbed oxygen species, resembling the ionization cross section for gas phase atomic oxygen species. This high cross-section ionization process for O_t species compared to bridging O^{2-} species can be due to several factors: (1) efficient resonant charge transfer between O_t and Ti^{5+}, (2) less efficient reneutralization of O_t^+ compared to O^+ from bridging O^{2-}, and (3) assignment of a charge of zero to O_t species, which means that only one electron would be transferred to Ti^{5+} to produce O^+.

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