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Positron-annihilation-induced ion desorption from TiO_2(110)

T. Tachibana,[1,*] T. Hirayama,[2] and Y. Nagashima[1]

[1]*Department of Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

[2]*Department of Physics, Rikkyo University, 3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan*

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We have investigated the positron-stimulated desorption of ions from a TiO_2(110) surface. Desorbed O^+ ions were detected in coincidence with the emission of annihilation γ rays. The energy dependence of the ion yields shows that the O^+ ions were detected at energies much lower than the previously reported threshold for electron impact desorption corresponding to the excitation energy of Ti($3p$) core electrons. These results provide evidence that core-hole creation by positron annihilation with electrons in the core levels leads to ion desorption.

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Positrons are used as sensitive probes that provide detailed information on atomic physics [1], elementary particle physics [2], fermiology of metals [3], and defect studies [4]. Slow positron beams have also been used to develop surface-sensitive techniques such as reemitted positron energy loss spectroscopy (REPELS) [5], positron-annihilation-induced Auger electron spectroscopy (PAES) [6], and reflection high-energy positron diffraction (RHEPD) [7].

Another promising use of positron probes has been proposed [8–10]. Electronic transitions induced by the annihilation of slow positrons may cause desorption of the topmost surface components. Studies of positron-stimulated desorption processes will provide insight into the fundamental nature of the dynamics of positron-surface interactions. Moreover, desorption from the topmost atomic layers can enable the exploration of new approaches to surface modification. However, the experimental field of positron-induced surface dynamics is in its infancy and little is known about desorption. In this Rapid Communication, we report an experiment that demonstrates a fundamental process for ion desorption from a TiO_2(110) surface by positron annihilation with core electrons.

When energetic electrons or photons are directed onto solids, they can cause desorption of atoms, molecules, and ions from near the surface region [11]. This phenomenon is referred to as desorption induced by electronic transitions (DIET). DIET is one of the most important processes in surface science that has been actively studied. In the DIET process, which involves both excitation of valence levels and core-hole creation following Auger decay, electronically stimulated desorption may also be caused by positron impact. Desorption via impact ionization by fast positrons is expected to be similar to that by energetic electrons. In contrast, for slow positrons with kinetic energies less than the threshold for electron- and photon-stimulated desorption (ESD and PSD), positron annihilation with electrons is the only possible stimulation process which results in the removal of one electron from the system. In addition, positrons may annihilate with core electrons, although the probability is lower than that for annihilation with conduction or valence electrons. Thus, the positron-induced ionization process leading to ion desorption can be performed using very-low-energy beams. It will provide gentle stimulation and extreme surface sensitivity. Unlike ESD and PSD, which involve an appreciable contribution from bulk excitation due to high-energy electrons and photons and an indirect desorption process caused by secondary electrons from bulk layers [12], positron-stimulated desorption can potentially provide selective information and modification on the topmost atomic layers.

In the present work, we observed ion desorption following slow positron bombardment on a TiO_2(110) surface. The O^+ ions were detected using a modified time-of-flight (TOF) technique. Signals were observed at energies much lower than the threshold for ESD and PSD.

The experiments were conducted using a slow positron generation system with a trochoidal $E \times B$ filter at Tokyo University of Science [13]. A slow positron beam was obtained using a tungsten mesh to moderate the energetic positrons emitted from a ^{22}Na radioactive source. An axial magnetic field generated by a series of Helmholtz coils ($\sim$0.01 T) was used to guide the beam. Before entering a target chamber, positrons were accelerated to the desired energies using an electrostatic acceleration tube.

The target chamber was evacuated to a pressure of approximately 3×10^{-8} Pa. The target, a single crystal of TiO_2(110) (Shinkosha, 15 mm $\times$ 15 mm $\times$ 0.5 mm) was mounted on a Si(110) wafer with a resistivity of 0.02 Ω cm for resistive heating (Fig. 1). The crystal surface was cleaned by repeated annealing cycles at 1000 K. This treatment created color centers and induced a pronounced color change from transparent to dark blue, indicating an increase in the n-type semiconducting property. Every 12 h during the experiment, the target was annealed to remove residual gas adsorbed on the surface.

An electric field perpendicular to the positron beam was applied in front of the target to deflect the ions emitted from the target. The field was created using two parallel square plates of 40 mm length with a separation 40 mm, which were placed along the path of the positron beam with a potential difference of 370 V between the plates. Since the positron beam trajectory was slightly deflected by $\boldsymbol{E} \times \boldsymbol{B}$ drift motion in this region, it was controlled before entering the target chamber using steering coils. After passing though the region, the beam was directed to the target through a hole of 13 mm diameter in the

*tachibana@rikkyo.ac.jp; Present address: Department of Physics, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan.

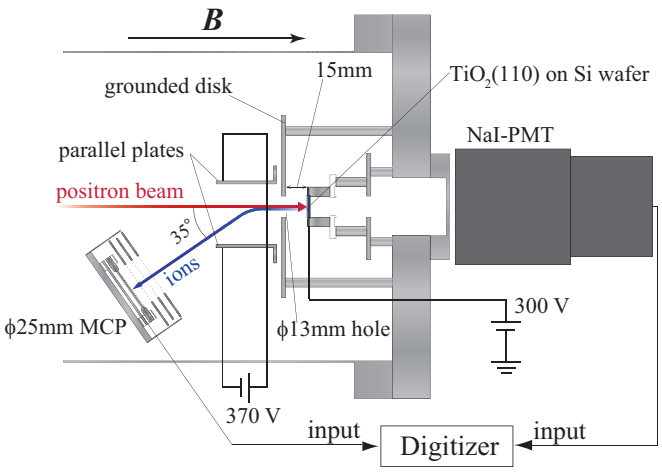

FIG. 1. (Color online) Schematic diagram of the measurement system.

center of a grounded disk. The distance between the disk and the target was 15 mm. The beam diameter at the target position, measured using a microchannel plate (MCP) with a phosphor screen, was 5 mm. A bias voltage of 300 V was applied to the target in order to accelerate ions desorbed from the surface.

The transport energy distributions of the positron beam measured using a retarding field energy analyzer are shown in Fig. 2. The values of E_a are the upper endpoint energies of the distributions. The shape and the intensity of the distributions did not depend on E_a. The energy spread of about 20 eV full width at half maximum (FWHM) is attributed to the characteristics of the mesh moderator and the nonuniform magnetic field, which reduced the longitudinal energy adiabatically. In the ion measurements, the positron beam was decelerated by the target bias of 300 V. Thus, the endpoint energy of the beam onto the target E_i is given by $E_a - 300$ eV.

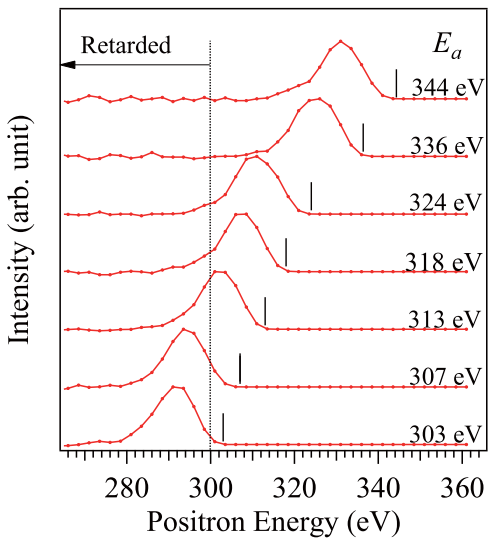

FIG. 2. (Color online) Energy distributions of the positron beam. The vertical solid lines indicate the endpoint energies E_a. The endpoint energies of the positrons onto the target E_i are given by $E_a - 300$ eV.

The positive ions emitted from the target were accelerated to 300 eV and extracted to the region between the parallel plates. This acceleration reduced the relative energy width and provided the smaller emission angle distribution of the desorbed ions, resulting in sufficient mass resolution and signal intensity in the TOF measurements. Although the desorbed ions were forced to spiral around the axial magnetic field due to the Lorentz force, the radius of the spiral motion was correspondingly large since the ions are much more massive. Thus, the accelerated ions were deflected by the electric field between the plates and were directed to another MCP of diameter 25 mm. The MCP was placed at a distance of 127 mm from the target and at an angle of 35° with respect to the beam axis. Annihilation γ rays were monitored by a NaI(Tl) scintillator coupled with a photomultiplier tube (Hamamatsu H6614) mounted downstream of the target. The output pulses from both the NaI(Tl) detector and the MCP were input directly to a personal computer with a built-in high-speed digitizer (National Instruments, NI PCI-5152). The TOF spectrum was obtained through analysis of the time interval between the pulses from the detectors.

Figure 3 shows the TOF spectra of the desorbed ions for several values of E_i between 3 and 44 eV. The spectra were normalized to the intensity of peaks around time 0, which are ascribed to the detection of the annihilation γ rays emitted from the target by the MCP. Another peak at 2.4 μs is clearly observed in each spectrum except that for 3 eV. These peaks are attributed to O^+ ion desorption from the target. The double peaks at 7 and 24 eV may be due to the statistics of the data.

We have also measured the ESD of ions using a pulsed electron gun to ensure the surface cleanliness of the target. Though O^+ ions with small amounts of H^+ ions were observed, which are typical ESD species from a well-prepared clean

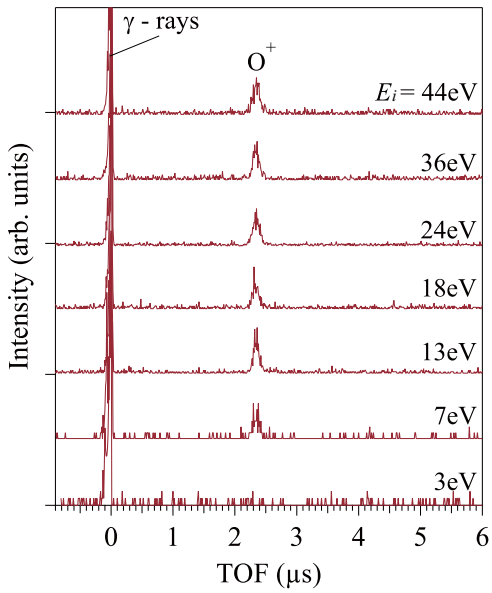

FIG. 3. (Color online) TOF spectra triggered by the emission of annihilation γ rays for positron impact energies between 3 and 44 eV. The spectra are normalized to the intensity of the peaks around time zero.

TiO_2 surface [14], F^+ ions from major contamination were not detected [15].

There are two possible contributions to the electronic excitation process leading to O^+ ion desorption. One is the impact excitation mechanism that occurs in the ESD process and the other is that of positron annihilation with electrons. The most widely accepted model for the DIET process on the TiO_2 surface was proposed by Knotek and Feibelman (KF) [16]. The model is based on their ESD measurements in which the threshold energy correlates with the core-excitation energy of Ti($3p$). In the KF model, the Ti($3p$) core hole created is filled with an electron via an interatomic Auger process from a neighboring O^{2-} lattice ion because there are no higher-lying occupied electronic states in the Ti^{4+} lattice ions. If three electrons escape from the O($2p$) valence orbital as a result of interatomic double Auger decay, the O^+ ion in the lattice desorbs due to Coulomb repulsion between the surrounding Ti^{4+} ions. The PSD of O^+ ions by the excitation involving other deep core levels such as O($1s$), Ti($2s$), Ti($2p$), Ti($3s$), and Ti($3p$) has been reported by Tanaka *et al.* [17]. They suggested that the interatomic charge-transfer process after the metal core excitation is much more efficient for O^+ ion desorption than the interatomic double Auger decay of the KF model. In addition, O^+ desorption by O($1s$) ionization is proposed to be due to a three-hole final state resulting from an intra-atomic double Auger decay [18]. Despite the differences in the charge-exchange processes, these models exhibit the same initial threshold corresponding to excitation of the Ti($3p$) electron at 34 eV and indicate that core-hole creation leads to O^+ desorption.

If positron-stimulated desorption is caused via impact ionization, the desorption threshold is not likely to differ from the value of ESD or PSD, although the ionization cross section of the positron impact near the threshold energy should be smaller than that of the electron impact because of Coulomb repulsion between the incident positrons and the nuclei [19]. The desorption of O^+ ions via the impact ionization process will not occur at positron energies less than the initial threshold of 34 eV. Hence, we conclude that the O^+ ions observed under E_i of 34 eV were desorbed via positron annihilation with electrons on the TiO_2 surface and that annihilation with a core electron is necessary.

It is well known that a fraction of slow positrons incident on metal surfaces lose their energy, diffuse back to the surfaces, and are trapped in the image potential well [20]. A small fraction of the trapped positrons annihilate with core electrons in the topmost atomic layers [6]. In the case of α-SiO_2, positrons are trapped on the surface as physisorbed positronium [21]. If such states exist on the TiO_2 surface, they may contribute to the ion desorption. Auger electrons are expected to be emitted from the surface in coincidence with the desorbed ions. However, these electrons cannot be detected in our experimental setup because the electric field between the target and the grounded disk to accelerate the ions retards the electrons.

Evidence that O^+ ions were desorbed via positron annihilation can be seen in the positron energy dependence of the desorbed O^+ ion yield (Fig. 4). The ESD yield of O^+ ions increases steeply above the threshold of 34 eV [16].

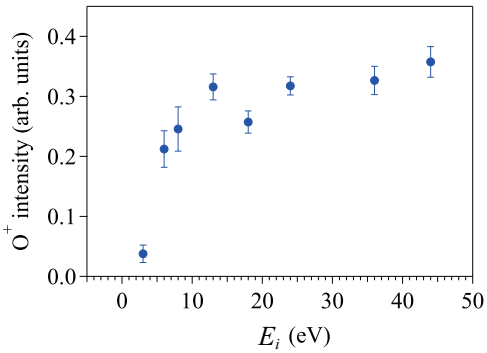

FIG. 4. (Color online) Desorption yields of O^+ ions from the TiO_2 surface plotted against the positron energy onto the surface E_i.

However, the O^+ ion intensities by the positron impact are nearly constant in the range of E_i above 7 eV. This result indicates that the desorption yields reflect the annihilation probability, which does not strongly depend on the positron energy in the range of the present experiments. With respect to the result for $E_i = 3$ eV, most positrons in the energy spread of 20 eV were retarded by the target bias and did not contribute to the ion emission. Hence, the result for $E_i = 3$ eV may be almost originated from the background signal due to accidental coincidences. Indirect ion desorption via surface atom ionization by annihilation γ rays emitted from the target are unlikely because such rays pass through the near-surface layers without any interaction with the atoms.

The probability of O^+ ion desorption via positron annihilation σ can be obtained from the present experiment as

$$\sigma = N_{\text{ion}}/N_{e^+}, \tag{1}$$

where N_{ion} is the total number of desorbed ions and N_{e^+} the total number of incident positrons. In the present measurements for E_i of 24 eV, the coincidence rate for the desorbed O^+ ion with the annihilation γ ray was approximately 7.5×10^{-3} s^{-1} for a count rate of 420 s^{-1} by the NaI detector. The ion-detection efficiency of the MCP for the 300 eV O^+ ion has been reported to be about 10% [22]. Thus, σ is estimated to be 1.8×10^{-4} for O^+ ion desorption from the TiO_2(110) surface.

The probability σ is also given by

$$\sigma = \delta P, \tag{2}$$

where δ and P denote the probability of positron annihilation with core electrons and that of ion desorption after core-hole creation, respectively. The parameter δ depends on the core-level binding energy of the annihilating electrons. Although core-hole creation by positron annihilation with O($1s$), Ti($2s$), Ti($2p$), Ti($3s$), and Ti($3p$) electrons in TiO_2 surface atoms may lead to O^+ desorption [17], theoretical calculations using the local density approximation indicate that the positrons mainly overlap the electrons of the O atoms in the TiO_2 lattice [23]. Hence, assuming O^+ ion desorption is due to positron annihilation with O($1s$) electrons, δ is estimated to be about 0.05% on the basis of the theoretical prediction of annihilation probability for electron binding energies [24]. In PSD measurements on the TiO_2(110) surface, the probability

ratio of O^+ ion desorption after O(1s) ionization and that after Ti(3p) ionization was estimated to be 44% [17]. In general, desorbed ions in the lattice are affected by the reneutralization process via interactions with the surface, which quenches desorption. However, very efficient ESD from the TiO_2(001) surface was recently reported: Desorption probability after Ti(3p) excitation for the O atoms on a pristine surface is implied to be close to unity [14]. The influence of the surface geometric structure on ion desorption from TiO_2(001) and TiO_2(110) by core-hole creation is uncertain, but we can conjecture that P does not differ much from 44%. Thus, σ can be estimated to be 2×10^{-4}, which is consistent with the estimation from the present experiment.

In summary, ion desorption induced by positron annihilation with core electrons has been successfully observed using ion-annihilation γ-ray coincidence TOF spectroscopy.

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