

Comparative Study of Ion Desorption from Clean and Contaminated TiO₂(110) Surfaces by Slow Positron Impacts*

Takayuki Tachibana[†] and Takato Hirayama

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

Yasuyuki Nagashima

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

(Received 31 December 2014; Accepted 13 May 2015; Published 30 May 2015)

We have compared positron-annihilation-induced ion desorption from clean and contaminated TiO₂ surfaces. While O⁺ ions from the clean surface were detected, H⁺ ion desorption was observed for the contaminated surface. These results indicate that positron-stimulated desorption is sensitive to changes in the surface environment.
[DOI: 10.1380/ejsnt.2015.261]

Keywords: Positron spectroscopy; Positron-solid interactions; Desorption induced by electronic transitions (DIET); Electron stimulated desorption (ESD)

I. INTRODUCTION

When energetic electrons impinge on solid targets, they can cause electronic excitation or ionization followed by ion desorption from the near-surface region [1, 2]. This phenomenon is referred to as electron-stimulated desorption (ESD). ESD in various materials has been extensively studied to gain insights into the mechanisms of molecular dissociation and their local binding properties.

Positron impact can also cause ion desorption. When low-energy positrons are incident onto the solids, they rapidly thermalize and diffuse in the bulk [3]. Some of the positrons reach the surface and annihilate there with valence or conduction electrons, producing two photons with the energy of 511 keV. In addition, positrons can annihilate with inner shell electrons of target atoms, and two photons of 511 keV are emitted, although the probability is smaller than that with valence or conduction electrons [4]. Thus, while desorption by energetic positrons is expected to be similar to ESD, slow positron impacts with the kinetic energy less than the ESD threshold lead to the desorption through core-hole creation by positron annihilation with inner shell electrons. This process occurs with low energy positrons yielding gentle ionization, and hence it may provide surface-specific information about the bonding and dynamical behavior of adsorbate molecules. Recently, we observed positron-annihilation-induced O⁺ ion desorption from a clean TiO₂ surface [5]. The O⁺ ions were detected employing a modified time-of-flight (TOF) technique. A peak attributed to O⁺ ion desorption was observed clearly even in the energy range below ESD threshold. In the present work, we have observed ion desorption from a contaminated TiO₂ surface and compared it with that from a clean surface.

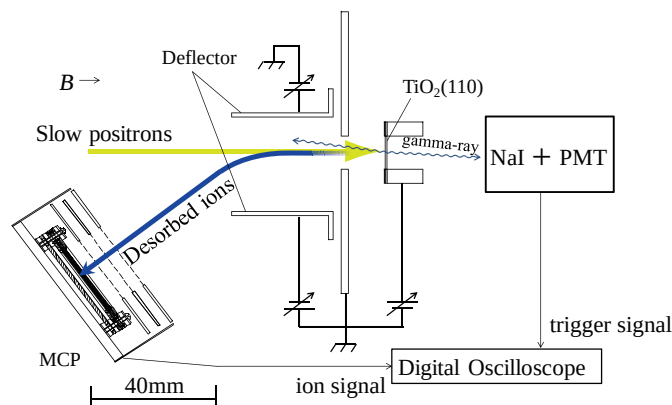


FIG. 1. Schematic of the TOF measurement system.

II. EXPERIMENTAL

The experimental system used was a magnetically-guided slow positron beam apparatus at Tokyo University of Science [6]. A slow positron beam was obtained by using a ²²Na positron source and an electro-polished tungsten mesh moderator.

The slow positrons were accelerated to 310 eV with a 20 eV FWHM energy spread and guided by an axial magnetic field (~0.01 T) to the target in an experimental chamber. The base pressure of the chamber was 3×10^{-8} Pa. The target employed was a TiO₂(110) single crystal, with dimensions 15 mm × 15 mm × 0.5 mm, mounted on a Ta foil for resistive heating. The clean TiO₂ surface was prepared by repeated annealing cycles at 1000 K and the contaminated TiO₂ surface was by poor annealing. The target was held at room temperature in TOF measurements.

Figure 1 shows schematically the TOF measurement system used in this experiment. Two parallel plates (40 mm × 40 mm) were placed along the path of the positron beam. After passing between these plates, the positron beam was directed towards the target. A bias voltage of 300 V was applied to the target. Incident positrons on the

* This paper was presented at the 7th International Symposium on Surface Science, Shimane Prefectural Convention Center (Kunibiki Messe), Matsue, Japan, November 2-6, 2014.

[†] Corresponding author: tachibana@rikkyo.ac.jp

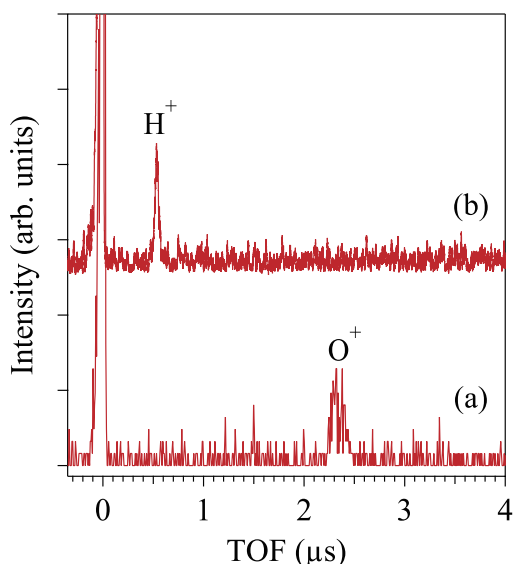


FIG. 2. TOF spectra of desorbed ions from (a) the clean TiO_2 surface and from (b) the contaminated TiO_2 surface by poor annealing. Positron impact energy is 10 eV.

target were decelerated to 10 eV by a potential difference between the target and a grounded disk placed in front of the target. Positive ions emitted from the target were accelerated to 300 eV.

The accelerated ions were deflected by the electric field between the parallel plates and then directed towards a 25 mm diameter micro channel plate (MCP). Although the ions undergo cyclotron motion around the guiding magnetic field lines, the cyclotron radius for the ions is correspondingly large, and the effect of the magnetic field on the ion trajectory was small. The MCP was placed at an angle of 35° with respect to the beam axis. The annihilation γ -rays were monitored by a NaI(Tl) scintillator coupled to a photomultiplier tube (HAMAMATSU, H6614) mounted downstream of the target. The output signals from both the MCP and the NaI(Tl) detector were recorded with a digital oscilloscope (Lecroy, WaveRunner 64Xi-A).

III. RESULTS AND DISCUSSION

Figure 2 shows the TOF spectra of desorbed ions from the clean TiO_2 surface and from the contaminated TiO_2 surface. The impact positron energy was 10 eV. The peak near time zero is due to detection of the annihilation γ -

rays emitted from the targets by the MCP. In the ESD from the clean TiO_2 surface, the desorption threshold of O^+ ions was reported to be 34 eV [7, 8]. Thus, this peak shows the desorption of O^+ ions induced via positron annihilation with core-electrons of TiO_2 surface [5].

Another peak at $0.5 \mu\text{s}$ is seen in the spectrum of the desorbed ions from the contaminated target. This peak is attributed to H^+ ion desorption. The H^+ ion is thought to be desorbed from chemisorbed water molecules which are the main residue in the UHV chamber. For the ESD from water chemisorbed on the TiO_2 surface, desorption of H^+ ions were also found. Their thresholds were 21 eV and 32 eV, respectively [9, 10]. This desorption was explained by the breaking of the OH bond of the Ti–OH species [8]. Hence, the peak shown in FIG. 2(b), which was obtained by the energy lower than these thresholds, indicates that positron-electron pair annihilation leads to the ionized dissociation of the OH bond and desorption of H^+ ions. Ionization of Ti–OH species may also lead to the desorption of OH^+ ions and O^+ ions [9, 10]. However, these peaks were not observed in the present experiment.

Signals of the positron-annihilation-induced ion desorption are sensitive to surface contaminations and top-most surface environment. This method can provide selective information on the topmost atomic layers.

IV. CONCLUSION

Positron-stimulated ion desorption from a TiO_2 (110) surface was observed using an ion-annihilation γ -ray coincidence TOF measurement system. While O^+ ions from the clean surface of TiO_2 were detected, H^+ ion desorption was only observed for the contaminated surface. Understanding of the positron stimulated desorption mechanism will enable the investigation of new approaches to surface analysis.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 23750023), a Grant-in-Aid for Scientific Research (S) (No. 24221006) from Japan Society for the Promotion of Science and in part by a grant by MEXT-Supported Program for the Strategic Research Foundation at Private Universities (No. S0901029) from the Ministry of Education, Culture, Sports, Science and Technology, Japan).

- [1] T. Madey, *Surf. Sci.* **299/300**, 824 (1994).
- [2] O. Dulub, M. Batzill, S. Solovev, E. Loginova, A. Alchagirov, T. E. Madey, and U. Diebold, *Science* **317**, 1052 (2007).
- [3] P. J. Schultz and K. G. Lynn, *Rev. Mod. Phys.* **60**, 1988 (1988).
- [4] K. O. Jensen and A. Weiss, *Phys. Rev. B* **41**, 3928 (1990).

- [5] T. Tachibana, T. Hirayama, and Y. Nagashima, *Phys. Rev. B* **89**, 201409(R) (2014).
- [6] Y. Nagashima, T. Hakodate, A. Miyamoto, K. Michishio, and H. Terabe, *J. Phys. Conf. Ser.* **194**, 012039 (2009).
- [7] M. L. Knotek and P. J. Feibelman, *Phys. Rev. Lett.* **40**, 964 (1978).
- [8] S. Tanaka, K. Mase, and S. Nagaoka, *Surf. Sci.* **572**, 43 (2004).
- [9] M. L. Knotek, *Surf. Sci.* **101**, 334 (1980).
- [10] M. L. Knotek, *Surf. Sci.* **91**, L17 (1980).