Experimental and computational studies of positron-stimulated ion desorption from TiO\(_2\)(1 1 0) surface

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Keywords: positrons, ion desorption, density functional theory (DFT)

Abstract

Experimental and computational studies of the positron-stimulated O\(^+\) ion desorption process from a TiO\(_2\)(1 1 0) surface are reported. The measured data indicate that the O\(^+\) ion yields depend on the positron incident energy in the energy range between 0.5 keV and 15 keV. This dependence is closely related to the fraction of positrons which diffuse back to the surface after thermalization in the bulk. Based on the experimental and computational results, we conclude that the ion desorption via positron-stimulation occurs dominantly by the annihilation of surface-trapped positrons with core electrons of the topmost surface atoms.

1. Introduction

When electrons impinge on solid surfaces, they can cause electronic excitation or ionization followed by ion desorption from the topmost surfaces [1–6]. This phenomenon, called electron-stimulated ion desorption (ESID), has been extensively studied for many years.

Recently, we have observed positron-stimulated O\(^+\) ion desorption from TiO\(_2\)(1 1 0) surfaces [7–10]. The results indicated that the O\(^+\) ion desorption efficiency via positron-stimulation is almost constant in the energy range between 10 eV and 500 eV and one order of magnitude higher than that from electron impact at 500 eV [10]. In order to understand the details of this phenomenon, it is important to investigate the relationship between ion desorption and positron behaviour over a wider range of positron incident energy than the previous work.

In the present paper, we report the results of experimental and computational studies of positron-stimulated ion desorption from a TiO\(_2\)(1 1 0) surface. We have measured the positron incident energy dependence of the O\(^+\) ion yields and positron annihilation Doppler-broadening from rutile-TiO\(_2\)(1 1 0) surfaces in the energy range 0.5–15 keV. The Doppler-broadening of the 511 keV \(\gamma\)-rays reflects the momentum distributions of the positron-electron pairs at the instant of their annihilation. We have also calculated a positron state at the rutile-TiO\(_2\)(1 1 0) surface using the framework of two-component density functional theory (TC-DFT) in order to understand positron behaviour at the surface.

2. Experimental procedure

The experimental system used in the present study was the same as that in the previous work except for the S-parameter measurement system [7–10]. Briefly, a slow positron beam was obtained by using a \(^{22}\)Na positron source and an electro-polished tungsten mesh moderator. The experiments were carried out in a UHV chamber with a base pressure of 3 \(\times\) 10\(^{-8}\) Pa. The energy of the positrons incident on the sample, \(E_\text{e}\), was varied from 0.5 keV to 15 keV. The sample, a commercially obtained rutile-TiO\(_2\)(1 1 0) single crystal (Shinkosha), of dimensions 15 \(\times\) 15 \(\times\) 0.5 mm\(^3\), was mounted on a Si wafer with a resistivity of 0.02 \(\Omega\) \(\cdot\) cm for resistive heating. A clean surface was prepared by annealing at 900 K in oxygen of \(\sim\)1 \(\times\) 10\(^{-4}\) Pa following a repeated annealing cycle at 1200 K in UHV. After this procedure, the surface becomes n-type semiconductor. The ion desorption yields and annihilation \(\gamma\)-ray spectra were measured for each value of \(E_\text{e}\) in a short time interval (600 s) and this was repeated several times to obtain statistically sufficient data.

The ion desorption from the TiO\(_2\) surface by positron impact was observed using a time-of-flight (TOF) technique. On applying a bias of 300 V to the sample, the desorbed positive ions were accelerated by the potential...
difference between the sample and the grounded disc in front of the sample and detected by a microchannel plate (MCP) placed at a distance of 127 mm from the sample. The annihilation $\gamma$-rays were monitored by a NaI(Tl) scintillation detector coupled to a photomultiplier tube (Hamamatsu H6614-70) placed behind the sample. The TOF spectra were obtained by measurement of the time interval between the signals from both detectors.

The Doppler-broadened $\gamma$-ray energy spectra were measured using a Ge detector with 20% relative efficiency connected to a multichannel analyser (MCA). The energy resolution of the Ge detector was 1.1 keV (FWHM) at 512 keV. The Doppler-broadening of the annihilation line shape is characterized by $S$-parameters, which are the counts in a narrow region around the 511 keV $\gamma$-ray peak divided by the total counts.

3. Experimental results

Figure 1 shows the TOF spectra of desorbed ions from a clean TiO$_2$(1 1 0) surface for positron incident energies of 0.5 keV, 3.0 keV, 5.0 keV and 15 keV. These spectra have been normalized to the number of incident positrons obtained from the count rate of the NaI(Tl) scintillation detector. Two peaks are observed at 0 and 2.4 $\mu$s. The large peak at time zero is due to the detection of positron annihilation $\gamma$-rays emitted from the sample by the MCP. The other peak, at 2.4 $\mu$s, is ascribed to O$^+$ ion desorption from the sample surface. As clearly seen in figure 1, the O$^+$ ion signal decreases with increasing $E_{\text{c.e.}}$.

Figure 2 shows the O$^+$ ion yields plotted against $E_{\text{c.e.}}$. The yields of O$^+$ ions were obtained from the integrated area of the O$^+$ ion peak in the TOF spectra by fitting it with the sum of a Gaussian function and a background. The O$^+$ ion yields were found to decrease monotonically in the energy range between 0.5 keV and 15 keV. In previous work, the O$^+$ ion yields were reported to be almost constant in the energy range between 10 eV and 500 eV [10], which was too narrow to reveal this energy dependence. The present data suggest that the O$^+$ ion desorption is closely related to the fraction of positrons which diffuse back to the surface as discussed in more detail in section 6.

Figure 2 also shows the $S$-parameters plotted against $E_{\text{c.e.}}$. As seen in figure 2, the $S$-parameters show a similar tendency to the O$^+$ ion yields, indicating that the O$^+$ ion yields are highly correlated with the $S$-parameters. Usually, $S$-parameters depend on the positron annihilation sites, i.e. in the bulk, at the surface, or in vacuum as self-annihilation of para-positronium emitted from the surface. We have estimated the yields of re-emitted positrons and emitted positronium atoms from the same surface to be almost zero within statistical errors using the method described in another work [11]. Thus, the increase of the $S$-parameters at low positron incident energy is attributed to the annihilation of surface-trapped positrons [12–15].

4. Computational detail

The present experimental results suggest that positron-stimulated ion desorption is closely related to positron diffusion in the bulk and capture to a surface state (see section 3). In the present work, we have carried out the calculation of a TC-DFT conventional scheme [16] using ABINIT code [17] within plane-wave basis sets and a projector-augmented wave method [18] framework. The rutile-TiO$_2$(1 1 0) surface was represented by a periodic structure with a thick vacuum.

For the electron calculations, the kinetic energy cut-off was 550 eV. The number of k-point sampling was $12 \times 6 \times 1$. The generalized-gradient approximation functional [19] was used for the exchange-correlation energy and potential. Cell optimization was done for rutile-TiO$_2$ and the lattice constants $a = b = 4.630$ Å and $c = 2.982$ Å were used for constructing the surface slab. The structure optimization without positrons was carried out for the slab until all the forces acting on the atoms became smaller than $5.0 \times 10^{-5}$ Ha/bohr.

For the positron calculations, the wave function was also represented by plane-wave basis sets and the kinetic energy cut-off was the same as that of the electronic system. Only the $\Gamma$-point ($k = 0$) was chosen in the k-point sampling. The local density approximation functional [20] was used for the positron-electron correlation energy and potential. The corrugated mirror model [21–23] (CMM) was adopted to represent the positron surface potential precisely. In the CMM, asymptotic behaviour of the image potential, $V_{\text{im}}(z)$, is adapted to the positron-electron correlation potential in the vacuum region. Since rutile-TiO$_2$ is a band-gap material, $V_{\text{im}}(z)$ is modified by the imperfect screening effect of semiconductors [24, 25]. Therefore, $V_{\text{im}}(z)$ at the semiconductor surface in CMM is represented by

$$V_{\text{im}}(z) = -\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 1/4(z - z_{\text{im}})} \varepsilon_1 \left( z > z_{\text{im}} \right),$$

where the z-axis is perpendicular to the surface. $z_{\text{im}}$ and $\varepsilon_1$ denote a position of effective image-plane and high-frequency dielectric constant, respectively. In the present study, a theoretical value of $\varepsilon_\infty = 6.31$ was used.\[1\]

\[1\] Theoretical value of $\varepsilon_\infty$ was determined by using many-body GW approximation, which solves band-gap problem [26]. The obtained dielectric constants $a = b = 5.97$ and $c = 7.00$ were averaged for each direction and the averaged value $\varepsilon_\infty = 6.31$ was used for constructing $V_{\text{im}}(z)$.\[1\]
5. Computational results

We have determined the electron and positron work functions ($\Phi_-, \Phi_+$) and positronium affinity ($\Phi_{Ps}$, expressed as $\Phi_{Ps} = \Phi_- + \Phi_+ - 6.8$ eV) using surface electron and bulk positron states (details of the determination for these values are described in the previous study [22]). The results of $\Phi_-$, $\Phi_+$ and $\Phi_{Ps}$ at the TiO$_2$(1 1 0) surface are 7.24 eV, 0.75 eV and 1.19 eV, respectively. These values indicate that positrons and positronium atoms cannot be emitted from the surface because $\Phi_+$ and $\Phi_{Ps}$ are positive. This is consistent with the present experimental results (see section 3).

Figures 3(a) and (b) show the positron density distribution and laterally averaged Kohn–Sham potential for positrons, $V_+(z)$, at the surface, respectively. As can be seen in figure 3(a), the positron density distribution is highly localized at the surface due to the existence of the image potential well displayed in figure 3(b). The positron binding energy, $E_b$, at the TiO$_2$(1 1 0) surface is 2.97 eV, which is greater than $\Phi_+$. This indicates that thermalized positrons which diffuse back to the surface can be trapped by the surface induced image potential.

6. Discussion

The O$^+$ ion yield is almost constant in the energy range between 10 eV and 500 eV [10] and decreases gradually with $E_e$ above 500 eV, as shown in figure 2. If we assume that the O$^+$ ion desorption is caused by positron impact inner shell excitation, the yield curve should show more complicated structures such as those observed in ESID
[1–6], where the desorption relates to electronic excitation at the surface and the yield strongly depends on the electron incident energy. Thus, the present data cannot be explained by the positron impact inner shell excitation model.

When slow positrons impinge on solid targets, they lose their kinetic energy until thermalized in the bulk and a significant fraction of them diffuse back to the surface. Figure 3(a) shows the positron density distribution at the surface, indicating that thermalized positrons can be trapped and localized at the surface. A small fraction of them annihilate with core electrons of the topmost surface atoms [27]. The removal of core electron by this process is thought to contribute to the O$^+$ ion desorption. In this case, the shape of the O$^+$ ion yield curve should be reflected by the fraction of positrons which diffuse back to the surface. We have analysed the data by using a positron stopping profile and positron diffusion model in the bulk as described below. The positron stopping profile, $P(z)$, is given by [28]

$$P(z) = \frac{mz^{m-1}}{z_0^m} \exp \left[-(z/z_0)^m\right],$$

(2)

where $m$ is the shape parameter and $z_0$ is the depth-related constant as

$$z_0 = \frac{\pi(E_{e+})}{\Gamma(1 + (1/m))},$$

(3)

$E_{e+}$ is the positron incident energy and $\pi(E_{e+})$ is the average positron stopping depth. $\pi(E_{e+})$ can be written as [29, 30]

$$\pi(E_{e+}) = AE_{e+}^{1.6},$$

(4)

where $A$ is a constant given using the mass density of the solid, $\rho$, as

$$A = \frac{40 \text{ nm} \cdot \text{keV}^{-1.6} \cdot \text{g} \cdot \text{cm}^{-3}}{\rho}.$$  

(5)

The fraction of positrons which diffuse back to the surface, $f_i(E_{e+})$, is given by

$$f_i(E_{e+}) = \frac{1}{1 + (E_{e+}/E_0)^{1.6}},$$

(6)

where $E_0$ is the positron incident energy at which half of the entered positrons return to the surface. If O$^+$ ions are desorbed through this process, the fraction of the O$^+$ ion desorption, $f_{O^+}(E_{e+})$, is written as

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**Figure 3.** (a) Contour map of positron density distribution at the surface. A colour bar for positron density distribution is shown on the right side of the contour map. The position of the contour plane passes through that of the outermost O atom. Light blue and red balls represent Ti and O atoms, respectively. (b) Laterally averaged Kohn–Sham potential, $V_+(z)$, for the positron at the surface. $z = 0$ and $V_+(z) = 0$, respectively, indicate the position of the outermost O atom and vacuum level.
\[ f_{O^+}(E_{e^+}) = \frac{f_0}{1 + (E_{e^+}/E_0)^{1.6}}, \]  
\[ S(E_{e^+}) = S_b + \frac{S_s - S_b}{1 + (E_{e^+}/E_0)^{1.6}}, \]

where \( f_0 \) is the \( O^+ \) is the fraction of the \( O^+ \) ion desorption for positrons at the surface. Thus, the value of the \( S \)-parameter, \( S(E_{e^+}) \), is written as \( S(E_{e^+}) = S_b + \frac{S_s - S_b}{1 + (E_{e^+}/E_0)^{1.6}} \), \( (7) \)

where \( S_b \) and \( S_s \) are the \( S \)-parameters for the positrons which annihilate in the bulk and at the surface, respectively.

The solid curves shown in figure 2 are from the least square fitting of equations (7) and (8) to the measured data. These curves are in a good agreement with the data. Therefore, the results of the present work indicate that the \( O^+ \) ion desorption via positron-stimulation is mainly caused by the removal of core electrons by the annihilation of surface-trapped positrons.

7. Conclusion

We have performed experimental and computational studies for positron-stimulated ion desorption from TiO\(_2\)(1 1 0) surfaces to investigate the relationship between ion desorption and positron behaviour near the surface. We have found that thermalized positrons can be trapped and localized at the TiO\(_2\)(1 1 0) surface. The results of the present work indicate that the ion desorption via positron-stimulation occurs dominantly by the annihilation of surface-trapped positrons with core electrons of the topmost surface atoms.

Acknowledgments

We thank Luca Chiari, Takato Hirayama, Masaru Nagira and Hisakuni Yabuki for valuable discussions and suggestions. This work was supported by JSPS KAKENHI Grant Numbers 24221006, JP16K05483, 23750023, 16K21424 and 17H01024. One of the authors (TT) acknowledges financial support by the Nippon Sheet Glass Foundation for Materials Science and Engineering. Parallelized calculations were performed on the supercomputers of the Institute for Solid State Physics, The University of Tokyo.

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Mater. Res. Express 4 (2017) 116303

T Yamashita et al
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