

XPS and STM study of TiO₂(110)-(1 × 1) surfaces immersed in simulated body fluid



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ABSTRACT

Rutile titanium dioxide (TiO₂) (110)-(1 × 1) surfaces prepared in ultrahigh vacuum (UHV) were removed from the UHV, immersed in Hank's buffered salt solution (HBSS), and then re-introduced to the UHV to be examined for an atomic-level study of the osteoconductivity of TiO₂. X-ray photoelectron spectroscopy (XPS) showed the adsorption of phosphate ions and divalent Ca ions from the HBSS. The density of the phosphate ions increased with the immersion time for up to 1 min and remained constant with further immersion time up to 1 week. Unlike in the case of the phosphate ions, the density of the Ca ions decreased with the immersion time after reaching the maximum value at 1 min immersion. Consequently, calcium phosphate was not formed on the (1 × 1) surface in the 1-week immersion. Scanning tunneling microscopy revealed molecule-sized spots covering the surfaces immersed for 1 min and longer. On the basis of density analysis by XPS, the spots were hypothesized to represent phosphate ions. Phosphate ions on the (1 × 1) surface are unable to undergo arrangement needed to facilitate the epitaxial growth of the brushite.

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1. Introduction

Osteoconductivity is the ability for the materials to bond to bones. Implants bond to bones via the hydroxyapatite layer. This process is characteristic of Ti and its alloys, which are unique materials for replacement implants [1]. Ti-based materials are naturally coated with an oxide layer. Hence, titanium oxide is responsible for the osteoconductivity of the Ti-based materials. Hydroxyapatite is generally known to form via the calcium phosphate precursor phase, but the type and formation mechanism of the calcium phosphate have not been fully explained [2]. Clarifying the process of calcium phosphate formation would thus aid in identifying the origin of the osteoconductivity and hence allow the enhancement of the rate and/or strength of the implant–bone bonding.

Ad-species from a body fluid have been investigated by immersing titanium dioxide (TiO₂) in simulated body fluids, which are simulated balanced electrolyte solutions with ion concentrations similar to those of human plasma. Hanawa et al. examined calcium phosphate layers formed on TiO₂ films covering Ti plates [3,4]. X-ray photoelectron spectroscopy (XPS) analysis revealed a higher concentration of hydrogen phosphate ions (HPO₄²⁻) in the calcium phosphate layer at its initial stage of growth. The authors proposed that the adsorption of the hydrogen phosphate ions and subsequent uptake of the Ca ions by the adsorbed hydrogen phosphate ions initiate the formation of calcium phosphate. The high ratio of hydrogen phosphate ions in the calcium phosphate

layer agrees with the results of secondary-ion mass spectroscopy reported by Chusuei et al. [5]. In this study, the authors examined the ratios of the PO₃⁻ and PO₂⁻ ions that reflect the composition of the calcium phosphate and concluded that dicalcium phosphate dihydrate (CaHPO₄·2H₂O), known as brushite, is a predominant form of calcium phosphate on the TiO₂ films. On the basis of results of depth analysis by Auger electron spectroscopy, the authors propose Ca-mediated bridging between O atoms of the surface and of hydrogen phosphate ions. Kokubo et al. reported that acid treatment followed by air-annealing results in a positively charge of the Ti plates and the promoted formation of hydroxyapatite thereon [6]. According to their model, the positively charged TiO₂ surface attracts phosphate ions (PO₄³⁻), which then lead to a negative charge of the TiO₂ surface and to the attraction of Ca and thus formation of amorphous calcium phosphate.

An atomically well-defined TiO₂ surface is expected to highlight the effect of microscopic surface structures on calcium phosphate formation. The (110) surface of rutile TiO₂ exhibits such a well-defined structure after sputter-anneal cleaning in ultrahigh vacuum (UHV) [7]. Fig. 1 shows the model of the clean (110) surface with a (1 × 1) structure corresponding to a simple truncation of the bulk crystal [8]. Oxygen atoms that bridge two Ti atoms, known as bridging O atoms (O_b atoms), form protruding rows along the [001] direction. Some of the O_b atoms are part of OH groups (OH_b groups), and some are missing (O vacancies) [9]. The OH_b groups are formed by the dissociation of residual H₂O

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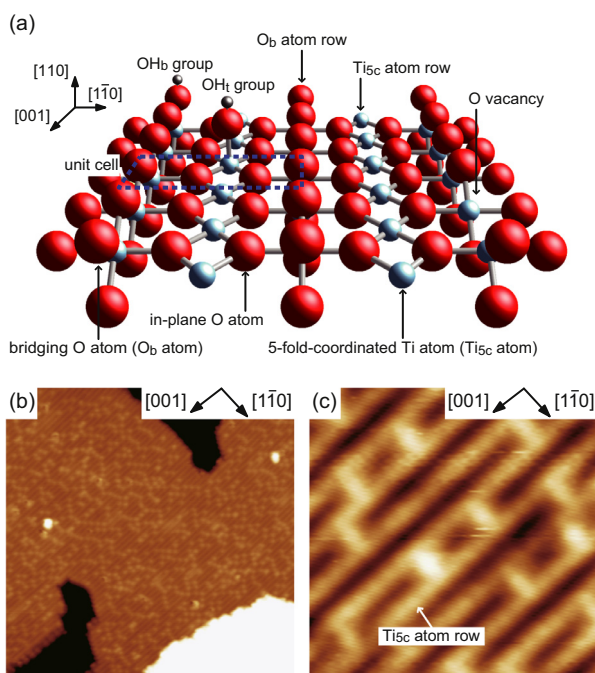


Fig. 1. (a) A ball-and-stick model of the $\text{TiO}_2(110)-(1 \times 1)$ surface. Light-blue balls and red balls represent Ti atoms and O atoms, respectively. The smallest gray balls bound to the O atoms represent H atoms. The OH_t group terminating the Ti_{5c} atom is added for reference. The unit cell indicated by the dotted line has dimensions of $0.30 \text{ nm} \times 0.65 \text{ nm}$. (b,c) STM images of the (1×1) surface. Scan sizes are (b) $40 \text{ nm} \times 40 \text{ nm}$ and (c) $5 \text{ nm} \times 5 \text{ nm}$. Sample bias voltage, $+1.4 \text{ V}$; tunneling current, 0.2 nA . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

molecules in the UHV chamber. At the troughs between the O_b atom rows, Ti atoms coordinated to five O atoms (Ti_{5c} atoms) are exposed. Oxygen atoms surrounding the Ti_{5c} atoms are called in-plane O atoms. The OH_t group is another type of OH group terminating the Ti_{5c} atom. It forms via the reaction of the OH_b group with O adatom (O_a atom) [10] and is absent on the (1×1) surface prepared in the UHV.

Fig. 1b and c show empty-state images of the (1×1) surface obtained by UHV-scanning tunneling microscopy (STM). The surface consists of flat terraces separated by monatomic steps 0.33 nm high. The bright lines along the $[001]$ direction correspond to the Ti_{5c} atom rows, and the short lines bridging the adjacent Ti_{5c} atom rows along the $[1\bar{1}0]$ direction are either OH_b groups or O vacancies. It is impossible to classify the short lines in Fig. 1c into either OH_b groups or O vacancies. The image height difference between them is $\sim 0.03 \text{ nm}$ even in optimized imaging conditions [9]. In separate experiments, we determined the densities of the OH_b groups and the O vacancies prepared by the method in this study to be $\sim 0.3 \text{ nm}^{-2}$ and $\sim 0.03 \text{ nm}^{-2}$, respectively [11,12]. Hence, most of the short lines in Fig. 1c represent OH_b groups. The (1×1) structure has been recently found to be retained in humid environments such as laboratory air and water [13].

In this work, we examined ad-species from the Hank's buffered salt solution (HBSS), a commonly used simulated body fluid, on the $\text{TiO}_2(110)-(1 \times 1)$ surface. We found that the phosphate ions and the Ca ions adsorbed on the (1×1) surface and that calcium phosphate did not form after 1-week immersion. The non-formation of the calcium phosphate disagrees with the commonly known osteoconductivity of TiO_2 and suggests that the osteoconductivity is sensitive to the atomic-scale structure of the TiO_2 surface.

2. Experimental methods

Surface cleaning and microscope experiments were conducted using a commercial UHV-STM system (JSPM4500S, JEOL). The system is com-

posed of the microscope chamber and the sample preparation chamber. The microscope chamber includes an STM stage, and the sample preparation chamber is equipped with an Ar^+ sputtering gun (EX03, Thermo) and low-energy electron diffraction (LEED) optics (BDL600, OCI). The base pressure of the chambers was $2 \times 10^{-8} \text{ Pa}$. The view ports of the chambers were shaded unless it was necessary to view the inside.

Mirror-polished TiO_2 wafers ($7 \text{ mm} \times 1 \text{ mm} \times 0.3 \text{ mm}$, Shinkosha) were clamped on a Si wafer that was used as a resistive heater. The surface was cleaned by cycles of sputtering with Ar ions and annealing. The ion beam energy, sample current, angle of the incident beam with respect to the surface normal, and time of the sputtering, respectively, were 2 keV , $0.5 \mu\text{A}$, 45° , and 1 min . The temperature and time for the annealing were 1173 K and 1 min , respectively. The temperature was monitored at the side faces of the wafers by an infrared thermometer. Hence, the temperature of the TiO_2 surface was probably lower than the monitored temperature because of incomplete contact between the TiO_2 and Si wafers. The wafers with the (1×1) surface were yellowish white, similar to the as-purchased wafers, but they were also very slightly bluish, indicating that the wafers were almost stoichiometric.

The cleaned TiO_2 wafers were cooled to room temperature, removed from the sample preparation chamber, and immersed in 100 mL of HBSS (with Ca and Mg and without phenol red; Nacalai Tesque). The perfluoroalkoxy alkane container for the HBSS was shaded and was placed at room temperature. The pH of the HBSS was ~ 7.0 and increased to ~ 7.6 after 1 day of preservation in the container, regardless of the presence or absence of the TiO_2 wafer. For the 1 week immersion, the HBSS was exchanged every day. After immersion, the TiO_2 wafers were rinsed with Milli-Q water for 1 min and re-introduced to the STM system. Empty-state STM images were acquired in constant-current mode at room temperature. Electrochemically etched W wires were used as a probe.

XPS analysis was performed at room temperature using a commercial instrument (Axis Ultra DLD, Kratos). The base pressure of the system was $6 \times 10^{-7} \text{ Pa}$. The TiO_2 wafers were removed from the STM system, placed in a shaded container, and transferred in laboratory air to the XPS system. A monochromatic Al $K\alpha$ line was used as an excitation source. Charging of the TiO_2 surfaces was reduced by a low-energy electron neutralizer. The photoelectron emission angle θ with respect to the perpendicular line on the surface was set to 0° . The pass energy of the analyzer and the energy step were 160 and 1.0 eV for wide scans, respectively, and 20 and 0.1 eV for narrow scans, respectively. The binding energy of the spectra was calibrated such that the Ti $2p_{3/2}$ peak from Ti atoms in a bulk TiO_2 crystal was 459.1 eV . With this calibration, the O $1s$ peak from O atoms in a bulk TiO_2 crystal (O_{bulk} atoms) was corrected to 530.3 eV . The spectra were deconvoluted into mixed Gaussian–Lorentzian curves (70:30) following Shirley-type background subtraction.

3. Results and discussion

A wide-scan XPS spectrum of the control, a (1×1) surface immersed in Milli-Q water for 1 day, is shown in Fig. 2 (spectrum (a)). The intense peaks at ~ 460 and $\sim 530 \text{ eV}$ are Ti $2p$ and O $1s$ peaks, respectively. Ar and C peaks were also detected. The residue from sputtering explain the Ar atoms, and the C atoms result from the adventitious contaminants. Spectrum (b) was obtained using the (1×1) surface that was immersed in HBSS for 1 day. In addition to the Ti, O, Ar, and C peaks, Ca and P peaks were observed. Elements other than P and Ca included in the HBSS, such as Cl, Mg, S, K, and Na, were not detected, consistent with previous studies [3,4].

Fig. 3 shows the narrow-scan spectra of the (1×1) surfaces that were immersed in either Milli-Q water or HBSS. The vertical scales of the spectra were normalized with respect to the height of the Ti $2p_{3/2}$ peak in each set of spectra. Spectra (a) were obtained from the surface that was immersed in Milli-Q water for 1 day. The O $1s$ spectrum shows an intense peak resulting from the O_{bulk} atoms. The shoulder on the high-binding-energy side of the O_{bulk} peak originates from low-coordination O atoms, OH groups, OOH groups, and contaminants [13]. The Ti $2p_{3/2}$ peak

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