

# Water surface coverage effects on reactivity of plasma oxidized Ti films



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## ARTICLE INFO

### Article history:

Received 2 September 2013  
Received in revised form 29 October 2013  
Accepted 29 November 2013  
Available online 11 December 2013

### Keywords:

Thin Ti films  
Water vapor plasma  
Surface reactivity  
TiO<sub>2</sub>

## ABSTRACT

The behavior of the adsorbed water on the surface of thin sputter deposited Ti films maintained at room temperature was investigated in dependence on the thickness of the resulting adsorbed water layer, controllably injecting water vapor into plasma. The surface morphology and microstructure were used to characterize the surfaces of plasma treated titanium films. Presented experimental results showed that titanium films immersed in water vapor plasma at pressure of 10–100 Pa promoted the photocatalytic activity of overall water splitting. The surfaces of plasma oxidized titanium covered by an adsorbed hydroxyl-rich island structure water layer and activated by plasma radiation became highly chemically reactive. As water vapor pressure increased up to 300–500 Pa, the formed water multilayer diminished the water oxidation and, consequently, water splitting efficiency decreased. Analysis of the experimental results gave important insights into the role an adsorbed water layer on surface of titanium exposed to water vapor plasma on its chemical activity and plasma activated electrochemical processes, and elucidated the surface reactions that could lead to the split of water molecules.

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## 1. Introduction

The interest in oxidized titanium surfaces is driven by many technological applications of TiO<sub>2</sub>, ranging from pigments, coatings, electronic devices, implants, gas sensors, photochemical reactions to catalysis. In all of them, the surface properties of oxidized titanium play a crucial role [1].

One of the most important properties of titanium is that it can be easily oxidized and reduced. The oxidation of titanium occurs in different oxidation atmospheres, such as air, oxygen and water vapor even at room temperature. At room temperature, the amorphous very thin (5–10 nm thickness) passive film is formed, which is composed of three layers: the first layer adjacent to metallic titanium is TiO, the intermediary layer is Ti<sub>2</sub>O<sub>3</sub>, and the third layer, in contact with the environment, is TiO<sub>2</sub> which is the most important layer responsible for the interaction with the adsorbate molecules and chemical compounds [2]. The thermal oxidation of titanium in the presence of water vapour proceeds according to a linear-parabolic rate law resulting from a reaction–diffusion mixed regime. The growth of TiO<sub>2</sub> takes place by rapid diffusion of

substitutional hydroxide ions generated at the gas–scale interface [3,4].

The controllability of reducibility of titanium oxides is essential for many applications in heterogeneous catalysis. In many cases, the reduced TiO<sub>2</sub> surfaces exhibit a much higher catalytic activity for water split reactions. One way to reduce the surface of oxidized titanium is to remove surface oxygen atoms. The presence of O vacancies strongly increases the reactivity of the surface resulting in a patchwork of nanoscale domains where hydroxyl groups become adsorbed, which produces the superhydrophilicity [5]. Among the many investigated processes, probably the best-studied surface reaction is the dissociation of water, which has been shown to occur at O vacancies, whereas on the stoichiometric parts of the surface the water molecules stay mostly intact [6]. The *ab initio* calculations dealing with TiO<sub>2</sub> terminated surfaces have demonstrated the outward relaxation of the second-layer O atoms [7].

There are different ways how to reduce the surface of oxidized titanium. The ultraviolet light removes some oxygen atoms from the surface of the titania. In vacuum experiments, O vacancies are easily created either by electron bombardment, ion sputtering, or simply by thermal annealing. It is established [8] that due to bombardment of the oxides by energetic particles oxygen atoms are preferentially removed from the stationary sites of oxide targets and suboxides as well as oxygen deficient surfaces are formed in the steady state. Oxygen vacancy concentrations are typically in

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the order of several percent [9], but it is not possible to remove all surface O atoms. The neutral water molecules arriving to the reduced  $\text{TiO}_2$  surface spontaneously oxidize Ti atoms as follows:  $\text{Ti}_x\text{O}_y + (2x - y)\text{H}_2\text{O} = x\text{TiO}_2 + (2x - y)\text{H}_2$  [4].

The situation becomes more complicated in the environment of water vapor plasma when oxidation and reduction reactions occur simultaneously at the same rate for steady state, and the predictions following classical thermodynamics become questionable. These coatings immersed in plasma are exposed to the fluxes of incident neutral water molecules, wide range of electromagnetic radiation, electron and ion bombardment [10]. Water vapor plasma can supply many radicals and atoms as well as some ions into the surface, and then layers with non-stoichiometric ratio would form on the stoichiometric  $\text{TiO}_2$  layer. Although thermal oxidation of titanium in the mixture of oxygen and water vapor has been investigated extensively, only a few studies on titanium oxidation and reduction in water vapor plasma are available [11,12]. Because of the large numbers of significant variables, the surface properties of samples of partially reduced oxides may be quite different and dependent on the details of the reduction process even for the same degree of reduction.

In order to access the complicated processes at the  $\text{TiO}_2$  surface, methodologically, we begin with the metal surface and study the evolution of titanium oxide phase and changes of surface morphology in dependence on the thickness of an adsorbed water layer, controllably injecting the water vapor into plasma. This study covers the synthesis of titanium oxide film by low-temperature oxidation of titanium immersed in water vapor plasma and explores how the presence of water layer on the surface changes the reactivity of titanium film.

## 2. Experimental technique

Thin Ti films were deposited using magnetron sputtering system onto the crystalline Si (111) substrates (10 mm × 20 mm). A circular magnetron was installed in the vacuum chamber of a PVD-75 model vacuum device. Pure titanium (99.99 at.%) of 76 mm diameter and 3 mm thickness was used as a target material and distanced 35 mm away from substrate holder. Pure argon was used as the sputtering gas. The discharge parameters have been controlled using a variable DC power supply (1 kV, 1 A). Prior the deposition, the target was plasma cleaned. Deposition time was chosen in order to obtain 200–600 nm thick Ti films for sputtering power supply of 300 W (1 A, 300 V). The thickness of the films was measured using nanoprofilometer by revealing the height of the step with an accuracy of ±10 nm.

After Ti film deposition the chamber was evacuated up to  $10^{-3}$  Pa, the vapor of distilled water was injected until steady state pressure was reached. The water vapor was introduced through a nozzle at designated flow rates. The water temperature was regulated using light radiation and the chamber pressure was controlled during the test with a throttle valve.

More reproducible results were obtained under RF power and negative polarization of treated samples. The plasma generator was activated at a power of 200–300 W. The kinetic energy of ions of 10–20 eV was enhanced by the negative bias voltage of 200–300 V. The samples were located on the water cooled cathode of magnetron and the temperature of substrates was always starting at room temperature, rising to 50 °C or less at the end of experiment. Treatment duration varied between 5 and 60 min.

The structure and phase composition of the samples were registered by the Bruker X-ray diffractometer (Bruker D8). The measurements were performed in the range  $2\theta = 20\text{--}70^\circ$  using  $\text{K}\alpha$  radiation of Cu cathode in steps of  $0.01^\circ$ . All X-ray diffraction peaks were indexed using International Centre for Diffraction Data (ICDD)

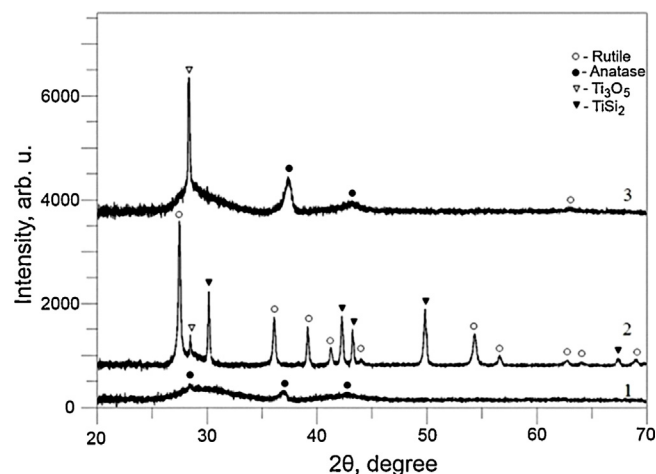


Fig. 1. XRD patterns of Ti films: as deposited – curve 1; and plasma treated at 10 Pa – 2, and at 300 Pa – 3.

current Powder Diffraction File (PDF-2 2006). EVA software used to determine peak positions and intensities and used to search-match or compare with all (or subset/restrictions) of the ICDD PDF-2 database. The surface analyses, chemical analysis and imaging of surface topography before and after water vapour plasma treatment were performed using a Scanning Electron Microscope (SEM, JEOL JSM – 5600) and optical (Nikon Eclipse Lv150) microscopies. The SEM was equipped with an Energy Dispersive Spectrometer (EDS, Bruker Quad 5040). SEM/EDS provides chemical analysis of the field of view. Surface height topography of Ti films was analyzed using the nanoprofilometer (AMBIOS XP 200). The measurements were performed in air at room temperature. The Data Analysis software was used for RMS surface roughness analysis.

## 3. Results

### 3.1. XRD patterns

X-ray diffraction was used to assess the effect of water vapour pressure on the plasma treated Ti film phase composition and crystallite size. Fig. 1 includes XRD patterns of Ti films: as-deposited – curve 1, and plasma treated at water vapor pressure of 10 Pa and 300 Pa – curves 2 and 3, respectively. A very small amount of anatase  $\text{TiO}_2$  embedded in the matrix of amorphous titanium was registered for an as-deposited Ti film (Fig. 1, curve 1). It is difficult to accurately locate the anatase peaks at low levels of crystallinity. The amount of oxidized Ti was observed to increase drastically with the introduction of water vapor at 10 Pa (Fig. 1, curve 2). The registered dominant phases were rutile  $\text{TiO}_2$  and  $\text{TiSi}_2$ . It indicates to the intensive structural and compositional transformations occurring in Ti film and at the interface titanium film/Si substrate immersed in water vapor under plasma radiation. The XRD pattern of Ti film plasma treated at water vapor pressure equal to 300 Pa (Fig. 1, curve 3) shows the presence of small amount of anatase  $\text{TiO}_2$ , and XRD peak corresponding to  $\text{Ti}_3\text{O}_5$  becomes dominant.

The line broadening corresponds to a mean crystallite dimension of 70–120 nm for the rutile  $\text{TiO}_2$  after plasma treatment at the pressure of 10 Pa, and 5–20 nm for the anatase  $\text{TiO}_2$  after plasma treatment at the pressure of 300 Pa, as calculated using the Scherrer formula. The formation of  $\text{TiSi}_2$  (Fig. 1, curve 2) is in agreement with literature data [13].

### 3.2. Optical microscopy

The optical surface views of films treated under different plasma conditions demonstrated general features of water adsorption. The

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