Research Article

Structural and Phase Transformations in Water-Vapour-Plasma-Treated Hydrophilic TiO₂ Films

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Received 23 March 2012; Revised 2 July 2012; Accepted 7 July 2012

Academic Editor: Markku Leskela

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We have investigated structural and phase transformations in water-vapor-plasma-treated 200–300 nm thick Ti films, maintained at room temperature, by injecting water vapor into radio frequency (RF) plasma at different processing powers. Scanning electron microscopy (SEM) combined with optical microscopy and surface nanotopography analysis were used to view tracks of adsorbed water layers and to detect bulges or blisters appeared on the surface of treated samples. Rough surfaces with different size of holes (5–20 μm) through the entire film thickness have been observed. X-ray diffraction results show that the oxidation rate of Ti film drastically increases in the presence of an adsorbed water on the hydrophilic layer. It is assumed that the defining factor which controls oxidation kinetics is the hydroxyl radicals formation.

1. Introduction

Exposition of Ti surfaces in water vapor results in the formation of an adsorbed layer on the surface. Rapid diffusion on the surface maintains quasiequilibrium between the molecules bound to islands and isolated adsorbed water molecules. Water molecules oxidize Ti atoms ($\text{Ti}_x\text{O}_y + (2x - y) \text{H}_2\text{O} = x\text{TiO}_2 + (2x - y) \text{H}_2$). These possible oxidation reactions are highly thermodynamically favorable and form nanostructured hydrated titanium oxide layer [1]. It is known that the thermal oxidation of titanium by water vapor proceeds according to a linear-parabolic rate law resulting from a reaction-diffusion-mixed regime. The growth of TiO₂ takes place by rapid diffusion of substitutional hydroxide ions generated at the gas-scale interface [2].

It is established [3] that the titanium coating exposed to ultraviolet light has the extraordinary property of complete wettability for water. The ultraviolet light removes some of the oxygen atoms from the surface of the titania, resulting in a patchwork of nanoscale domains where hydroxyl groups became adsorbed, which produces the superhydrophilicity. It is proved that the Ti³⁺ ions are closely associated with the hydrophilicity of TiO₂ [4, 5].

Titanium coatings immersed in plasma are exposed to ultraviolet radiation and ion bombardment [6, 7]. Due to

radiation coming from the plasma, oxygen atoms are preferentially removed from the surface of titania and the formation of suboxides as well as an oxygen deficient surface in the steady state is registered [8]. The water molecules arriving at the plasma activated surface due to hydrophilicity tend to spread out over the entire surface, as schematically shown in Figure 1.

Under plasma radiation the split of hydroxyl radicals, resulting from dissociation of water molecules and oxidation of Ti, into their atomic components: hydrogen and oxygen occurs [4]. The hydrogenation of growing titanium oxide TiO₂ takes place [9].

The present paper reports the study of the structural and phase transformations in thin Ti films treated by water vapor plasma in dependence to the surface coverage by hydrophilic layer at different levels of processing power.

2. Experimental Technique

The vacuum 80 L volume stainless steel chamber is equipped with a water inlet valve, which permits the introduction of water vapor from outside the chamber. The Ti samples to be treated are placed onto the water-cooled substrate holder. The reaction chamber is evacuated using a turbomolecular

FIGURE 1: Formation of water layer on the hydrophilic surface: (a) adsorbed water on a plasma nonactivated surface and (b) water layer on a plasma-activated surface.

vacuum pump down to a pressure of about 10^{-3} Pa and then connected to the source of water vapor. Once the steady state of water vapor pressure of about 5 to 10 Pa in the chamber at ambient temperature is reached, the Ti sample is exposed to low-pressure RF plasma. The discharge characteristics have been controlled using a variable RF power supply by changing input power levels from 50 to 300 W. Without an applied axial magnetic field, plasma ionization degree increases linearly with plasma dissipated power. With an axial magnetic field, ionization degree jumps to a maximum value at about 300 W and then saturates. The positive ion density and electron density of the vapor plasma of around $5 \cdot 10^{10} \text{ cm}^{-3}$ and the electron temperature between 1.2 and 1.6 eV were measured by a Langmuir probe at processing power of 300 W. It is in close agreement with the experimental results presented in [6].

The microstructure of the samples was characterized by X-ray diffraction (XRD) method using Bruker diffractometer (Bruker D8). The measurements were performed with 2θ angle in the range 20° – 70° using Cu cathode $K\alpha$ radiation in steps of 0.01° . All X-ray diffraction peaks were indexed using software together with Search-Match function and PDF-2 database from International Centre for Diffraction Data (ICDD). The thickness and surface topography of Ti films were measured using the nanoprofilometer (AMBIOS XP 200). The spatial resolution was several nanometers. The surface views were investigated before and after plasma treatment by the scanning electron (SEM, JEOL JSM-5600) and optical (Nikon Eclipse Lv150) microscopes. The distribution profiles of oxygen in Ti films were measured by Auger Electron Spectroscopy (AES, PHI 700XI). The distribution profiles of hydrogen in Ti films after hydrogenation were measured by Glow Discharge Optical Emission Spectroscopy (GDOES, Spectrums Analytica GmbH).

3. Experimental Results

Water vapor condenses on the hydrophilic Ti surface in plasma surrounding to produce adsorbed water layer. The

distribution and size of water island layers on the surface of thin hydrophilic Ti film surface were investigated by trace analysis of islands on the surface of plasma-treated samples using optical and scanning electron microscopes. It was found that water island layers were randomly distributed on the surface with an average size of about $8 \mu\text{m}$.

Figure 2 includes SEM surface views of plasma-treated Ti films: (a) at 50 W for 60 min and (b) at 300 W for 5 min. We observed that Ti films treated upon lightly ionized water vapor plasma (at RF power equal to 50 W) are homogeneous and smooth (Figure 2(a)). After treatment by highly ionized water vapor plasma (at RF power equal to 300 W), holes throughout the entire film thickness were observed (Figure 2(b)). With an increase in the power dissipation in plasma, the density of holes increased while the mean size remained about the same. The SEM surface view also reveals the circular bumps distributed between the holes (Figure 2(b)).

Figure 3 includes surface height profiles of untreated Ti film (Figure 3(a), curve 1) and plasma treated at 50 W for 60 min (Figure 3(a), curve 2). It was registered that the surface topography, initially flat with a mean roughness of about 2 nm, becomes periodically bumpy with a height amplitude equal to 8 nm and a period equal to $15\text{--}18 \mu\text{m}$ after treatment at 50 W for 60 min. As the output power of the RF power amplifier increased, the surface was subjected to the development of various bumps and blisters. After exposition to the water vapor plasma at 300 W for 5 min, thin film that covered blisters was lifted and film contained randomly distributed small holes throughout the entire film thickness (Figure 3(b)), a process known as “plasma-cut”. The location of the cuts correlates well with the wetted areas on the surface and can be explained by damage-induced in-plane stress and the corresponding elastic out-of-plane strain. We suppose that a rapid uptake of oxygen and hydrogen through the surface areas covered by island layers of adsorbed water occurs and deduces that fast H transients because of their high mobility may be responsible for the high compressive stresses which lead to film surface plastic deformation (50 W, Figure 3(a), curve 2) and detachment in

FIGURE 2: SEM surface views of plasma-treated Ti films: (a) 50 W for 60 min and (b) 300 W for 5 min.

FIGURE 3: Surface height profile of Ti film: (a) untreated (Figure 3(a), curve 1) and plasma treated at 50 W for 60 min (Figure 3(a), curve 2), (b) plasma treated at 300 W for 5 min (Figure 3(b)).

a form of buckling or debonding from the surface of the substrate (300 W, Figures 2(b) and 3(b)).

In all cases, the mean surface roughness increases after plasma treatment. It is in agreement with other observations [10]. In the presented work, it was registered that the mean surface roughness of untreated samples is equal to 2–4 nm. It increases from 24 nm for samples treated at 200 W during 5 min and up to 180 nm for samples treated at 300 W during 5 min. It is established that the dominant technological parameter to the surface roughness is the RF power, while the plasma treatment time has significantly less effect.

Water-plasma-treated hydrophilic Ti films, which had been completely covered by water layer, were subsequently analyzed by XRD technique. Figure 4 includes XRD patterns of untreated (curve 1) and plasma-treated Ti films: curve 2 for 5 min at 200 W, curve 3 for 20 min at 200 W, and curve 4 for 5 min at 300 W. It is seen that phase and structural transformations in metallic Ti depend on the RF power dissipated in the plasma. SEM analysis showed that the Ti films entirely covered by hydrophobic layer were broken and lifted from the substrate after treatment at 300 W for 5 min. It is in agreement with observation of lifting, rupture, and formation of holes for a film covered by water island layers registered by SEM (Figures 2(b) and 3(b)).

Figure 5 includes the distribution profiles of O and H atoms (curves 1 and 2, resp.) in Ti film treated at 200 W for 5 min. The Auger oxygen depth profile (Figure 5, curve 1) shows a sharp decrease of oxygen concentration from 75 at. % at the surface followed by a gradual decrease through the entire film thickness in the bulk to the values around the maximum solubility of oxygen in titanium (34 at. %), while H atoms are homogeneously distributed over the estimated film thickness of about 500 nm (Figure 5, curve 2) except the sharp increase near the surface where the mobile H atoms are trapped at radiation defects in TiO_2 . Titanium film treated at 300 W for 5 min becomes completely oxidized, while the distribution profile of H atoms does not change significantly in the bulk, and H maximum appears at the film-substrate interface. As a result of H accommodation at the interface, the surface is subject to the development of various bumps and blisters.

4. Discussions

Water molecules present in plasma are excited, ionized, and disassociated in dependence on the plasma processing power. In this surrounding, the oxygen atoms are preferentially removed from the oxidized titanium surface

FIGURE 4: XRD patterns of Ti film after plasma treatment: 1 as deposited, 2 for 5 min at 200 W, 3 for 20 min at 200 W, and 4 for 5 min at 300 W.

FIGURE 5: Distribution profiles of O and H atoms (curves 1 and 2, resp.) in Ti film treated at 300 W for 5 min.

due to radiation coming from plasma. An oxygen-deficient surface with suboxides becomes highly reactive. Taking into account superhydrophilic properties of titania, adsorbed water molecules and water drops converge to island layers rapidly. The adsorbed water molecules quickly hydrate the surface leading to increased hydroxyl group density on the surface and transformation of reduced oxides into TiO_2 . The concentration of hydroxyl groups on the surface depends on the oxidation state of titanium oxide. Irradiation of surface area covered by adsorbed water layer leads to the split of hydroxyl radicals into their atomic components hydrogen and oxygen [7, 10]. These factors contribute to the increase of oxidation rate of surfaces covered by water layers. This increase is predominantly determined by the plasma radiation intensity. Additionally, the outermost layer becomes highly defected and new pathways for the transport of water molecules and atoms become possible.

The splitted H atoms in the near-surface region of TiO_2 are trapped at radiation defects while the mobile H atoms detrapped from trapping centers diffuse through the oxide layer into the bulk and, taking into account titanium's high

affinity for hydrogen, are absorbed by the titanium and consequently are stored in the bulk. Substantial excess of atomic hydrogen present may be accommodated in the crystal lattice, resulting in gas bubbles. Lifting in the form of "popping off" discrete blisters was observed. The size distribution of the holes correlates well with the topology of island water layers observed by SEM. One of the main issues concerning their mechanical performance is the type and magnitude of residual stresses around the crystalline TiO_2 phase in the matrix of Ti. Residual stresses may or may not generate microcracks around the precipitates depending on their magnitude, crystal size, and film thickness.

5. Conclusions

In summary, it emerges from our results that the study of structural and phase transformations in water-vapor-plasma-treated Ti films in dependence on the processing parameters provides an information for an advancing knowledge of the behavior of adsorbed water molecules on the surface of titanium oxide under plasma radiation. Adsorbed water molecules on the hydrophilic surface converge to water island layers leading to increased hydroxyl group density on the oxidized Ti surface and its transformation into TiO_2 . The H atoms are trapped at radiation defects in the near-surface region of TiO_2 , while the mobile H atoms diffuse through the oxide layer and tend to form gas bubbles in the bulk and at the film-substrate interface.

Acknowledgments

This research was funded by a Grant (ATE-2011/2012) from the Research Council of Lithuania. The authors are grateful to the Science Council of The Lithuanian Energy Institute and Vytautas Magnus University for the support of this research.

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