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On the Oxygen Transport Mechanism in Titanium Thin Films under Irradiation by Molecular Water Ions

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The behavior of oxygen atoms in (0.5 – 1.0) μm thick Ti films is investigated under high-flux, low-energy molecular water ion irradiation. The anomalously deep penetration of oxygen without formation of new compounds observable by XRD has been registered after 10 min of irradiation at room temperature using Auger Electron spectroscopy analysis.

The mechanism driving oxygen atoms from the surface into the bulk is discussed. It is based on the results of experimental studies of surface topography and assumption that the surface energy increases under ion irradiation, and relaxation processes minimizing the surface energy initiate the atomic redistribution on the surface and in the bulk. Two processes minimizing the surface free energy are considered: (i) the mixing of atoms on the surface, and (ii) the annihilation of surface vacancies by the atoms transported from the bulk to the surface.

Keywords: hydrogen, water vapor, plasma, ion implantation.

1. INTRODUCTION

Titanium and its oxide is widely used material in both the energy and environmental applications, ranging from photovoltaics and photocatalysis to photo-electrochromics and sensors [1, 2]. It has been shown [3], that titanium oxide doped with hydrogen demonstrates photocatalytic properties under visible light radiation.

It is known that oxidation mechanism of titanium is modified by the presence of water vapor in oxidant environment. Such changes include microstructural changes in the scale, enhancement or decrease in the oxidation rate and changes in oxygen transport mechanism through the oxide [4]. In publication [5], it is concluded that the fast oxygen transport in titanium is caused by rapid matter transport and have to be related to the high reactivity of oxygen arising from water vapor. It is shown [6] that the presence of water vapor leads to the development of a double-layered structure consisting of an innermost multilayered structure and an outermost recrystallized layer. The complete explanation of the effect of water during oxidation has not been given yet.

Situation becomes more complicated if oxidation of titanium takes place in the ionized water vapor. There are several publications on water vapor plasma oxidation of titanium [7, 8]. Low and atmospheric plasmas have been used. The oxidation of titanium is strongly affected by the presence of plasma and the predictions following classical thermodynamics become questionable. The outermost layer becomes highly defected and new pathways for the transport of water molecules and hydrogen atoms become possible. The possible oxidation-reduction reactions of partially oxidized titanium by hydrogen plasma have been considered in publication [9].

Oxygen transport mechanism from the surface into the bulk and through the TiO_2 layer involves many processes including interfacial charge transfer, adsorption and trapping. They are influenced by properties of the oxide such as chemical composition and structure, hydrogen solubility, the presence of interstitials and oxygen vacancies, the type and concentration of impurities, and the oxide thickness and porosity [10, 11]. The mechanism by which the oxide layer influences oxygen transport into Ti is still not well established.

In general, it is difficult to evaluate the rate of oxygen transport through a TiO_2 film and how many oxygen atoms, arriving to the TiO_2 surface, reach the Ti layer. In this work, we study the oxygen transport in thin Ti films under water vapor plasma treatment.

2. EXPERIMENTAL TECHNIQUES

A vacuum system (PVD-75) including rotary and cryogenic pumps enabled a base pressure of $2 \cdot 10^{-4}$ Pa. The titanium films of (0.5 – 1.0) μm thickness were deposited on 2 mm thick stainless steel and 0.2 mm thick Si(111) substrates employing magnetron sputter deposition technique. Water vapor was injected into vacuum chamber from heated water container as shown in Fig. 1, a. The flow and pressure of water vapor were controlled by mass flow controller (MFC). Plasma treatment was performed at 5 Pa pressure of water vapor. A radio-frequency (RF) power supply provided the power needed to generate plasma. The power dissipated in plasma was verified in the range 50 W – 300 W.

Samples were located at the different sites of PVD-75 vacuum device (Fig. 1, b): A – at the distance 2 cm – 3 cm from the magnetron cathode outside its sputtering zone, and B – on the surface of water cooled Ti cathode of magnetron. Two surface areas of the sample located on the cathode were analyzed: (i) affected by low, and (ii) high-flux radiation. In this way, three irradiation regimes were

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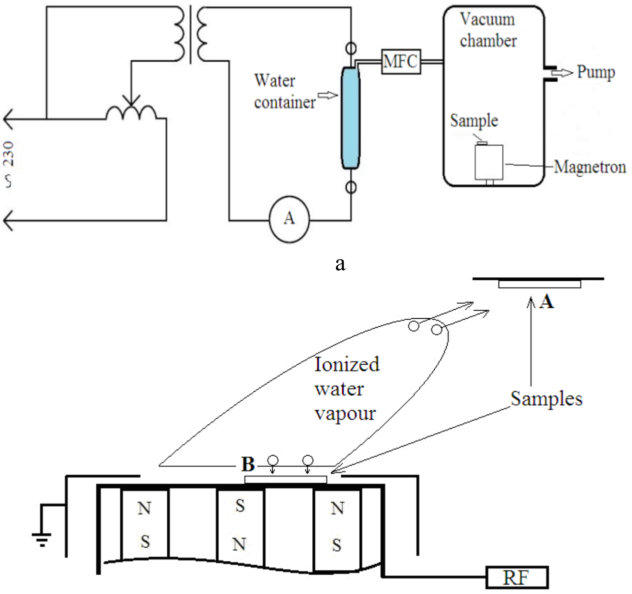
realized: 1 – case A, the ion current density to the substrate is equal to about 5 μA/cm^2, 2 – case B, the surface area affected by low-flux irradiation with ion current density of about 1.5 mA/cm^2, and 3 – case B, the surface area affected by high-flux irradiation with ion current density of about 10 mA/cm^2.



a

b

Fig. 1. The schemes of: a) experimental technique and b) samples location inside vacuum chamber

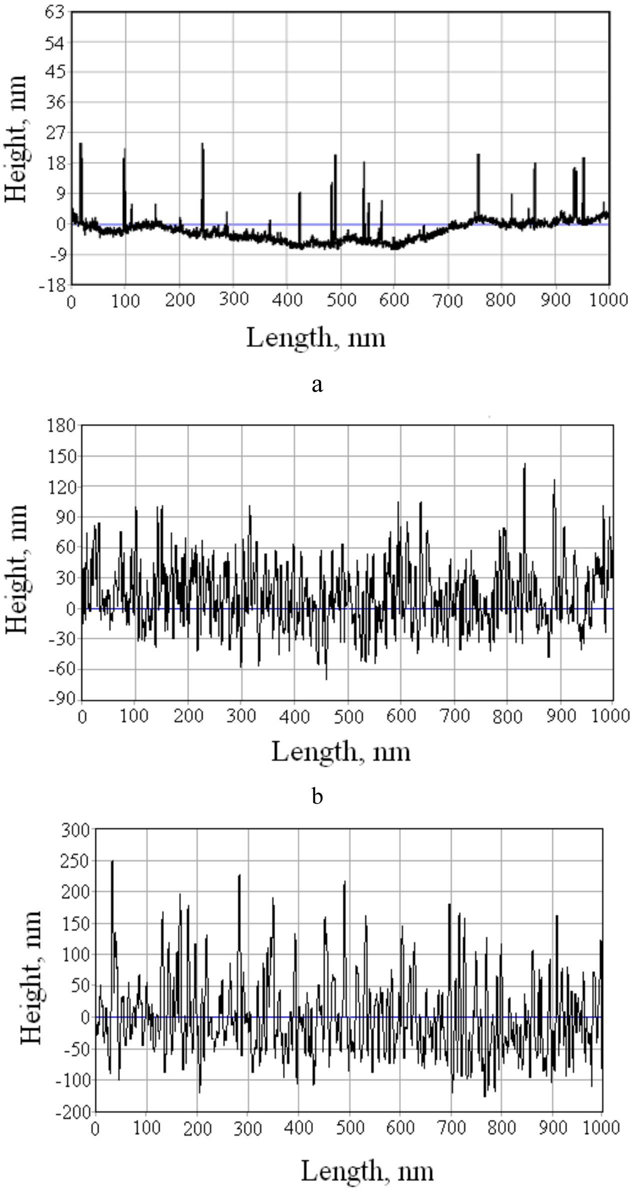
The microstructure of the samples was characterized by X-ray diffraction (XRD) method using Bruker diffractometer (Bruker D8). The measurements were performed with $\theta - 2\theta$ modification in the range 20° – 70° using Cu K_α radiation in steps of 0.01°. The identification of peaks has been done using the Search – Match software. The thickness and surface topography of Ti films were measured using the nanoprofilometer (AMBIOS XP 200). The surface views before and after hydrogenation were investigated by a scanning electron microscopy (SEM, JEOL JSM-5600). The elemental composition of plasma treated films was analyzed by energy dispersive X-ray spectroscopy (EDX, Bruker Quad 5040). The distribution profiles of oxygen in titanium films after plasma treatment were measured by Auger Electron spectroscopy (AES, PHI 700XI AUGER NANOPROBE).

3. EXPERIMENTAL RESULTS

3.1. Analysis of Surface Topography

The studies of surface nanotopography profiles at the boundary between the non-irradiated and water vapor plasma treated surface areas have shown that the step height does not exceed 4 nm. In this way, it was concluded that the steady state surface erosion and surface growth rate due to accommodation of implanted species in the near-surface region are approximately equal for irradiation parameters used in the present work.

The studies of surface roughness on a nanometric scale revealed that surfaces of Ti film after water plasma treatment become rough. Fig. 2 includes images of surface topography height profiles: a – for as-deposited, b – after plasma treatment for 10 min, and c – 60 min. The root mean square (RMS) of surface roughness is equal to 10, 25 and 47 nm, respectively. The surface roughness approaches steady state values. The steady state surface roughness and the characteristic approach to the steady state time depend on the parameters of irradiation and the initial state of surface.



a

b

c

Fig. 2. The surface height profiles: a – for as-deposited; b – after plasma treatment for 10 min; c – after plasma treatment for 60 min

3.2. XRD Analysis

All samples that had been treated by the water vapour plasma were subsequently analysed by XRD technique. All X-ray diffraction peaks were indexed using EVA software together with Search-Match function and PDF-2 database from International Centre for Diffraction Data (ICDD). A typical XRD spectrum from the samples irradiated by low intensity ion flux (case A) during 30, 45 and 60 min are shown in Fig. 3, curves 1 – 3, respectively. The XRD spectrum of the sample treated by water vapour plasma discharge for 30 minutes indicates that the sample is predominantly metallic, with small amounts of titanium suboxide Ti_6O. The XRD patterns of Ti films irradiated by ions extracted from water vapour plasma during 30, 45 and 60 min (curves 1, 2 and 3, respectively, Fig. 3) show one wide and asymmetric peak which is interpreted as superposition of two peaks – Ti and TiO_2. It seems that the Ti film is partially oxidized transferring it to an anatase at room temperature even after 30 min of plasma treatment under low-flux ion irradiation.

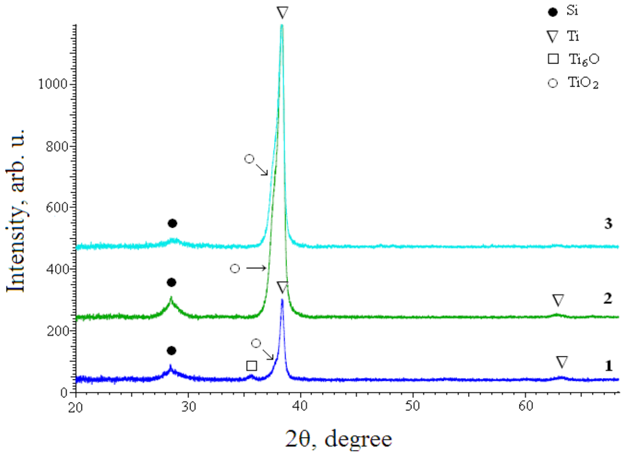
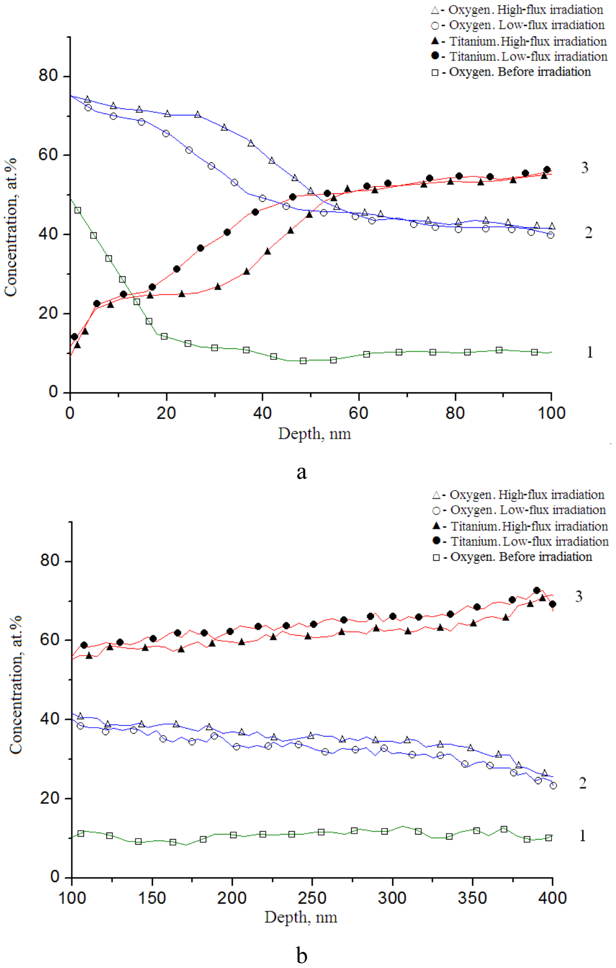


Fig. 3. The XRD patterns of Ti films after different durations of irradiation



a

b

Fig. 4. The Auger depth distribution profiles of O and Ti atoms: a – near surface layer; b – in the bulk

3.3. Depth Distribution of O Atoms

The Auger depth distribution profiles of O atoms in Ti film after irradiation for 10 min are shown in Figs. 4, a and b: curves 1 and 2 – for O atoms in as-deposited Ti film and after its high and low-flux irradiation, respectively, and curve 3 – for Ti atoms after high and low-flux ion irradiation for 10 min. Two regions have been distinguished: a – the near surface region with thickness of 100 nm, and b – the underlying region in the range from 100 nm through the entire film thickness. It is seen that the oxygen concentration decreases from 75 at.% to 40 at.% in the near surface layer (Fig. 4, a), and the concentration of oxygen gradually decreases from 40 at.% to 25 at.% from the depth equal to 100 nm across the entire film thickness (Fig. 4, b). It is seen that the intensity of irradiation has a small effect on the shape of distribution profiles.

4. DISCUSSION

According to the widely accepted concept of molecular surface science the surface may be treated as a separate phase with a different structure, composition and electronic properties [12, 13]. These experimental studies reveal that processes of relaxation and reconstruction relocate surface atoms from their bulk-like positions and indicate to the unique importance of surface defects (roughness) in controlling surface phenomena. At rough edges the atoms relax by a large amount in order to smooth the surface irregularities. In this work, the main emphasis is made on analysis of the role of surface height topography instabilities on the mechanism of oxygen transport in Ti film under water vapor plasma treatment.

The surface dynamic state is prerequisite for the surface topography formation and relaxation kinetics. The atom on the surface is located in some adsorption site determined to first order by the local crystal structure. It oscillates in the potential well and may be displaced from it if the oscillation energy exceeds the binding energy (thermal displacement). This process has been verified in publication [13]. Additionally, the ballistic atomic displacements take place if surface is under ion irradiation.

At steady state, the generation and annihilation rates of surface vacancies and adatoms are balanced. This condition may be fulfilled in two ways. First, the stochastic mixing of displaced atoms on the surface is supported by thermal and ballistic atomic displacements and, second, the annihilation of surface vacancies and adatoms takes place by the balanced fluxes of atoms arriving from the bulk to the surface and from the surface into the bulk.

Above mentioned processes may be interpreted in the following way. As the surface roughness is low, the stochastic mixing of atoms on the surface of Ti film initiates surface roughening, and the surface roughness increases. In many cases the increase of roughness is correlated with the increase of surface energy. The increase of surface roughness, or surface energy (i. e. the number of broken links multiplied by the pair-interaction (bond) energy), cannot be infinite. When surface free energy reaches critical value, its relaxation starts. Two balanced atomic fluxes take part in the stabilization of surface energy and surface topography at steady state (Fig. 5, b).

Both fluxes are equal and have opposite directions according to the mass-conservation law and continuity of material.

Transport of oxygen atoms into the bulk becomes problematic if one or both of these fluxes are physically non-realizable. Let us consider some examples, which are in consistence with the existing observations: 1) the efficient oxidation starts at temperatures when thermal displacements of surface atoms begin; 2) the presence of the thin oxide layer on the surface acts as barrier for O atoms transport from the surface into the bulk, and in this way hinders efficiency of oxygen transport from the surface into the bulk. On the contrary, the pretreatment processes removing surface barrier layers and related with the generation of defects increases the efficiency of the transport of oxygen. The prebombardment of materials by non-reactive Ar ions increases efficiency of oxygen transport.

In this way, two O transport mechanisms may be in action under ion irradiation: (i) the transport of O atoms as result of stochastic mixing of displaced atoms on the surface, and (ii) the transport of O by atomic fluxes driven by surface energy relaxation processes. The presented model is in consistence qualitatively with the obtained experimental results. The first mechanism explains the existence of the highly saturated by O atoms near-surface region, and the second one explains the homogeneous O distribution along the entire Ti film thickness.

5. CONCLUSIONS

The study results show that the O penetration in Ti films treated by ion irradiation with ions extracted from the water vapor plasma is correlated with the surface roughness. The anomalously deep O penetration into Ti film at room temperature has been registered experimentally. It is supposed that the relaxation processes stabilizing surface roughness initiate a local and long-range restructuring and atomic mixing on the surface and in the bulk.

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