

## OXYGEN IMPLANTATION AND BEHAVIOUR INTO TI THIN FILMS FROM WATER VAPOUR PLASMA

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### ABSTRACT

The behavior of O atoms in Ti film is investigated under high-flux, low-energy molecular water ion implantation. After 10 min of irradiation at room temperature, the anomalously deep penetration of oxygen without formation of new chemical compounds observable by XRD has been registered in Ti films using Auger spectroscopy analysis.

It is shown that the surface energy increases under ion irradiation, and the relaxation processes minimizing the surface energy initiate the redistribution of atoms. Two surface energy relaxation processes are considered: (i) the mixing of atoms on the surface resulting in annihilation of surface vacancies; and (ii) the annihilation of surface vacancies by atoms transported from the bulk. The theoretical considerations are in agreement with the experimental results if to assume that the mass-transport in the bulk is controlled by the processes on the surface and the adsorption of reactive atoms or molecules leads to local and long-range restructuring and adatom relocation at the surface.

**Key words:** hydrogen, water vapour, plasma, ion implantation

### INTRODUCTION

Titanium and its alloys have many industrial applications thanks to their excellent corrosion resistance and high specific strength. Generally, titanium is covered by a passive titanium oxide (TiO<sub>2</sub>) film. Though very thin (usually a few nanometers), this compact film acts as a protective layer against corrosion.

Oxygen permeation through TiO<sub>2</sub> films and its transport in the bulk is a complex process involving interfacial charge transfer, adsorption, absorption, trapping, and transport, and, thus, is inherently influenced by properties of the oxide, such as the chemical composition and structure, the presence of Ti<sup>i+</sup> interstitials and/or oxygen vacancies, the type and concentration of impurities, hydrogen solubility, the adsorption characteristics of the surface, and the oxide thickness, porosity and uniformity [1,2]. The mechanism by which the oxide barrier layer influences oxygen permeation into Ti is still not well established.

The retardation of oxygen permeation by TiO<sub>2</sub> films may be due to a

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combination of low oxygen absorption at the oxide surface and/or slow oxygen transport in the oxide. In general, it is difficult to predict the rate of oxygen transport through a  $\text{TiO}_2$  film and how many oxygen atoms, generated on the  $\text{TiO}_2$  surface, reach the Ti substrate. In this work, we study feasible physical models explaining oxygen permeation through a thin Ti film.

### EXPERIMENTAL TECHNIQUE

The 0.5 - 1  $\mu\text{m}$  thick Ti films were deposited on 2 mm thick stainless steel and Si(111) substrates using magnetron sputter deposition technique. Samples were located at different sites of PVD – 75 vacuum chamber. Details of experimental technique are published in [3, 4]. Three cases were distinguished: (i) case A, the ion current density from plasma to the sample was about 5  $\mu\text{A}/\text{cm}^2$ , (ii) case B - 1.5  $\text{mA}/\text{cm}^2$ , and (iii) case C - 10  $\text{mA}/\text{cm}^2$ .

A vacuum system including rotary and cryogenic pumps enabled a base pressure of  $2 \cdot 10^{-4}$  Pa. The water vapour was injected into vacuum chamber using heated water container (Fig. 1).

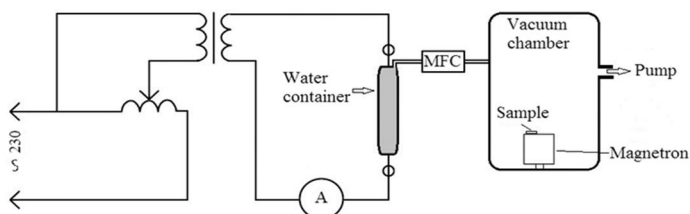


Fig. 1 - The scheme of the experimental technique

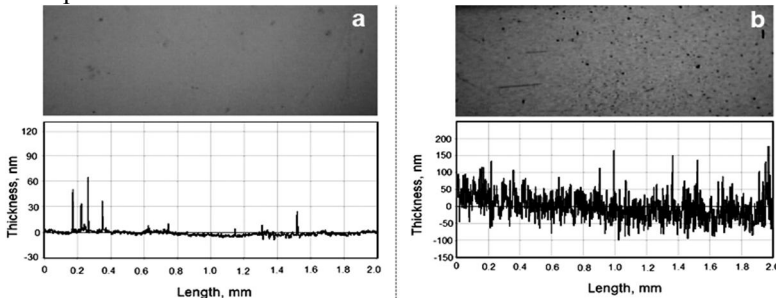
Plasma implantation was performed at 10 Pa pressure of water vapour. Flow of water vapour was continuously controlled by mass flow controller. The plasma was generated using DC and RF energy sources. The dissipated power in plasma was verified in the range 100 - 300 W.

The microstructure of the samples was characterized by X - ray diffraction (XRD) method using Bruker diffractometer (Bruker D8). The measurements were performed with  $2\theta$  angle in the range  $20^\circ - 70^\circ$  using  $\text{Cu K}\alpha$  radiation in steps of  $0.01^\circ$ . The identification of peaks has been done using *Search - Match* software. The thickness and surface topography of Ti films were measured using the nanopprofilometer (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 hydrogenation were measured by Auger Electron Emission spectroscopy (AES, PHI 700XI AUGER NANOPROBE).

**EXPERIMENTAL RESULTS: ANALYSIS OF SURFACE TOPOGRAPHY**

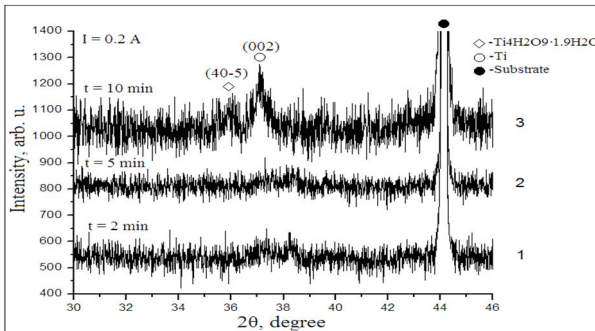
The height of a step on the boundary between the non-irradiated and water plasma irradiated areas has been investigated in [3]. It has been shown that under water plasma irradiation the elevation height between irradiated and non-irradiated areas does not exceed 2 nm. On the basis of these experimental results it has been concluded that for irradiation parameters used in the present work the steady state surface erosion and surface growth due to accommodation of implanted species rates in the near-surface region are approximately equal.

The studies of surface roughness on a nanometric scale revealed that surfaces of Ti film after water plasma treatment become rough. Fig. 2 includes the surface topography profiles of the as-deposited Ti film - Fig. 2a, and after plasma treatment during 5 min - Fig. 2b. The surface roughness increases from ~10 nm up to ~75 nm.



**Fig. 2** - The profiles of surface topography: a) - profile of as-deposited Ti film, and b) – profile of Ti after plasma treatment during 5 min

**EXPERIMENTAL RESULTS: XRD ANALYSIS**



**Fig. 3** - XRD patterns after different durations of hydrogenation

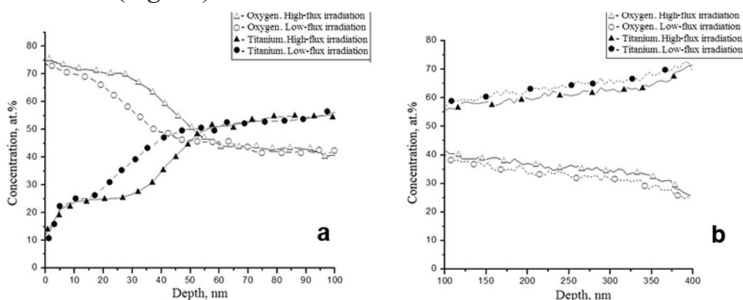
Fig. 3 includes XRD patterns of Ti film after different durations of irradiation: curve 1 - 2 min, curve 2 - 5 min, and curve 3 - 10 min. It is seen that structural reconstructions and formation of a new Ti4H2O9

phase begins after 10 min of irradiation. Characteristic peak of Ti shows that

initially amorphous film becomes nanocrystalline with the mean size of crystallites estimated using Scherrer equation is equal to about 60 nm.

### Distribution of o atoms

The Auger depth distribution profiles of O and Ti atoms in Ti film after irradiation during 10 min by ions extracted from the water plasma are shown in Fig. 5a and Fig. 5b. Two regions may be distinguished: (i) in the near surface layer with thickness less than 100 nm, the oxygen concentration decreases from 75 at.% to 40 at.% (Fig. 5a), and (ii) in the bulk in the range from 100 nm across entire film thickness, the concentration of oxygen decreases from 40 at.% to 25 at.% (Fig. 5b).



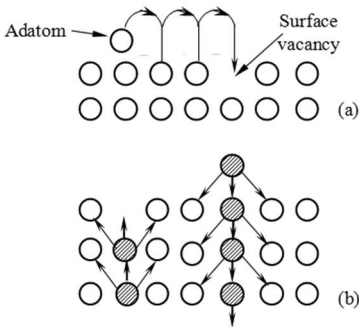
**Fig. 5** - The Auger distribution profiles of O and Ti atoms in Ti film after irradiation during 10 min by ions extracted from the water plasma

### Discussions

According to the new concept of molecular surface science the surface may be treated as a separate phase with a different structure, composition and electronic properties. It reveals that processes of relaxation and reconstruction relocate surface atoms from their bulk-like positions and indicates to the unique importance of surface defects (roughness) in controlling surface phenomena. This phenomenon is consistent with the latest discoveries in molecular surface science [5]. At rough edges, such as at stepped surfaces, the atoms at the step 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 topography instabilities on the mechanism of oxygen transport in Ti film under molecular water ion irradiation.

Two dominant surface topography relaxation mechanisms are distinguished: (i) the dynamic relocation of surface adatoms and annihilation of surface vacancies (Fig. 6a), and (ii) the transport of O atoms from the surface into to the bulk and Ti atoms from the bulk on the surface (Fig. 6b).

For modeling of oxygen behavior in Ti films some assumptions are needed. Let us assume that at elevated temperatures surface adatoms under the thermal or ballistic displacement effects are mobile.



**Fig. 6** - Schematic presentation of atom transport mechanisms

where  $E_d$  is the height of the potential well, or the activation energy, for surface diffusion;  $m$  is the adatom mass, and  $a$  is the width of the well.

The effect of the ion irradiation is to increase the relocation frequency above the thermal levels. The total frequency relocation probability is the sum of thermally activated jumps plus the ion impact induced jumps

$$w_i = \frac{DI_0}{C} + w_{i0} e^{-\frac{E_d}{kT}}, \tag{1}$$

where  $D$  is the number of displaced atoms on the surface by one incident ion,  $I_0$  is the flux of ions and  $C$  is the surface atom concentration. The Eq. (1) is valid if thermal and “ballistic” relocations are independent.

Mathematically the flux of displaced  $i$  atoms is equal to  $w_i c_i$ , where  $w_i$  is the frequency probability of surface displacements defined by the Eq.(1) and  $c_i$  is the partial surface concentration of  $i$  atoms. The flux of readsorbed atoms is equal to  $\alpha_{ij} \beta_i w_i c_i$ , where  $\beta_i$  is the probability of readsorption and  $\alpha_{ij}$  is the sticking probability of  $i$  atom to  $j$  atom on the surface. At steady state, when all displaced atoms are readsorbed,  $\alpha_{ij} \beta_i = 1$ .

For simplicity and in accordance with experimental observations, the behavior of broken oxygen atoms in Ti film will be considered in the following way. The affinity of Ti atoms to oxygen is high and they tend to form Ti-O bonds. The surface atoms are buried by the displaced and readsorbed O and Ti atoms. In this way, the oxidation kinetics may be limited by the transport of Ti atoms from the bulk to the surface or O atoms from the surface into the bulk. The conservation of continuity of material requires that these fluxes would be balanced.

The rate equations including processes of atom displacement and readsorption have been analyzed in [7]. It has been shown that the stochastic mixing of atoms on the surface may be described by the diffusion equation written in finite increments with step one monolayer  $h_0$  and the effective diffusion coefficient equal to  $D = h_0^2 (V_d + V_a)$  and surface movement velocity equal to  $V = h_0 (V_d - V_a)$ , where

This assumption is verified in publications [6]. The surface dynamic state is prerequisite for stochastic mixing of atoms between neighboring monolayers. The adatom on the surface is located in some adsorption site determined first order by the local crystal structure. It oscillates in the potential well at a frequency  $w_{i0} = \left( E_d / 2ma \right)^{1/2}$

, where  $E_d$  is the height of the potential well, or the activation energy, for surface diffusion;  $m$  is the adatom mass, and  $a$  is the width of the well.

$$V_d = \sum_j w_j c_j \quad \text{and} \quad V_a = \sum_i \sum_j \kappa_{ij} c_j. \quad (2)$$

The balanced dynamic state on the surface is realized if atom displacement and readsorption rates are equal,  $V_d \approx V_a$ . This regime may be realized in two ways: 1) if the generation rate of surface vacancies is equal to the annihilation rate of surface vacancies by mobile adatoms, and 2) if the annihilation of surface vacancies takes place by atoms arriving from the bulk in the balanced way. Atomic motion minimizes surface energy and stabilizes the surface roughness. The wells of the surface are filled by atoms which are transported from the bulk, and atoms from the surface elevations are moved into the bulk.

Above mentioned processes may be interpreted in the following way. The stochastic mixing of atoms on the surface initiates surface roughening. The roughness depth increases in time as  $(Dt)^{1/2}$ . In many cases the increase in 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), can not be infinite. When surface energy reaches critical, the stabilization of the surface energy starts. The stabilization of surface energy by diffusion of adatoms and annihilation of surface vacancies and occupation of empty sites on the surface is dominant process in the range of low temperatures (*Fig. 6a*). The transport of atoms from the bulk into the empty sites on the surface and annihilation of surface vacancies becomes dominant at elevated temperatures when point defects are mobile in the matrix of bulk material (*Fig. 6b*). The more open (rougher) surface topography, the larger relaxation fluxes are.

The above presented model considers two balanced fluxes. Both flux are equal and have opposite directions. They follow to the mass-conservation law and continuity of material. Transport of oxygen atoms into the bulk becomes inefficient if one or both of these fluxes are physically non-realizable. Let us consider some examples, which are in consistence with the experimental results: 1) the efficient oxidation starts at temperature when Ti atoms become mobile and take part in the relaxation mechanism of surface topography; 2) the presence of the thin  $\text{TiO}_2$  layer on the surface of Ti acts as barrier for atom transport from the surface into the bulk, and in this way hinders efficiency of oxygen transport from the surface into the bulk and stops it when continuous dielectric film is formed. On the contrary, the pretreatment processes removing barrier layers on the surface and related with the generation of defects on materials 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 transportation mechanisms from the surface into the bulk of Ti film are in action under ion irradiation: (i) the penetration of O atoms as result of stochastic mixing of atoms on the surface, and (ii) the transportation of O atoms by fluxes driven by surface energy relaxation processes. The first mechanism forms near-surface region highly saturated by O atoms and the second one explains distribution of O atoms along the entire Ti film thickness.

## CONCLUSIONS

It is shown that the oxygen transport from the surface into the bulk is controlled by the processes on the surface, and the adsorption of reactive atoms or molecules leads to local and long-range restructuring and adatom relocation at the surface. Experimentally, the anomalously deep penetration of oxygen has been registered in Ti films without formation of chemical compounds observable by XRD after molecular water ion irradiation during 10 min at room temperature (*Fig. 3*).

Surface topography analysis results showed that after irradiation surfaces become rough and for considered irradiation parameters the balance between the surface erosion and surface growth due to accommodation of implanted species in the near-surface region exists. The experimental observations are explained assuming that processes on the surface (surface roughening) initiate the transport of oxygen atoms from the surface into the bulk. The relaxation of surface energy and reconstruction of surface topography relocate surface atoms from their bulk-like positions and drive into the underlying monolayers.

### *Acknowledgement*

This research was funded by a grant (Nr. ATE-02/2010) from the Research Council of Lithuania. The authors are grateful to professors V. Girdauskas and A. Kanapickas for their useful discussions, doctoral student K. Gedvilas for his contribution in experimental work. Authors highly appreciate prof. D. Milčius, the head of the Center for Hydrogen Energy Technologies, for the access to the experimental technique.

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