# SURFACE TOPOGRAPHY ANALYSIS OF WATER VAPOR PLASMA IRRADIATION INDUCED EFFECTS IN Ti FILMS

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### ABSTRACT

In the present work, the changes of surface topography driven by interaction of ions extracted from low-pressure water vapor plasma are studied. Titanium 0.5-1 μm thickness films were deposited on silicon wafer substrates using magnetron sputtering technique and immersed in water vapor plasma at pressure 1-10 Pa. The samples were located on the cathode of magnetron and affected by high-flux, low-energy ions extracted by 250-300V bias negative voltage. The used Ti and W cathodes were water cooled.

It is shown that the surface roughness of irradiated films changes in dependence of irradiation fluence and intensity. The experimental results are explained on the basis of the analysis of the selective erosion of oxide phases synthesized in the near-surface region. Three sputtering modes are distinguished: (i) metallic, (ii) oxide and (iii) composite: metallic with clusters of oxide.

**Key words***: Titanium; Water vapor; Plasma; Surface roughness*

### INTRODUCTION

Due to the enormous variety of applications, going from catalysis to medicine, the study of titanium is a continuously growing field of work [1-8]. For instance, metallic Ti is a key material in aircraft construction [9] and its malleability and chemical activity promotes its use as a getter material [10]. On the other hand, its large biocompatibility comes from the formation of a surface oxide layer and the catalyst capability is also related to the properties of the metallic Ti films grown on it [11-16]. Thus, the interest goes from metallic Ti to its different oxides, including the chemical behavior of the different metal–metal and metal–oxide interfaces. The interest on the oxidation of titanium in the thin film regime goes also from applied points of view to basic ones.

Protective coatings against corrosion is a good example within the first group [17], and surface to bulk oxidation transition and the interface effects, as well as the knowledge about driving forces involved in oxidation process are included in the second one [16, 18]. In a recent work [19] it is shown that the

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oxidation kinetics of Ti thin films is strongly dependent on the film thickness.

The process of titanium surface oxidation has been largely studied by means of the most important surface characterization techniques, such as XPS, Auger electron spectroscopy (AES), EELS, SIMS, UPS and so on. Thus, the kinetics of titanium oxidation is well characterized: it begins with a fast oxygen adsorption, followed by a slowing down of the process until the saturation. This experimental behavior has been explained in two different ways: a fast adsorption stage followed by a slow oxidation one [20], or a fast oxidation stage followed by a slowing down due to the formation of a passivating film [21,22]. Azoulay et al. [23] found that the titanium oxidation state is strongly dependent on the type of surface, giving a possible explanation for the discrepancies between different authors.

In this work we study the changes of surface topography of Ti films initiated by plasma treatment under low and high-flux irradiation by ions extracted from water vapor plasma.

### *EXPERIMENTAL TECHNIQUE*

Titanium 0.5-1 μm thickness films were deposited on silicon wafer substrates using magnetron sputtering technique in PVD-75 vacuum system. The samples were located on the cathode of magnetron and affected by incident ions accelerated under 250-300V negative bias voltage. The used Ti and W cathodes were water cooled. All samples were divided into two groups: the samples of the first group were affected by low-flux (the ion current density about 1 mA/cm2), and the samples of the second group were affected by high-flux (the ion current density about 10 mA/cm$^2$) ion irradiation. In the following, the samples after low-flux ion irradiation are denoted by letter L, and the samples after high-flux ion irradiation are denoted by letter H.

The thickness and surface topography of Ti films were measured using the nanoprofilometer (AMBIOS XP 200). The mean surface roughness depth (Rz) was evaluated as the average length of the peak-to-valley values calculated over the all scanned length. It corresponds to Rz ISO standard called "Ten Point Average Roughness". The average height value is calculated using values of 5 the highest peaks (Yp), and 5 the deepest valleys (Yv), as shown in *Fig. 1* and using Eq.1.
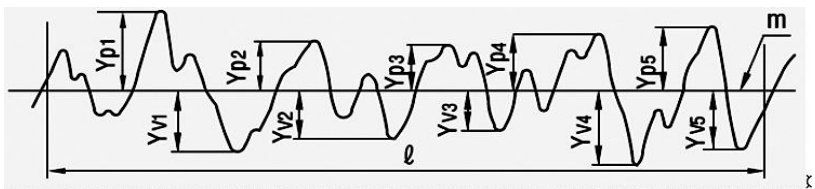


**Fig. 1** – Ten-point mean roughness (Rz)

$$Rz = \frac{|Y_{p1} + Y_{p2} + Y_{p3} + Y_{p4} + Y_{p5}| + |Y_{v1} + Y_{v2} + Y_{v3} + Y_{v4} +|}{5} \qquad (1)$$

In this study Rz has been calculated over the entire scanned length when the numbers of Yp and Yv are variable in dependence on the surface roughness (Eq.2).

$$Rz = \frac{|\sum Y_{pi}| + |\sum Y_{vi}|}{n}, \qquad (i = 1..n) \qquad (2)$$

The surface roughness of sample was calculated as the arithmetic average of Rz for different places of the sample.

The surface analysis was done by a scanning electron microscopy (SEM, JEOL JSM – 5600) before and after hydrogenation.

### EXPERIMENTAL RESULTS

*Fig. 2* illustrates typical profiles of surface topography for different samples: a – as-deposited Ti film, b – after plasma treatment (L, time – 60 min), and c – after plasma treatment (H, time – 60 min). *Table 1* summarizes measurement results of surface roughness for different samples.
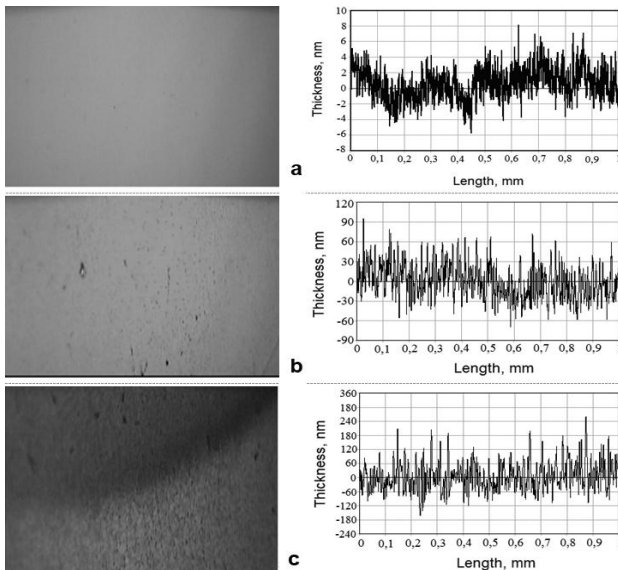


Fig. 2 – Surface topography of as-deposited Ti film – a, and after plasma treatment by high-flux – b, and low-flux ion irradiation - c

Plasma treatment parameters, such as duration and power dissipated in plasma, are included in table. Letters L and H indicate low and high-flux treatment modes, respectively. Low-flux corresponds to ion current density about 1 mA/cm2, and high-flux – 10 mA/cm2. The average surface roughness was equal to 4.5 nm for all as-deposited Ti film samples. It is seen that for all cases the surface roughness increases after plasma treatment. However, the magnitude of this increase is different for

different samples. We have distinguished two groups of samples: (i) the average roughness increase to 4-16 nm (samples 1, 2, 4-6, 8, 9 and 10), and (ii) the average roughness increase to 54-361 nm (samples 3, 7, 11 and 12). Large differences in magnitudes of surface roughness for samples of these two groups can be explained if to assume that different mechanisms operate for development of surface topography under ion irradiation.

**Table 1 –** Measurement results of surface roughness.

| Time, min | 5 | | | | | | 20 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plasma power, W | 200 | | 300 | | | | 200 | | | | | |
| Sample Nr. | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
| Irradiation intensity | H | L | H | L | H | L | H | L | H | L | H | L |
| Roughness, nm | 4,5 | 6,2 | 4,5 | 6,5 | 54,5 | 62,5 | 9,5 | 16,5 | 2,5 | 4,5 | 8,5 | 3,5 |

| Time, min | 20 | | | | 60 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plasma power, W | 300 | | | | 200 | | 300 | | | | | |
| Sample Nr. | 7 | | 8 | | 9 | | 10 | | 11 | | 12 | |
| Irradiation intensity | H | L | H | L | H | L | H | L | H | L | H | L |
| Roughness, nm | 85,5 | 64,5 | 1,5 | 4,5 | 13,1 | 1,5 | 12,5 | 10,5 | 105,5 | 43,5 | 361,5 | 111,5 |

We noted that the mean roughness of surface area affected by high-flux irradiation is less than the mean roughness of surfaces affected by low-flux irradiation for the majority of samples of the first group. For example, for sample 2H - 4.5 nm and 2L – 6.5 nm; sample 4H – 9.5 nm, and 4L – 16.5 nm; for sample 8H - 1.5 nm, and 8L – 4.5 nm, etc.

At the same time, the mean roughness of the surface area affected by high-flux irradiation is higher than the mean roughness of surfaces affected by low-flux irradiation for the majority of samples of the second group. For example, for sample 7H- 85.5 nm and 7L – 64.5 nm; sample 11H – 105.5 nm, and 11L – 43.5 nm, sample 12H – 361.5 nm, and 12L – 111.5 nm. Some exceptions were registered (samples 3, 6, 9 and 10).

Studies of surface topography views obtained in SEM revealed some complementary results. It was noted that SEM surface views, in the similar way as surface roughness results, may be divided in two groups. *Fig. 3* (a and b) includes SEM surfaces views of Ti films after irradiation in 300 W activated water vapor plasma under low-flux ion irradiation during 5 and 60 min, respectively. It is seen that the contrast of surface is homogeneous indicating to homogeneity of emission properties and, presumably, to the homogeneity of surface structure and composition. For 60 min of irradiation, some topographical formations are seen (*Fig. 3b*) which manifests the formation of new phases in the bulk. SEM surface views included in *Fig. 4a* and *Fig. 4b* reveals that in some cases for the same treatment parameters surface becomes uneven and consists of many nanocrystallines of different phases (see *Fig. 4b*).
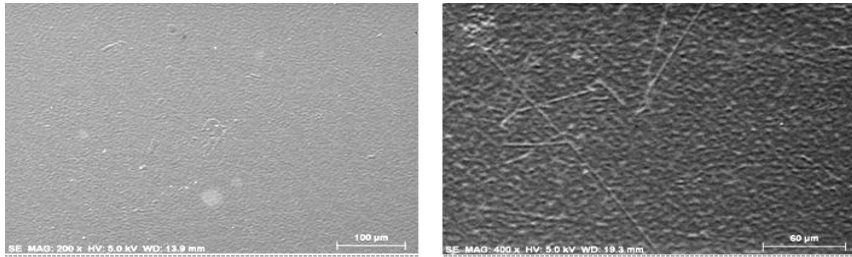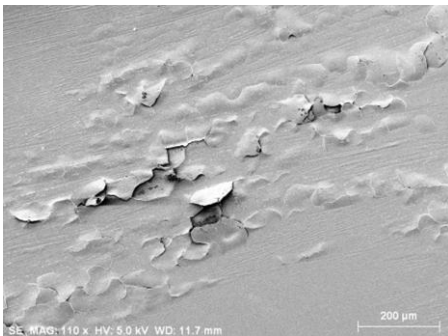
a) 5 min, 300 W, L                                b) 60 min, 300 W, L

**Fig. 3** – SEM surface views
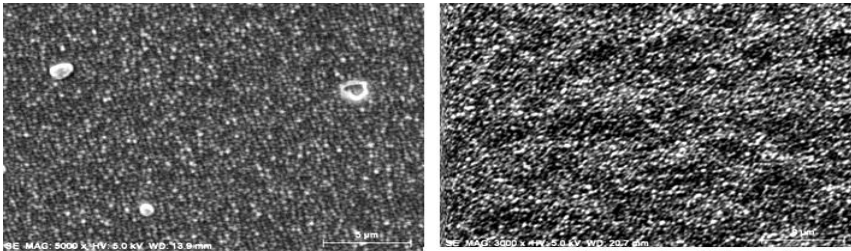


a) 5 min, 300 W, L                                b) 60 min, 300 W, L

**Fig. 4** – SEM surface views.



**Fig. 5** – SEM surface view

It is important to note, the lifting has been observed of Ti films from substrate in some sample areas as it is shown in *Fig. 5*.

### DISCUSSIONS

For incident ions extracted from water vapor plasma, the altered chemical composition of the surface layers leads to changes in surface topography. At high fluences, a saturation concentration of trapped ions is reached, which is determined by a balance among the incident ions flux, the diffusion of the implanted ions into the bulk and back to the surface, and surface removal due to sputtering. Most often a reduction of the sputtering yield for the target atoms is observed due to the dissolution of the target atoms in the surface layer. Changes of the surface binding energy, as well as the development of the collision cascades in the altered layer, may lead both to increased or decreased physical sputtering yields. Finally, surface diffusion

or segregation of implanted ions and target atoms may lead to the formation of surface molecules with different binding energies to the surface.

It is necessary to divide the surface changes on the microscopic (atomic) and macroscopic level. The development of surface structures is closely related to the range and trapping mechanism of implanted gas ions and to the properties of the gas-solid system. It means that the development of surface geometry depends on the type and energy of incident ions. In the range of low ion energies and heavy ions, penetration process is negligible and sputtering process prevails in the formation of surface geometry. It will produce the rearrangement of the first atomic layer and the appearance of micro non-homogeneities.

In many cases the surface structures which develop due to gas ion implantation into solids are predominantly caused by the action of stresses and internal gas pressure in the implanted layer while erosion by sputtering contributes only a minor part.

If the implant is the gas which is chemically bound by the target material, the concentration of implanted atoms saturates at about 0.3-1 gas atom per target atom. At these saturation concentrations a modification of the structure in the implanted layer occurs. Cracks or channels can be formed by which gas from deeper layers may be released to the surface. Also, the density of occupied trapping sites may become sufficiently high to allow the transport of gas atoms along chains of interacting sites towards the surface by percolation.

The compositional changes of chemical compounds are explained involving different processes. The main of them are as follows: (i) mass effect; (ii) bonding effect, and (iii) sputtering via electronic processes. Surface enrichment by the atoms of heavier component follows from the energy sharing between atoms of different masses in the collision cascade. These effects have often been suggested as an explanation for oxygen deficiency in oxides because oxygen is the lighter component in most cases. However, in some cases, the experimental results cannot be explained by the mass effect.

Changes in the sputtering yields depending on the partial pressure of reactive gases are well known in experiments on the production of thin films sputter deposited in a glow discharge and containing reactive ions [24].

In another cases it is assumed that oxygen atoms, adsorbed at the surface, shield the metal atoms from being sputtered. As sputtered oxygen atoms are continuously renewed from the residual gas at high partial pressures the partial sputtering yield of metal atoms is strongly reduced.

If the surface regression due to sputtering is high, the steady state concentration profile of the implanted atoms is built and it does not change with the increase of irradiation fluence. If implanted atoms are light gas ions having low sputtering rates (hydrogen), the gas concentration inside the lattice reaches a critical value of about 0.3-1 gas atoms per target atom, the implanted surface layer may separate partly or completely from the bulk causing a surface modi-

fication known as blistering and flaking (Fig. 5).

There are differences in the development of surface topography in the case of heavy and light ion irradiation. In the case of heavy ions, the penetration ranges of ions are relatively small while damage production and sputtering is relatively large, so that the surface topography which develops is dominated by erosion. For light ion bombardment, the ion ranges in the solid are large, while sputtering is much smaller and therefore high concentrations of the implanted gas can accumulate in the near surface layer. The surface topography under such conditions exhibits blistering, flaking, and spongy structures (*Fig. 5*).

There are two opposite effects observed when examining ion irradiation of materials as a function of fluence. In one case, initially somewhat rough surfaces become smooth (Table 1, samples 1-5 and 8 ). It is well known that the stress fields around defects can lead to lower surface binding energies, hence higher sputtering yield. On the other hand, when the initial surface is relatively poorly prepared, initial roughness may be amplified to give rise to ridges, cones, trenches and pits originating from scratch marks and other major perturbations (*Table 1*, samples 6, 7 and 9-12).

Intergranular effects describe those processes which occur as a result of differential macroscopic sputtering yields between neighboring grains, because of the dependence of sputtering yield upon crystal orientation, and give rise to the creation of grains of different elevation across the surface (*Fig. 4*).

In view of both fundamental physical interest and substantial technological interest the problem of surface topography after ion irradiation is still not resolved. Wide applications of surface pre-sputtering process to clean solids from surface contamination require deeper understanding of the physics of generation of surface defects and the development of surface topography.

However, as was mentioned above, the surface topographies after irradiation with heavy and light ions are different. There are a very large number of publications on this topic. However, it is not yet possible to give a completely consistent picture of the processes involved.

### *CONCLUSIONS*

It is shown experimentally that surface roughness of Ti films increases after treatment in water vapor plasma. The initial stages of the development of surface structures on the initially smooth surface (on the atomic scale) are determined by the stochastic nature of the sputtering process. The evolution of surface roughness depends on the intensity of irradiation.  The roughening mechanisms and dominant processes are discussed. The comparative analysis of surfaces affected by high and low-flux ion irradiation have been conducted. In one case, initially rough surfaces become smooth after high-flux ion irradiation, and on the other hand, when the initial surface is relatively poorly prepared, initial roughness is amplified. It is assumed that oxygen atoms, adsorbed

at the surface, shield the metal atoms from being sputtered. As sputtered oxygen atoms are continuously renewed from the residual gas at high partial pressures the partial sputtering yield of metal atoms is strongly reduced.

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