Development and characterization of Ta-based PVD coatings

A.V. Taran[1], I.E. Garkusha[1,2], I.O. Misiruk[1], O.I. Tymoshenko[1], Ya.O. Kravchenko[3], S.P. Romaniuk[4]

[1] Institute of Plasma Physics, NSC "Kharkiv Institute of Physics and Technology", 1 Akademichna Str., 61108, Kharkiv, Ukraine
[2] V. N. Karazin Kharkiv National University, School of Physics and Technology, 4 Svobody sq., 61022, Kharkiv, Ukraine
[4] Sumy State University, 2 Rimsky Korsakov Str., 40007, Sumy, Ukraine
[4] The State Biotechnology University, Kharkiv, Ukraine

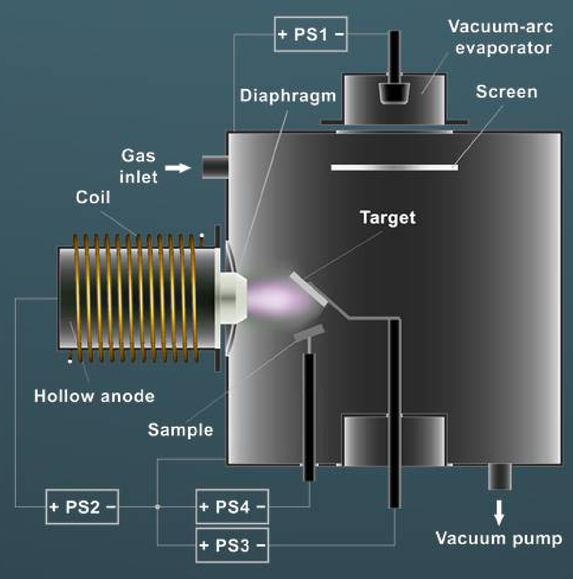
Abstract

Tantalum nitride (TaN) and tantalum oxide (Ta_2O_5) coatings were manufactured by using sputtering with non-self-maintained gas discharge in Bulat-type facility. Characteristics of the obtained coatings, including surface morphology, nanohardness, Young's modulus, and biocompatibility, were investigated. According to the test results, the average value of the elastic modulus for the sample coated with TaN was 426.07 GPa and TaO - 172.36 GPa, respectively. The maximum nanohardness reached 37.75 GPa (Fig. 5, a). At the same time, the TaN coating is characterized by stable performance (the spread in the obtained data does not exceed 9.78 %). The level of nanohardness for the Ta_2O_5 coating is significantly lower and ranges from 9.73 to 10.92.

Introduction

Among the different transition metal nitrides (TiN, CrN, ZrN, etc.), tantalum nitride (TaN) is gaining increasing interest due to its excellent chemical and physical properties. TaN is a widely used material for producing hard coatings, wear resistant layers, thin film resistors, diffusion barriers in integrated circuits, and mask layers for X-ray lithography [1-4]. Ta_2O_5 coatings are used in medicine research as a new type of biomaterials. Ta_2O_5 coatings have an excellent biocompatibility, good dielectric properties, and high corrosion resistance [5]. It was reported in [6] that Ta_2O_5 coating promotes the biocompatibility, anticorrosion and antibacterial behaviors of NiTi substrate. Hydrophilic and cytocompatible Ta_2O_5 films are providing substantial amounts of opportunities in the bone repair areas, owing to the easing the new bone in-growth [7,8]. There are a lot of methods to produce Ta based coatings. Non-self-sustained gas discharge, in which the additional charge carriers are produced by a vacuum-arc evaporator, is characterized by high values of current and degree of ionization [9]. Such type of discharge may be easily excited in widely used vacuum-arc deposition set-ups. Power sources in such set-ups provide, as a rule, the arc current ranging from tens to hundreds of amperes at a voltage of a few tens of volts between metallic cathodes and anode. With easy switching on such equipment, one can obtain a discharge in a gas with almost the same values of current and voltage. Due to enhanced plasma density and degree of ionization, the processes of surface treatment in such gas discharge are much more intense than they are in a self-sustained glow discharge [9]. In the present research the TaN and TaO coatings have been deposited by sputtering using non-self-maintained gas discharge in Bulat-type facility. The surface morphology, chemical composition, mechanical properties and biocompatibility have been investigated.

Experimental Set-up



Tantalum nitride and oxide coatings were obtained by sputtering a tantalum target with argon ions in the vacuum chamber of the Bulat type facility. The flux of argon ions was generated in the non-self-sustained gas discharge with hollow anode. A vacuum-arc evaporator with a titanium cathode was used as a source of additional charges. The evaporator was separated from the chamber by a screen to prevent titanium ions from penetrating the sample surface. The tantalum target was placed at an angle of 45° to the direction of ion flow. The polished steel samples AISI 430 were installed at a distance of a few centimeters from the tantalum target. After pumping the chamber to 7×10^{-3} Pa, it was filled with argon to a pressure of 5×10^{-1} Pa through the gas supply system. After starting the vacuum-arc evaporator and turning on the PS2 source, a non-self-sustained gas discharge ignited between the walls of the chamber and the hollow anode, from the aperture of which a stream of ions was emitted into the chamber. The non-self-sustained gas discharge current reached 90 A, and the ionic current at the target was 3.5 A. Initially, a negative potential of 1000 Volts from PS3 and PS4 sources was applied to the target and the sample, resulting in cleaning of surfaces with argon ions for 40-60 seconds. Next, the potential of the sample was reduced to -100 Volts, or to floating, and coating was performed. The sputtering rate of the tantalum disk surface was several tens of microns per hour. The deposition rate of tantalum coating on the surface of the sample reached 13 μm/h. To obtain tantalum nitride or oxide, a mixture of 75% by volume Ar and 25% N_2, or 75% Ar and 25% O_2, respectively, was fed into the chamber. The deposition rate of such coatings was about 10 μm/h.

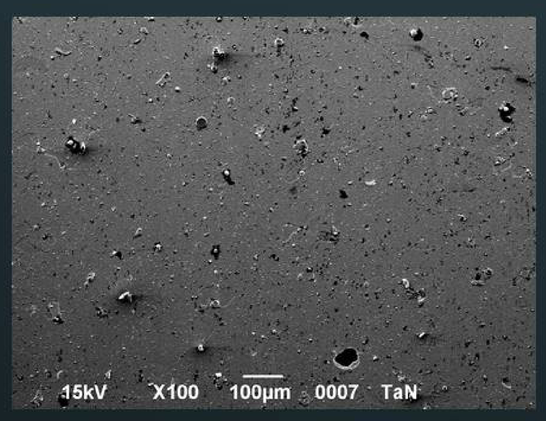
Diagnostics

The surface topography of the coatings was studied using JEOL JSM-6390LV scanning electron microscope (SEM) with an accelerating voltage of 20 kV, chemical composition was examined using energy-dispersive X-ray analysis (EDX).

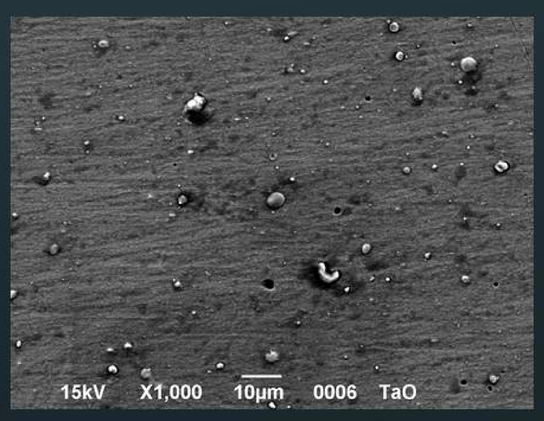
Energy dispersive spectrometer SPRUT-K (AO Ukrrentgen, Ukraine) was used for X-ray fluorescent analysis. Film thickness was determined by XRF examinations and comprised ~1.5 μm for both tantalum nitride and oxide samples.

The measurement of nonohardness was carried out with a Nanoindenter G200 nanoindentor from the USA, using Berkovich diamond triangular pyramid. 3-4 probes were applied on the sample at a distance of 15 μm from each other and the results were averaged.

Scanning Electron Microscopy



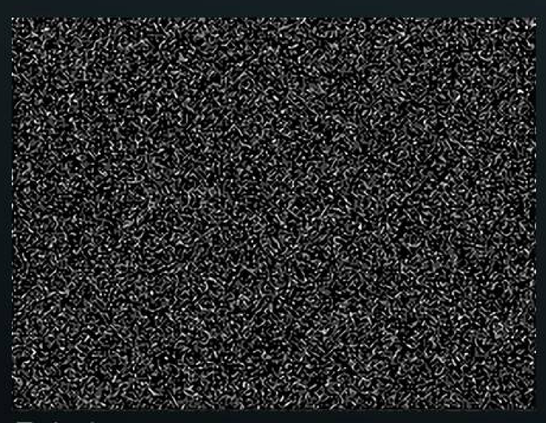
Surface morphology of TaN coating.



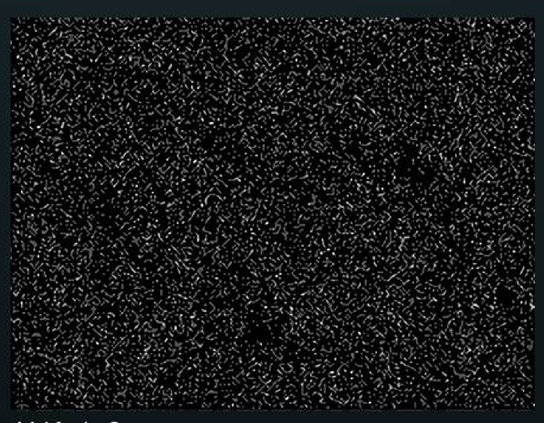
Surface morphology of Ta_2O_5 coating.

The surface morphology of TaN and Ta_2O_5 coated samples was examined by scanning electron microscopy. The surface of the coatings is typical for PVD-type deposition with some amount of macroparticles sized from 0.2 to 5 μm.

Energy Dispersive Spectroscopy



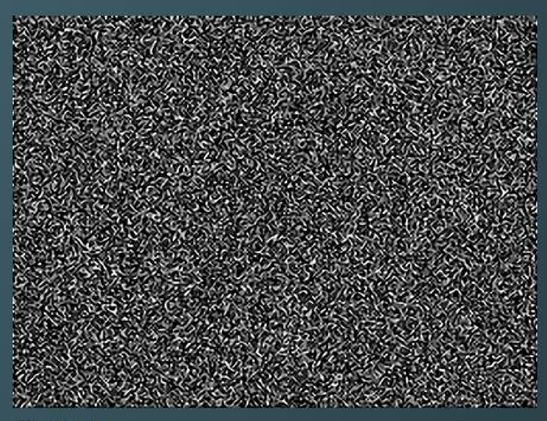
Ta La1



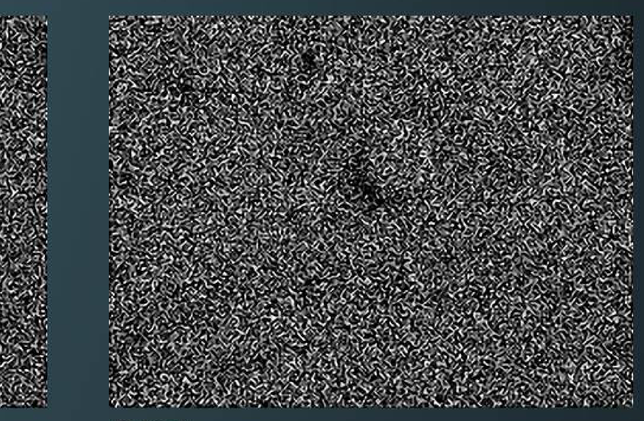
N Ka1_2

EDS mapping for TaN coating

Energy Dispersive Spectroscopy



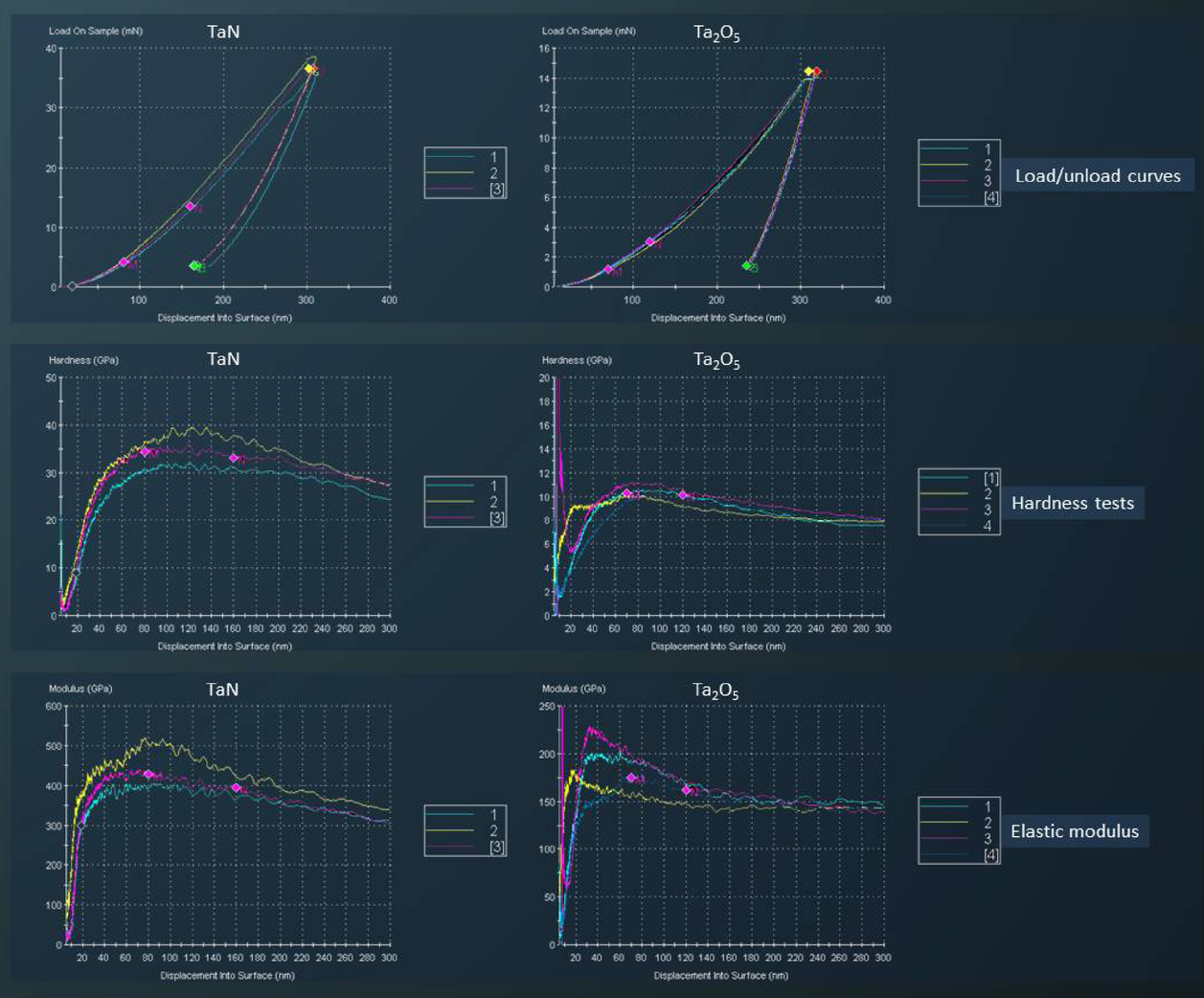
Ta La1



O Ka1

EDS mapping for Ta_2O_5 coating

Nanohardness



Physical-technical characteristics

Coating	Thickness, μm	Test	H/E	H^3/E^2	E*, GPa	H^3/E^{*2}	G, GPa	σ_T, GPa
TaN	1,5	1	0,080	0,198	415,65	0,174	243,55	10,36
		2	0,079	0,235	510,87	0,206	299,34	12,58
		3	0,084	0,245	436,92	0,215	256,01	11,51
		Mean	0,081	0,225	454,48	0,198	266,30	11,48
Ta_2O_5	1,5	1	0,057	0,033	195,46	0,029	114,53	3,47
		2	0,064	0,040	162,14	0,035	95,01	3,24
		3	0,059	0,038	196,46	0,034	115,12	3,64
		4	0,059	0,035	181,34	0,031	106,25	3,35
		Mean	0,060	0,037	183,85	0,032	107,73	3,43

Conclusions

The ability of the coating material to resist elastic deformation of fracture was evaluated by the H/E ratio. As a result of the research, it was found that the maximum elastic fracture strain is characteristic of the TaN coating and is 0.084. The coefficient of resistance to plastic deformation for the TaN coating is 6.08 times higher than for Ta_2O_5. Typical ratios for ceramics and cermets do not exceed 0.2 GPa. For the studied nanostructured TaN coating, the H3/E2 ratio reached 0.245, which, according to the literature data, may indicate high wear resistance. The maximum ability of the material to resist shape change while maintaining its volume reaches 299.34 GPa (for TaN). This indicator is much lower for the Ta_2O_5 coating and does not exceed 115.12 GPa. As a result of the analysis, it was found that the maximum stress that the TaN coating can withstand will be 12.58 GPa and, above which, the probability of its destruction may increase.

References

[1] Coatings 2017, 7, 209; doi:10.3390/coatings7120209 Microstructure and Mechanical Properties of TaN Thin Films Prepared by Reactive Magnetron Sputtering Anna Zaman ID and Efstathios I. Meletis*
[2] Hieber, K. Structural and electrical properties of Ta and Ta nitrides deposited by chemical vapour deposition. Thin Solid Films 1974, 24, 157–164. [CrossRef]
[3] Bhushan, B.; Gupta, B.K. Handbook of Tribology: Materials, Coatings, and Surface Treatments; McGraw-Hill Book Company: New York, NY, USA, 1991; p. 1168.
[4] Kim, S.K.; Cha, B.C. Deposition of tantalum nitride thin films by D.C. magnetron sputtering. Thin Solid Films 2005, 475, 202–207. [CrossRef]
[5] Sui, S.Y.; Chang, J.H.; Huang, H.H. Corrosion resistance and biocompatibility of titanium surface coated with amorphous tantalum pentoxide. Thin Solid Film. 2013, 528, 130–135.
[6] K. McNamara, O. Kolaj-Robin, S. Belochapkine, F. Laffir, A.A. Gandhi, S.A.M. Tofail Surface chemistry and cytotoxicity of reactively sputtered tantalum oxide films on NiTi plates Thin Solid Films, 589 (2015), pp. 1-7, 10.1016/j.tsf.2015.04.070
[7] Jh. Dhal, S. Bose, A. Banyopadhyay Influence of pentavalent dopant addition to polarization and bioactivity of hydroxyapatite [J. Mater. Sci. Eng. C Mater. Biol. Appl., 33 (5) (2013), pp. 3061-3068, 10.1016/j.msec.2013.03.043]
[8] Y.Y. Chang, H.L. Huang, H.J. Chen, Ch.H. lai, Ch.Y. Wen Antibacterial properties and cytocompatibility of tantalum oxide coatings J. Surf. Coat. Technol., 259 (2014), pp. 193-198 https://doi.org/10.1016/j.surfcoat.2014.03.061
[9] Misiruk I.O., Timoshenko O.I., Taran V.S., Garkusha I. E. Non-self-sustained discharge with hollow anode for plasma-based surface treatment. NUKLEONIKA 2016; 61(2): 195-199. doi: 10.1515/nuka-2016-0033