THE EFFECT OF NITROGEN PRESSURE DURING VACUUM-ARC TiN COATINGS DEPOSITION ON THE EROSOIN RESISTANCE IN PLASMA OF MAGNETRON TYPE DISCHARGES

G.P. Glazunov, A.A. Andreev, O.V. Sobol'[1]*, M.N. Bondarenko, A.L. Konotopskiy, V.A. Stolbovoy*

Institute of Plasma Physics NSC "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;
[1]*National Technical University "Kharkiv Politechnical Institute", Kharkiv, Ukraine*

E mail: glazunov@ipp.kharkov.ua

The erosion process was investigated of TiN coatings which were made with the vacuum-arc sputtering of Ti at the different nitrogen pressures ($10^{-4}…5·10^{-3}$ Torr). The erosion rates were measured by the weighting on analytical balance before and after treatment by plasmas of magnetron type, axial symmetrical discharges in nitrogen atmosphere, at the temperatures of 500…1100ºC. It was shown that an erosion rate of TiN coatings deposited at low pressures (~10^{-4} Torr) is essentially (up to 1.5 times) lower than that for coatings produced at the more high pressures ($5·10^{-3}$ Torr). For samples produced in the regime with high voltage pulses supply on substrate the erosion is lower than for coatings deposited in the regime without pulses supply. Taking into account the results of X-ray diffraction measurements, the physical mechanisms are suggested to explain such character of erosion behavior.

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INTRODUCTION

It was shown yearly [1-2] that nitrogen pressure during TiN coating deposition can strongly impact on film characteristics: micro-hardness (H), phase composition, concentration of nitrogen (C), etc. It is accepted as incorrect, to use e.g., TiN coatings produced at low nitrogen pressure as wearproof, due to their high brittleness[1-2]. But when one use TiN coatings in plasma devices, such criterions as erosion resistivity and thermocyclic resistivity are most important. It was shown in the work [3] that absolute value of erosion rates of TiN coatings deposited at low pressure can be essentially lower than that for samples produced at more high pressures. This result was explained by the difference in nitrogen concentration (C) in coatings produced at different pressures. But these data had preliminary character and was obtained only for two pressures ($2·10^{-3}$ and $5·10^{-3}$ Torr). So in this work more systematic investigations were carried out of an erosion behavior of TiN coatings deposited at different nitrogen pressures, including very low (10^{-4}Torr).

1. EXPERIMENTAL AND RESULTS

The experiments were carried out at the DCM-1 device (bench for diagnostic of materials under plasmas irradiation) under operating conditions of magnetron-type cylindrical-symmetry discharge [4]. The scheme of the experiment is clear in Fig. 1. The typical discharge parameters were as follows: magnetic field in the region of discharge ~ 0.05 T, working gas pressure 0.2 Pa, discharge voltage 0.55 kV, the discharge current varied within 60 to 180 mA (at the same time sample temperature was changed from 500 to 1100ºC). The Langmuir probe was used to measure the plasma column edge characteristics such as electron temperature T_e, electron density n_e, plasma potential φ , which determine according to method described in [5].

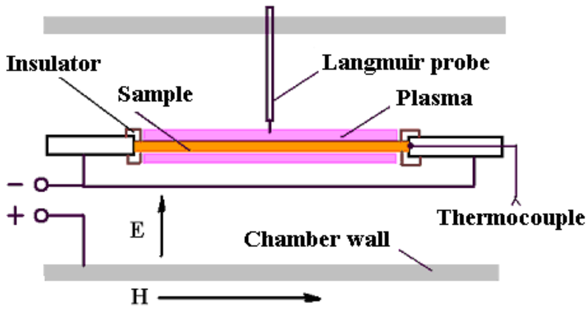


Fig. 1. Experiment scheme

The typical edge plasma characteristics of magnetron-type discharges in nitrogen atmosphere were: T_e ~ 10…20 eV, n_e ~ 10^9 cm^{-3}, φ ~ -100 V. The samples presented 200×10×0.3 mm straps from stainless steel 12Kh18N10T, on both sides of which 10…15 μm thick titanium nitride coatings were deposited by two different technologies: i) with feeding HV negative potential pulses to the substrate [6], and ii) without feeding the mentioned pulses (traditional technology [7]). TiN coatings were produced in "Bulat-6" device with two Ti vacuum-arc evaporators placed along horizontal axis of chamber, on its butt ends. It was prepared two series of samples. The first batch of samples was produced in the typical regime without supply of high-voltage (HV) pulses on substrate. In this case the current of arc discharge was 95 and 110 A, substrate potential was -230 V, nitrogen pressure in the chamber was changed from $1·10^{-4}$ to $5·10^{-3}$ Torr, deposition time was 3 hours. Coating thickness was calculated from overweight after deposition, and its absolute average values were 12.1 μm. The second serious of samples was produced under the same arc parameters and deposition time, but with feeding HV negative potential pulses to the substrate (-2000 V). Pulse duration was 10 ms, pulse-repetition frequency was 7 kHz. TiN coating average thickness in this case was 10.5 μm. It was prepared four batches of samples at the nitrogen pressures of $5{\cdot}10^{-4}$, 10^{-3}, $5{\cdot}10^{-3}$ Torr with feeding HV negative potential pulses to the substrate and four batches without supply of HV pulses. Color of samples made at the low pressures (~10^{-4} Torr) was straw, made at pressures $5x10^{-4}…10^{-3}$ Torr – golden-yellow and made at pressure $5x10^{-3}$ Torr – red-gold color.

The influence of nitrogen pressure during TiN coatings deposition on sputtering coefficient in plasma of magnetron type discharges in nitrogen is presented in Figs 2, 3. Axis of abscises in Fig. 2 is nitrogen pressure in "Bulat-6" device. Ordinate axis is sputtering coefficient multiplied on 10. In this figure the micro-hardness (H) literature data (blue circles) [1] and nitrogen concentration (C) in TiN (black circles) are shown, too. In the last case only character of nitrogen concentration behavior are presented but not its absolute value.

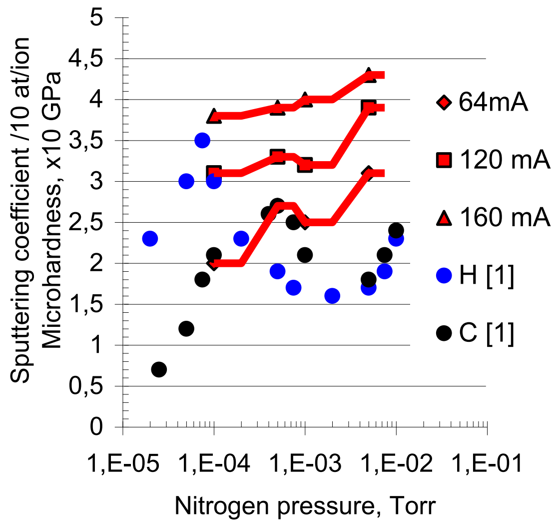


Fig. 2. Sputtering coefficient in plasma of magnetron type discharges in nitrogen vs nitrogen pressure during TiN coatings deposition (red curves)

Note, according to data of electron microscopy it was not essential difference in microstructure of the samples produced by different methods. But thickness of coatings made with the same time of deposition (3 hours) was essentially lower in the regime with supply of HV pulses: average value was 10.5 μm instead of 13.5 μm for regime without HV pulses supply. Here, for the case with HV pulses good agreement is observed between values of coating thickness determined from the data of electron microscopy and weight-loss method. TiN coatings produced without HV pulses have average thickness 12.1 μm, instead of 13.5 μm obtained from the electron microscopy data. So such films have about 10 % porosity. At the same time for the films deposited in regime with HV pulses on substrate the density is about theoretical one because the density value obtained from optical measurements is equal to value measured by weight loss method. Note, this conclusion is unrelated to coatings produced at the $5{\cdot}10^{-3}$ Torr pressure, when thickness and density of coatings produced by different methods are practically equal.

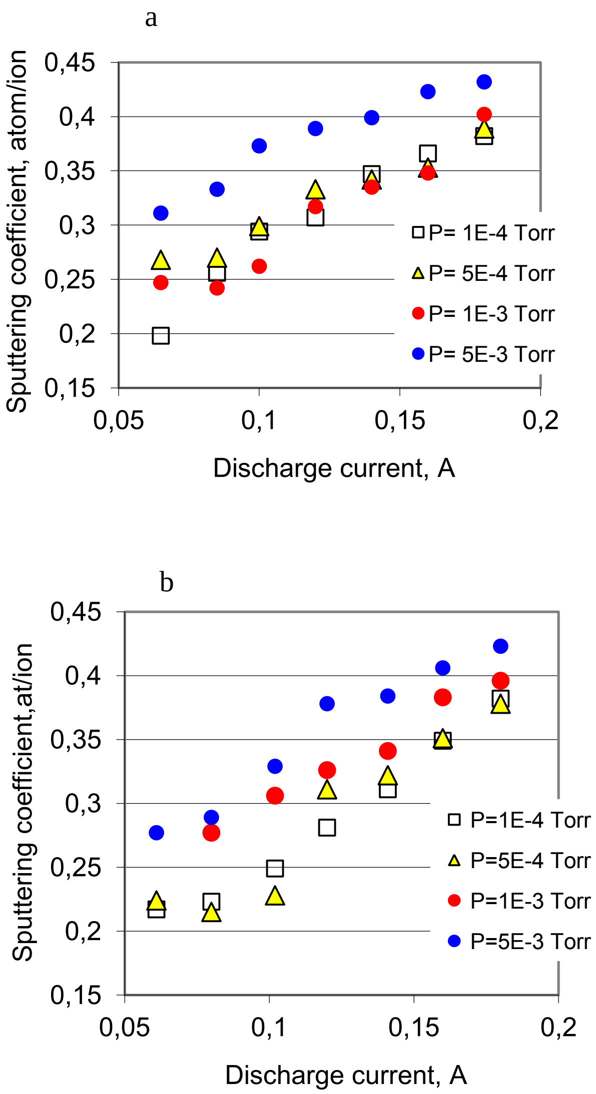


Fig. 3. Sputtering yield dependence on the discharge current value under impact of magnetron type discharges in nitrogen: (a) coatings were deposited at the various nitrogen pressure in regime without HV pulses on substrate;(b) the same, but with HV pulses supply

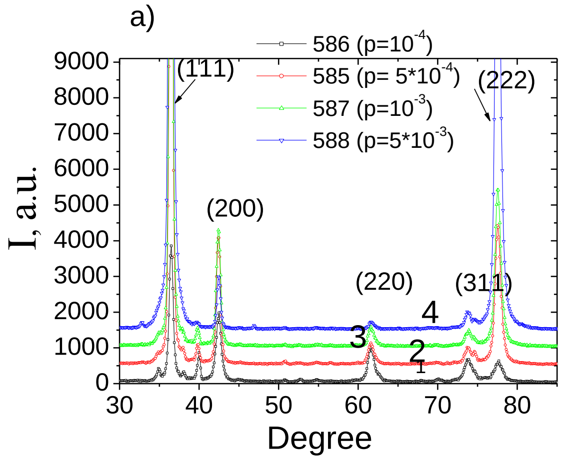
2. DISCUSSION

It is obvious from Figs. 2, 3 that low level of erosion is observed for TiN coatings deposited at low (~$1{\cdot}10^{-4}$Torr) pressures and not large values of discharge currents. The maximal magnitudes of erosion yield were observed for coatings produced at nitrogen pressure of $5{\cdot}10^{-3}$ Torr and high values of discharge current. Here the difference in erosion rate values decreases with discharge current value increase for both methods deposition. It is followed from Fig. 2 that erosion yield is minimal for samples with maximal micro-hardness (H). With nitrogen pressure increasing micro-hardness decreases and nitrogen concentration(C) in the samples increases. Here the erosion increases. Specially this effect is expressed at the rather low sample temperature (low currents). At 64 mA current (about 500ºC) the difference in erosion rate is about sesqui-time. In the ~10^{-3} Torr nitrogen pressure range erosion weakly changes as micro-hardness and nitrogen concentration (C) in the samples weakly depends on the pressure. Then erosion increases independently on the character of behavior of micro-hardness and nitrogen concentration (C). Note, that at the such different pressures as 10^{-4} Torr and 10^{-3} Torr concentration of trapped nitrogen atoms practically is the same, and erosion yield differs in sesqui-time. So the reason of erosion decreasing is not nitrogen concentration in TiN coating, but different structure, crystal grain dimension and macro-, micro-deformations of the samples deposited at different nitrogen pressures.

The analysis of TiN coating structure state by the X-ray diffraction method had shown that the TiN cubic phase with NaCl type crystal grating determines the phase state. With nitrogen pressure increase the transition is observed from random-orientation state to textured state with the main crystal grain orientation along the axis [111] (the specters 1 and 4 in Fig. 4). For HV pulse regime the width of peaks is less, that says about more high perfection of texture. The analysis of substructure characteristics (crystal grain dimension, micro-deformation), carried out from the change of peak widths, had shown that crystal grain dimension increases from 50 to 59 nm and from 35 to 71 nm , accordingly, for regimes with HV pulses and without pulses. Micro-deformation in the grain decreased with nitrogen pressure increase from 0.45 to 0.29% and from 0.39 to 028%, accordingly, for pulsed and non-pulsed regimes. Macro-deformation state of tension, determined by "a-sin$^2\psi$"- method [9, 10] increased with nitrogen pressure increase from -1,3 to -1,9 % in the case of HV pulsed regime and from -0,9 to -1,85 % in non-pulsed regime.

By the data of X-ray diffraction method investigations, with nitrogen pressure increase the transition is observed from random-orientation state to textured state with the main crystal grain orientation along the axis [111]. It could be reason for coating hardness and density changes. What about micro-hardness (H) of the samples produced in the work, this parameter for samples deposited in HV pulse regime is higher on 30% than for samples made in regime without HV pulses supply. Possible, it is caused by high density of such coatings.

Note, that examined TiN coatings produced at low nitrogen pressure has not only low level of sputtering in plasmas, but are resisted to thermal cycling. In special experiments it was shown the resistibility to thermal cycling for such coatings is not worse than for coatings deposited at more high pressures. After more than 10 thermal cycles (heating to 1000^0C and next cooling to room temperature) it was not found any damages – micro cracks, shelling, etc.



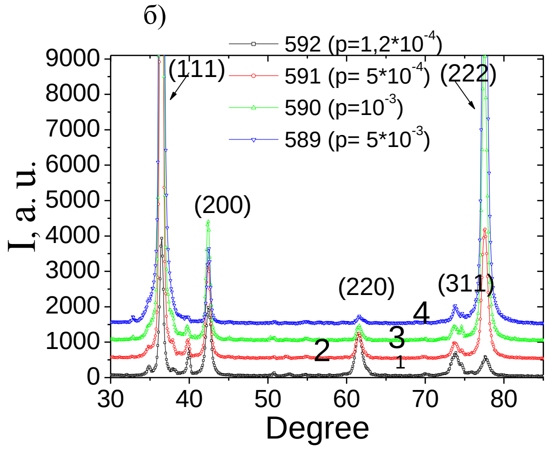


Fig. 4. Diffraction specters of TiN coatings produced in non-pulsed (a) and HV pulsed regimes (b) in dependence on nitrogen pressure: 1 – 10^{-4} Torr; 2 – $5\cdot10^{-4}$ Torr; 3 – 10^{-3} Torr; 4 – $5\cdot10^{-3}$ Torr

CONCLUSIONS

The erosion rate of TiN films deposited at low nitrogen pressures (~$1\cdot10^{-4}$ Torr) essentially (up to 1.5 times) lower, than that for the coatings deposited at more high pressures ($5\cdot10^{-3}$ Torr). Taking into account the results of X-ray diffraction measurements such erosion behavior can be caused by different texture and levels of micro and macro-deformations of TiN coatings deposited at the different nitrogen pressures. For samples produced in the regime with supply of HV pulses the erosion is lower than that for coatings deposited in the regime without HV pulses on substrate. It could be caused by more complete texture and high (up to theoretical one) density of TiN films deposited in regime with HV pulses. Resistibility to thermal cycling for examined coatings is not worse than for coatings deposited at more high pressures. So, from the point of view of TiN coatings use in plasma devices, the nitrogen pressure range during coatings deposition in the "Bulat" type devices could be determined as ~10^{-4} Торр.

REFERENCES

1. I.I. Aksyonov, Yu.N. Antuf'ev, V.G. Bren', et al. The influence of gas pressure in reaction volume on process of nitrides synthesis under metal plasma condensation // *Chemistry of high energies*. 1986, v. 20, № 1, p. 82-86.
2. A.A. Andreev, A.P. Sablev, S.N. Grigor'ev. *Vacuum-arc coatings*. Kharkov: NSC KIPT, 2010, p. 318.
3. G.P. Glazunov, A.A. Andreev, M.N. Bondarenko, A.L. Konotopskiy, V.E. Moiseenko, V.A. Stolbovoy. Erosion of vacuum-arc TiN coatings and stainless steel under impact of plasma of magnetron-type stationary discharges // *Physical surface engineering*. 2011, v.9, № 3, p. 250-255.
4. G.P. Glazunov, M.N. Bondarenko, A.L. Konotopskiy, et al. Erosion behavior of tungsten coatings in magnetron type discharges with hot cathode // *Problems of Atomic Science and Technology. Series "Plasma Physics"*. 2008, № 6, p. 107-109.
5. P.C. Stangeby and G.M. McCracken. Plasma boundary phenomena in tokamaks // *Nucl. Fusion*. 1990, v. 30, № 7, p. 1225-1379.
6. A.A. Andreev, V.M. Shulaev, B.F. Gorban', V.A. Stolbovoy. Deposition of super hard vacuum-arc TiN coatings // *Physical surface engineering*. 2004, v. 3,4, № 3, p. 179-183.
7. I.I. Aksenov, A.A. Andreev, A.A. Bren', et al. Coatings produced by condensation of plasma flows in vacuum (method of condensation with ion bombardment) // *Ukrainien physical J.* 1979, v. 24, № 24, p. 515-525.
8. L.S. Palatnik, M.Ya. Fuks, V.M. Kosevich. *Mechanism of forming and sub-structure of condensated films*. Moscow: "Science", 1972.
9. A.P. Shpak, O.V. Sobol', Yu.A. Kunitskiy. Mechanisms of forming of phase-structural state of condensates deposited by ion sputtering // *Advance of metal physics.* 2008, v. 9, № 3, p. 357-370.
10. G.P. Glazunov, E.D. Volkov, D.I. Baron, et al. Effect of low/high hydrogen recycling operation on palladium sputtering under steady state plasma impact // *Physica Scripta.* 2003, v. 103, p. 89-92.

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ВЛИЯНИЕ ДАВЛЕНИЯ АЗОТА ПРИ ОСАЖДЕНИИ ВАКУУМНО-ДУГОВЫХ ПОКРЫТИЙ TiN НА ИХ ЭРОЗИЙНУЮ СТОЙКОСТЬ В ПЛАЗМЕ РАЗРЯДОВ ТИПА МАГНЕТРОНА

Г.П. Глазунов, А.А. Андреев, О.В. Соболь, М.Н. Бондаренко, А.Л. Конотопский, В.А. Столбовой

Исследован процесс эрозии TiN-покрытий, полученных вакуумно-дуговым распылением титана при различных давлениях азота ($10^{-4}…5\cdot10^{-3}$ Торр). Скорости эрозии измерялись методом взвешивания на аналитических весах до и после плазменной обработки в атмосфере азота при температурах 500…1100ºC. Обнаружено, что скорость эрозии TiN-покрытий, осажденных при низких давлениях ($\sim1\cdot10^{-4}$ Торр), существенно (до полутора раз) ниже, чем для покрытий, нанесенных при более высоких давлениях азота ($5\cdot10^{-3}$ Торр). Для образцов, полученных в режиме с подачей импульсов на подложку, эрозия в среднем несколько ниже, чем у покрытий, осажденных в безимпульсном режиме. С учетом результатов исследований покрытий методом рентгеновской дифракции предложены и обсуждаются возможные физические механизмы для объяснения такого характера поведения эрозии.

ВПЛИВ ТИСКУ АЗОТУ ПРИ ОСАДЖЕННІ ВАКУУМНО-ДУГОВИХ ПОКРИТТІВ TiN НА ЇХ ЕРОЗІЙНУ СТІЙКІСТЬ У ПЛАЗМІ РОЗРЯДІВ МАГНЕТРОННОГО ТИПУ

Г.П. Глазунов, А.А. Андрєєв, О.В. Соболь, М.Н. Бондаренко, А.Л. Конотопський, В.А. Столбовий

Досліджено процес ерозії TiN-покриттів, отриманих вакуумно-дуговим розпилюванням титану при різному тиску азоту ($10^{-4}…5\cdot10^{-3}$ Торр). Швидкості ерозії вимірювалися методом зважування на аналітичних вагах до і після плазмової обробки в атмосфері азоту при температурах 500…1100ºC Виявлено, що швидкість ерозії TiN-покриттів, осаджених при нижчому тиску ($\sim1\cdot10^{-4}$ Торр), істотно нижче, ніж для покриттів, нанесених при вищому тиску азоту ($5\cdot10^{-3}$ Торр). Для зразків, отриманих у режимі з подачею імпульсів на підкладку, ерозія в середньому декілька нижча, ніж у покриттів, осаджених у безімпульсному режимі. З урахуванням результатів досліджень покриттів методом рентгенівської дифракції запропоновані і обговорюються можливі фізичні механізми для пояснення такого характеру поведінки ерозії.