Modification of TiN_x coatings in the course of deposition by periodic electron beam stimulation of N_2/Ar medium

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Contents

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Introduction

Hard single-layer coatings based on TiN are characterized by high hardness and low impact elasticity, which decreases the effectiveness of their use under shocks impacts, i.e. for protection of the compressors blades of turbine engines from abrasive erosion [1].

Using multilayer coatings (MLC) with alternation of soft and hard layers Ti/TiN provides decrease of the level of intrinsic stresses and hampers the cracks propagation [2].

Traditional PVD methods of deposition of multilayer Ti/TiN coatings based on periodic change of N_2 partial pressure for controlling the layers properties are inertial.

Alternatively, periodic change of plasma parameters at the same N_2 flow can influence the phase composition of coatings by changing of active N_2 concentration [3].

1. D.A.Glocker, S.I.Shah (Eds), Handbook of thin film process technology, V.2, IOP Publishing, Bristol and Philadelphia,1995.

2. V.Bonu,M.Jeevitha,V.P.Kumar, H.C. Barshilia // Surf. Coat. Technol.,vol.35715,p.204-211, 2019.

3. O.V.Krysina, V.V.Shugurov, N.A.Prokopenko // Proc. of Int. Sci. and Tech. Conference. Modern Technologies and Advanced Materials, TPU, Tomsk, Russia, 2017, p.182-184

Introduction

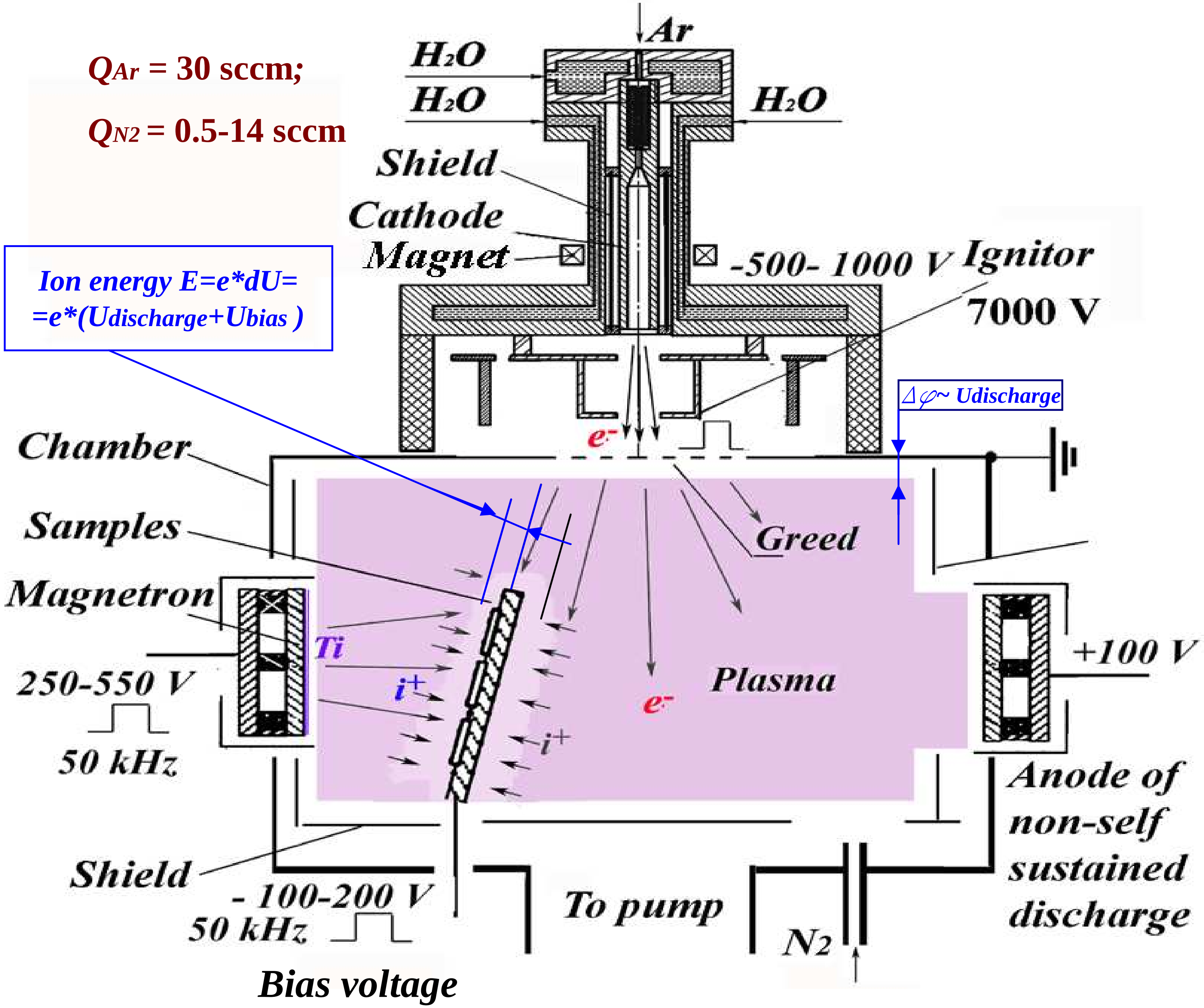
The present work is devoted

to study of the effect of injection of wide (100 cm^2) low energy (100-150 eV) high current (>10 A) electron beam into plasma of magnetron discharge in Ar/N_2 mixture on properties of TiNx coatings.

to deposition of multilayer coatings based on titanium nitride and investigation of TiNx/TiN composition with thin layer thickness 6-150 nm obtained under conditions of periodic ionizing of gas medium with low partial pressure of nitrogen by electron beam.

The aim of work was to research an application of high-current non-self-sustained discharge supported by electron emission of a plasma cathode based on discharge with self-heated hollow cathode for pulse-periodic stimulating of gas medium simultaneously with reactive magnetron deposition for production of nanostructural multilayer coatings with the minimal thickness of interlayer interface.

Experimental setup



An ion current density from plasma of NSS discharge is mach more than one of electron beam plasma

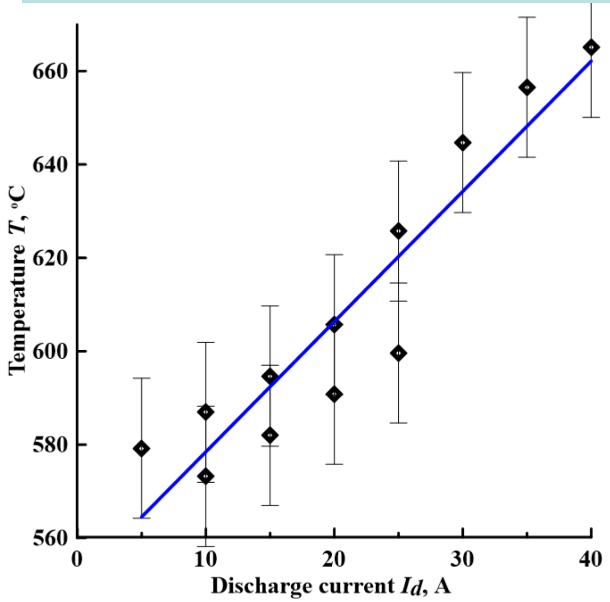
-The one-layer coatings of Ti or TiN_x were deposited for 30 min from ~ 5 (Ti) till ~1.5 (TiN_x)μm thick.

- *Wide electron beam was emitted by discharge with self-heated cathode into working chamber .*
E=100 eV , S= 100 cm²
and I= 5-15 A.

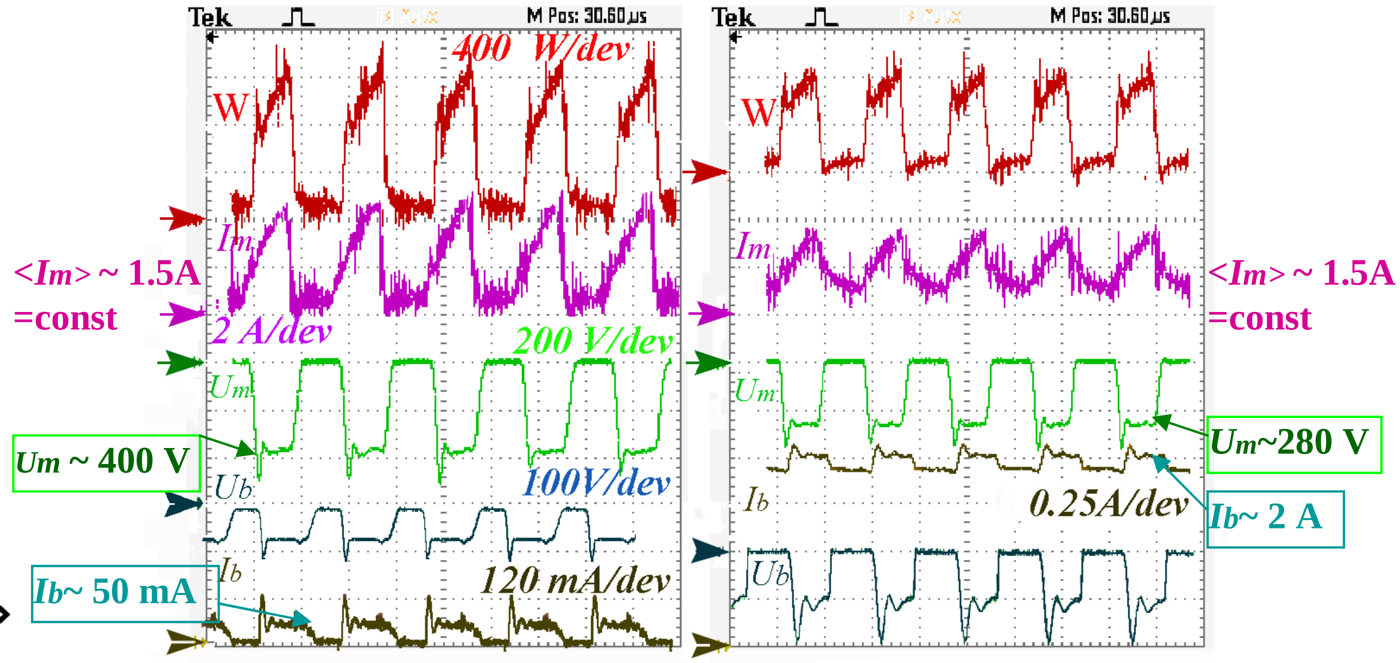
- *Non-self-sustained (NSS) discharge*
(I_d=15-40 A, U_d=100 V)
was initiated by this electrons oscillated in working chamber, which serves as hollow cathode.

Experimental conditions

Samples temperature and ion current density vs. non-self-sustained discharge current



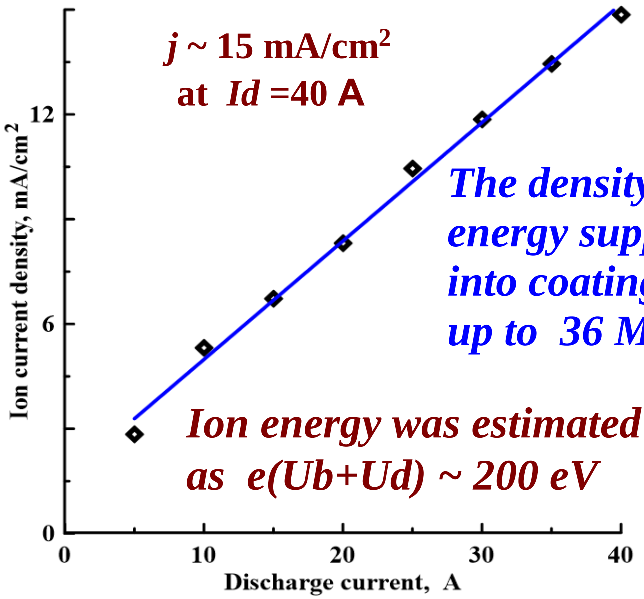
Voltage and current oscillograms of magnetron discharge (*Um* and *Im*), of bias (*Ub* and *Ib*) and of calculated magnetron power W = *Im* x *Um*



f **= 50 kHz, *P*~ 0.25 Pa, Q_{Ar} = 30 sccm.**

Without plasma ***With plasma. Id=35 A***

The plasma of NSS-discharge caused a decline of the magnetron discharge voltage (till 400-250 V) and, as result, decrease of the deposition rate.



j ~ 15 mA/cm²
at *Id* =40 A

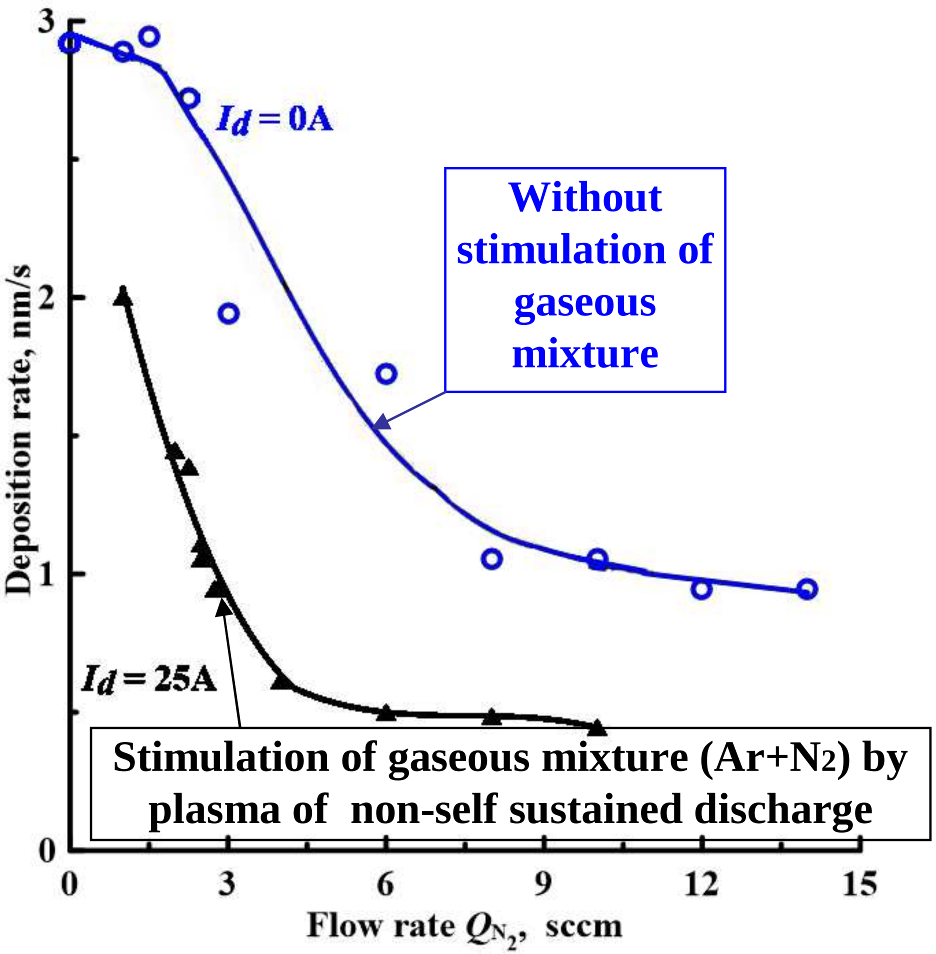
The density of energy supplied into coatings was up to 36 MJ/cm³.

Ion energy was estimated as e(Ub+Ud) ~ 200 eV

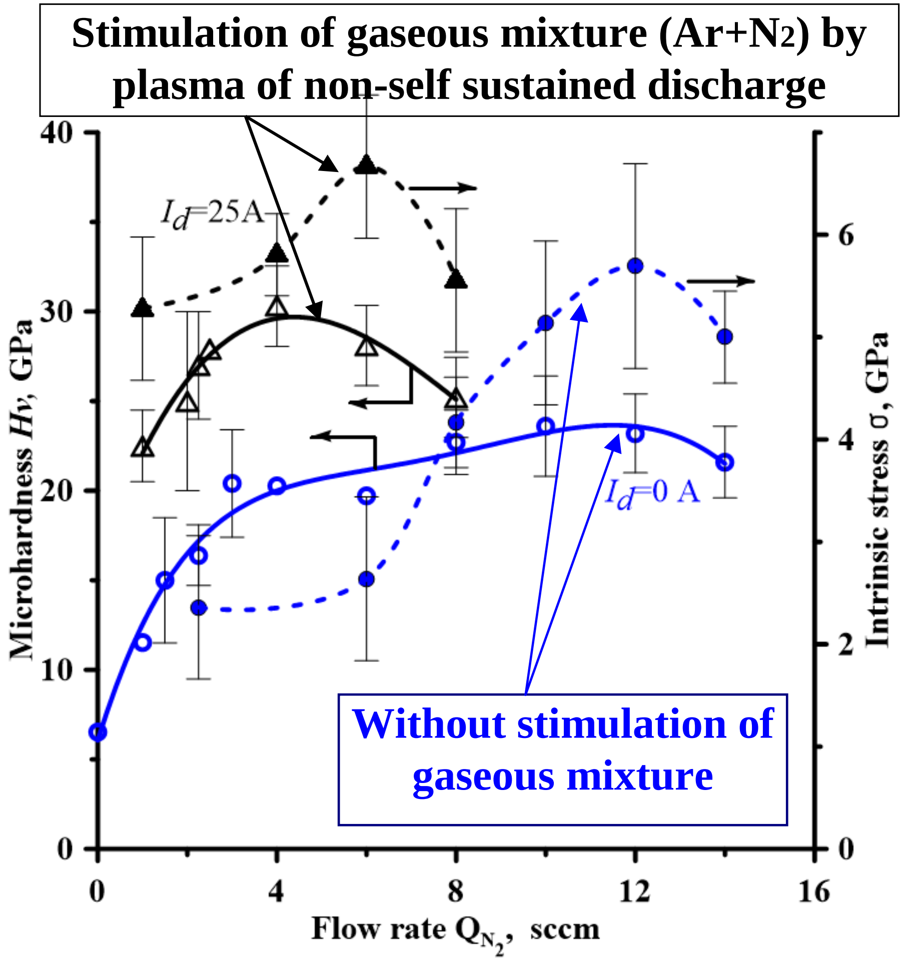
Ion current density on substrate from plasma of NSS glow discharge was estimated by both methods: from bias current and from radiating power calculated from temperature of samples.

Properties of single-layer TiNx coatings

Deposition rate of TiNx vs. nitrogen flow



Microhardness *Hv* and intrinsic stresses coatings vs. nitrogen flow rate



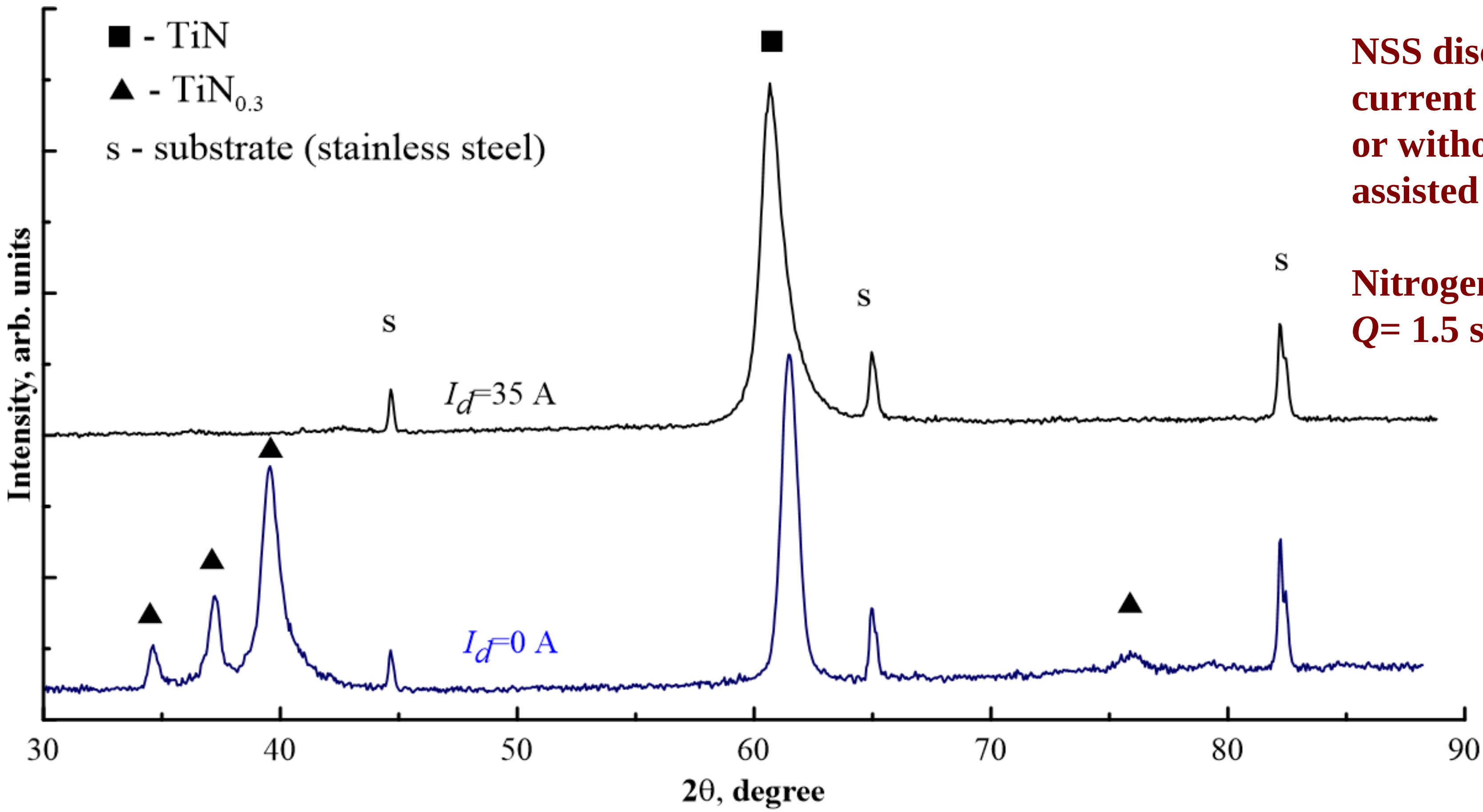
NSS discharge current *Id* = 25 A or 0A.

The shift of maximums of stresses and hardness towards the region of low nitrogen flow rate was induced by intensive ion assisting. The growth of intrinsic stresses connected with initiation of structural defects, crystal lattice distortion, changes in grain size or additional phase's formation etc.

In our experiments, at low nitrogen flow rate 2.25 sccm and ion current density 10 mA/cm² cubic titanium nitride with microhardness 27 GPa was obtained.

Properties of single-layer coatings

X-ray diffraction patterns of one-layer coatings



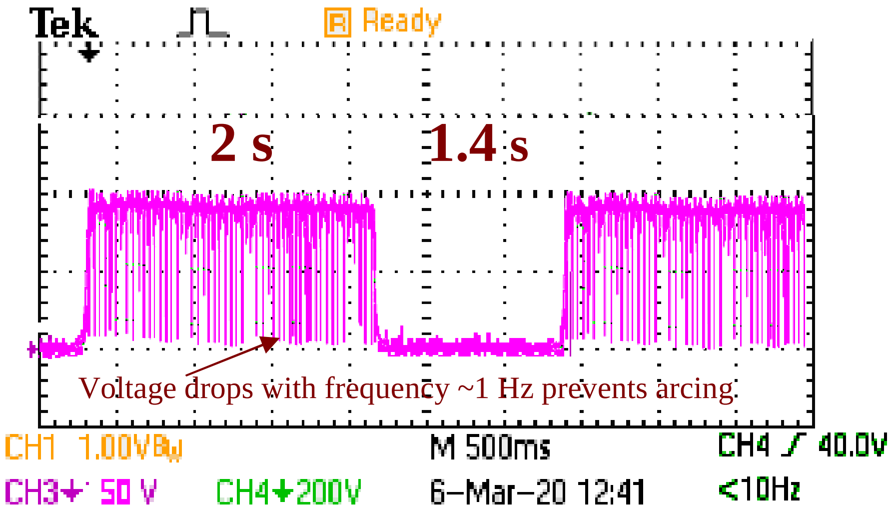
NSS discharge current *Id* = 35 A or without ion assisted deposition

Nitrogen flow rate *Q*= 1.5 sccm.

Generation of dense plasma with enhanced content of active nitrogen (atomic and ionized) and intensive ion bombardment of the coating during deposition provide formation of the phase of cubic TiN at lower nitrogen flows. Single-layer with the non-stochiometric phase of $TiN_{0.3}$ is formed without ion assisting at the same low nitrogen partial pressure.

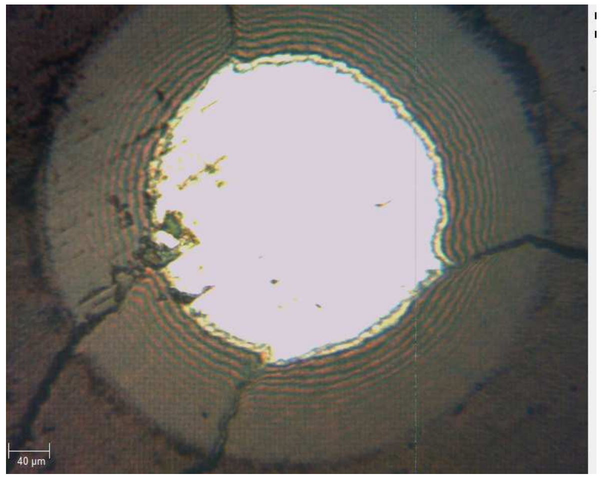
Multilayer coatings deposition

Typical oscillogram of pulse-periodic voltage *Ud* of non-self-sustained discharge



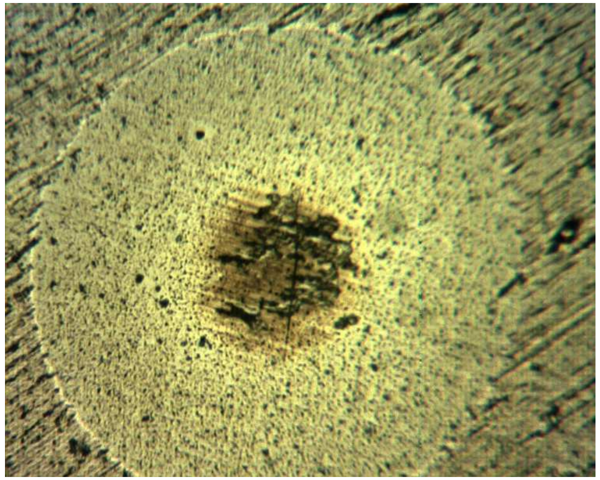
The formation time non-self sustained discharge from the moment of voltage pulse initiating Ud and falling edge of the current pulse did not exceed 100-150 ms.

Optical images of the Calotest ball impresses on multilayer coatings



0.55 mm x 0.45 mm

Double layer ($TiN+TiN_x$) thickness h_D ~ 200 nm. Time of pulse *tpulse* is 70 s; time of pause *tpause* - 33 s.

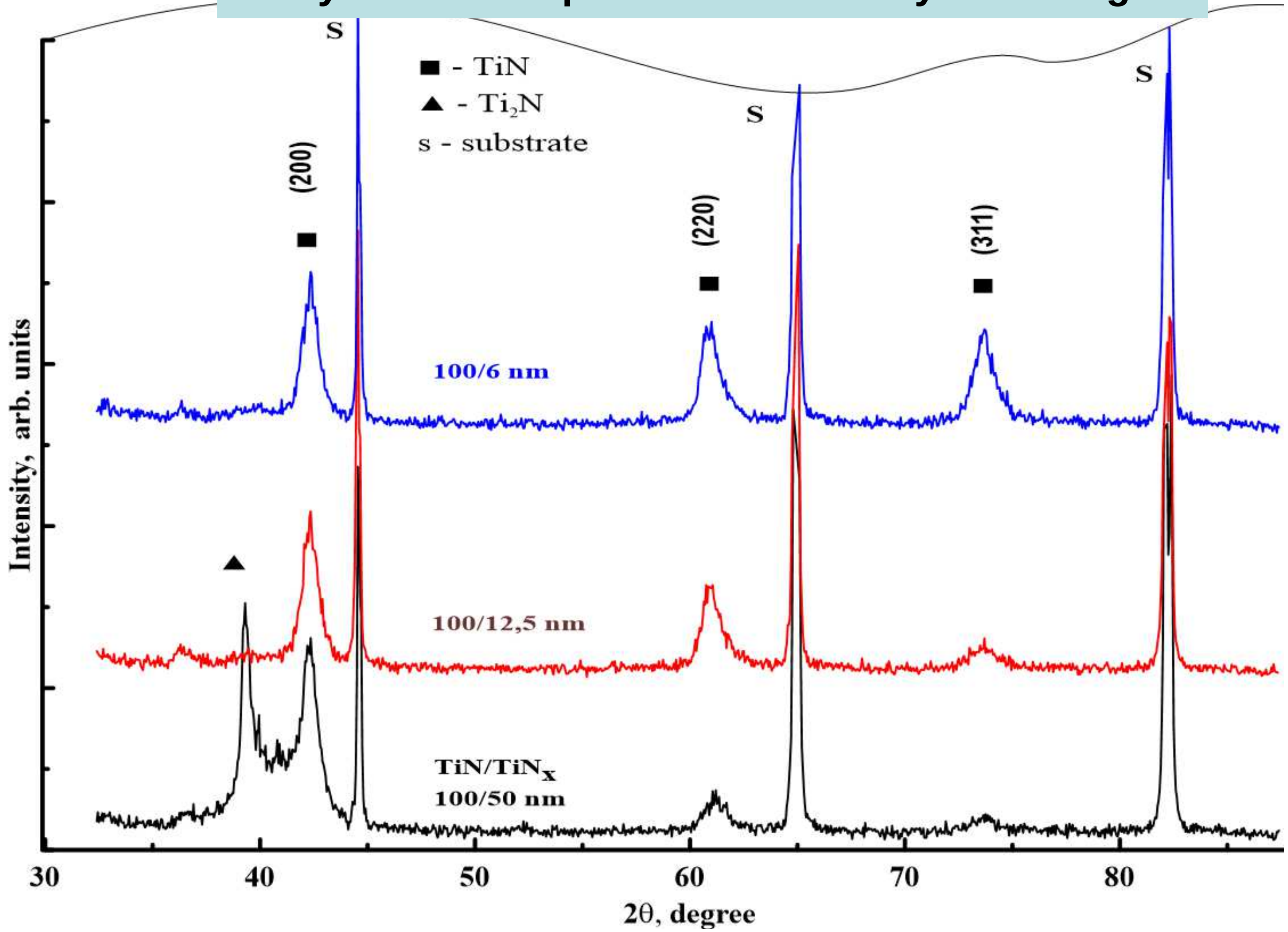


h_D ~ 51 nm; *tpulse* = 18 s; *tpause* = 8 s

During multilayer coating deposition the alternation of hard and soft layers (TiN/TiN_x) of the given thickness was achieved by change of pulse duration of the NSS discharge and of pause between the impulses.
Interlayer's interfaces at fast time of discharge formation were not exceed some nanometers.

Multilayer coatings characteristics

X-ray diffraction patterns of multilayer coatings



Nitrogen flow rate
Q = 1.75 sccm.

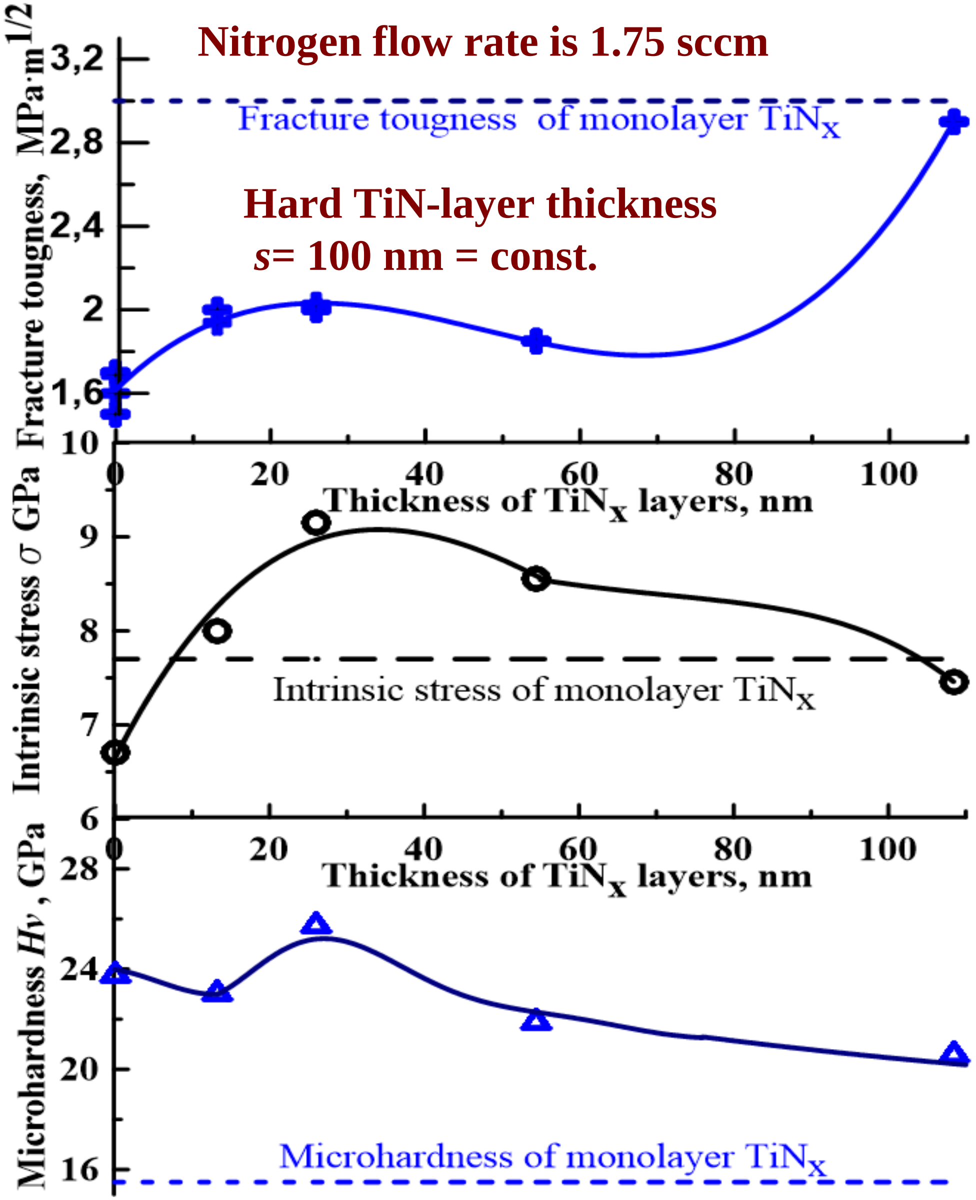
Hard TiN-layer thickness
s= 100 nm = const.

The size of CSR in TiN layer with reduction of thickness of soft TiNx layer from 50 till 6 nm increases from ~ 17 till 20 nm.

At lower thickness of the soft non-stoichiometric titanium nitride TiNx layers the coating becomes one-phase (TiN).
Phase $TiN_{0.3}$ was modified into tetragonal phase $TiN_{0.5}$.
Obviously, the intensive ion flux and high temperature of samples caused a nitrogen diffusion from TiN layers into TiNx layers.

Multilayer coatings properties

Hardness, intrinsic stresses and critical coefficient of stress intensity (fracture toughness) of TiN/TiNx coatings vs. thickness of soft TiNx-layer



MLC hardness did not exceed that of one-layer TiN deposited with ion assistance.

The main positive effect of the use of multilayer structure is the increase of fracture toughness.

The increase of thickness of soft layer TiNx of non-stoichiometric titanium nitride allowed to rise the critical coefficient of stress intensity up to 2.9 MPa·m$^{1/2}$.

Conclusion

- The injection of low energy (100-150 eV) electron beam (up to 11A) leading to ignition of non-self-sustained discharge with hollow cathode (up to 40 A) in the working volume of magnetron system for stimulation of gaseous medium was realized.

- High ion current density from Ar/N_2 plasma (up to 15 mA/cm^2) on substrate and high power input density to deposited coating (up to 36 MJ/cm^3) were achieved.

- It is shown, that ion assisted deposition by reactive magnetron sputtering leads to a change in the composition of nitride coating from $TiN_{0.3}$ to TiN at low partial pressure of nitrogen in gas mixture.

- Using pulse-periodic mode of electron beam generation at fixed low nitrogen flow, multilayer nanocrystal TiNx/TiN coatings (MLC) with widely regulated ratio of layer thickness (6-100 nm) were obtained.

- This MLC differ significantly in microhardness and the structure of crystal lattice and possess increased fracture toughness.

- The reduction of TiN coating hardness along with the decrease of nitrogen flow rate restricts the possibilities of such method for hard multilayer TiN/TiNx coatings deposition.


Thank you for attention!
HVPS-25/200