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ENERGY AND MASS DISTRIBUTIONS OF IONS DURING DEPOSTITION OF TiN BY TRIODE ION PLATING IN BAI 730 M

ENERGIJSKE IN MASNE PORAZDELITVE IONOV MED DEPOZICIJO TiN v TRIODNEM SISTEMU BAI 730 M

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On the basis of the results of the energy and mass spectroscopy it was found that low voltage arc in combination with the arrangements of electrodes and coils to form the weak mirror magnetic vessel very efficiently ionize the gas and evaporate metal species in triode ion plating system BAI 730 M. Results show that the 95% of the Ti ion flux during the deposition of TiN consists of double charged Ti^{++} ions accelerated toward the substrate with energies from 90 to 120 eV. The rest (≈5%) of Ti ions have energies from 45 - 60 eV (Ti^{+}) and about 0.1% even have energies over 135 eV.

Key words: plasma spectroscopy, TiN, ion plating

Na osnovi rezultatov energijske in masne spektroskopije smo ugotovili, da je možno v triodnem depozicijskem sistemu BAI 730 M z nizkonapetostin lokom s kombinacijo elektrod in tuljav na način, ki formira šibko zrcalno magneto posodo, zelo efektivno ionizirati plin in izparevati kovine. Rezultati kažejo, da 95% ionskega toka predstavljajo dvakrat nabiti ioni Ti^{++}, ki bombardirajo površino podlag z energijo 90-120 eV. Ostanek (≈5%) so enkrat nabiti ioni Ti^{+} z energijo od 45-60 eV, medtem ko je delež trikrat nabitih ionov Ti^{3+} energijo preko 135 eV okrog 0,1%.

Ključne besede: spektroskopija plazme, TiN, ionsko prekrivanje

1 INTRODUCTION

Low pressure plasma is a basic media used in triode ion plating systems for preparation of hard coatings like TiN, CrN and Ti(C,N). The triode ion plating system (Balzers BAI 730) uses a filament-based ionization source. It forms a low voltage (LV) arc, which expands into the vessel. Such plasma is an efficient source of low energy electrons, used primarily for enhancing the ionization during deposition, secondary as an efficient heating source and thirdly as a source of electrons for the melting of evaporation material. Argon ions from LV arc plasma are also used for physical cleaning of the substrate surfaces needed to assure good adhesion of hard coatings. Heating and etching processes by the LV arc plasma are used prior to the deposition itself to improve the coating adhesion and microstructure[1,2,3].

The processes on the surfaces of the substrates during heating, etching and deposition depend strongly on the mass and energy distribution of the principal species in plasma, especially of the heavy particles. The mass and energy distributions are influenced by arc current, pressure in the chamber as well as the overall chamber geometry and plasma confinement in the chamber by the variable magnetic field.

This paper compares mass and energy distributions of ions during heating, etching and deposition sequence of the standard TiN thin film deposition process as measured by an energy-resolved mass spectrometer. Plasma parameters were determined by the standard Langmuir probe diagnostics[4].

2 EXPERIMENTAL

Description of the system

The energy distribution of positive ions was measured in the commercial triode ion plating systems Balzers BAI 730 M schematically represented in **Figure 1**. The system consists of an axially symmetrical vacuum vessel containing a crucible, an auxiliary anode and substrate holders with substrates. Two Helmholtz coils producing an axial magnetic field are placed at the top and bottom of the vessel. Centrally on the top of the system a filament-based ionization source forms the LV arc. The power supply for the LV arc is electrically floating with respect to the chamber walls. Its negative pole is connected to the arc cathode, while the positive one can be connected to different anodes, depending on the operation mode (heating, etching and evaporation).

During the heating mode the substrates serve as the anode for the LV arc. In the etching mode the primary electron flux is directed to the auxiliary anode and ions produced in the plasma are extracted by a negative potential to the substrates. After etching, the crucible is connected in the way to form the anode of the arc discharge. The LV arc is focused by the axial magnetic field

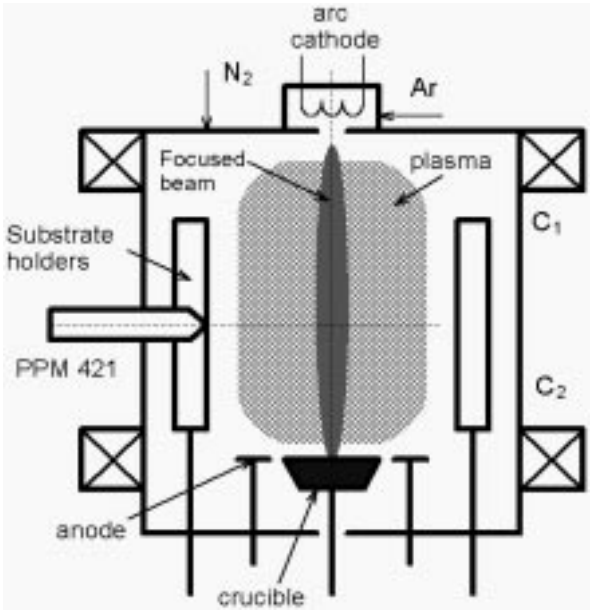

Figure 1: Scheme of the triode ion plating system Balzers BAI 730 M
Slika 1: Shematični prikaz triodnega depozicijskega sistema Balzers BAI 730 M

and directed towards the crucible containing the metal (Ti) to be melted (evaporation mode).

For TiN deposition, titanium is evaporated in a mixture of argon and nitrogen gases. The Ar inlet is in the LV ionization source chamber and N_2 comes directly into the main vessel through the chamber wall. The crucible is surrounded by the auxiliary anode in the form of a concentric ring with the outer diameter of 26 cm. This anode is used mainly for etching and it is electrically floating during the deposition.

The spectrometer is located at a side of the chamber in the middle of its height at the analyzer axis is horizontal, crossing the chamber axis. The entrance electrode of the spectrometer is located 1 cm behind an aperture with 5 mm hole which serves also as an shutter. This aperture is electrically connected to substrates and lined with the inner circle of the dummy substrates approximately 20 cm from the center axis.

The standard parameters and measured voltages on the crucible and the auxiliary anode for heating, etching and deposition are summarized in **Table 1**.

Energy and mass spectrometry

The energy distributions of positive ions was measured using the energy and mass analyzer Balzers PPM 421. The orifice of the energy and mass analyzer was grounded. The ions are focused by the ion optics, filtered by the cylindrical mirror energy analyzer and then pass through the quadrupole mass analyzer. The secondary electron multiplier counts the ions. It can give readings from 0.1 to 10^7 counts per second (CPS). More details are given in ref.[3].

The analyzer can perform a mass scan at selected ion energy or an energy scan at selected mass numbers. The measured energy spectrum is actually a spectrum of stopping potential, and for multiple charged ions the real energy is the product of the stopping potential and the ion charge.

3 PPM ENERGY SPECTRA FOR STANDARD CONDITIONS

Energy spectra of $Ar^{+,++}$ ions (m/q = 40, 20) and other important positive ions for standard heating, etching and TiN deposition are represented in **Figure 2**.

Energy spectra for standard heating

The energy spectrum measured during the heating mode **(Figure 2a)** reveal besides the single and double charged Ar ions, (Ar^+, m/q = 40 and Ar^{++}, m/q = 20), high concentration of water (H_2O^+, m/q = 18), oxygen (O^+, m/q = 16) and nitrogen (N^+, m/q = 14). As the result of high temperature inside the vessel, final temperature reaches values over 300°C after 30 min, the intensity of water, oxygen and nitrogen decreases for more than one decade.

The peak of the energy distribution is close to the highest positive potential in the chamber. In the case of heating this is the potential of the substrates. The reason for the second peak at around 35 eV is most probably related to some kind of discrimination in the spectrometer.

Energy spectra for standard etching

The energy spectrum in **Figure 2b**, measured during standard etching step, shows beside the single and double charged Ar ions also the presence of Ti ions (Ti^+, m/q = 48, Ti^{++}, m/q = 24) from TiN deposited on the substrate holders. Ti ions appear after a certain period. As the in-

Table 1: Parameters and measured voltages parameters for standard operating conditions

Mode	p_{Ar} (mbar)	p_{N2} (mbar)	I_{arc} (A)	I_{coil} (A)	crucible position (cm)	$U_{substr.}$ (V)	U_{arc} (V)	U_{anode} (V)	$U_{cruc.}$ (V)
Heating	2.5E-03	/	150	8/8	bottom	14	49	-0.6	-12.5
Etching	1.5E-03	/	130	8/8	bottom	-130	55	8.3	-20.6
TiN Deposition(1)	1.5E-02	5.0E-03	200	15/15	bottom	-125	56	50	53
TiN Deposition(2)	1.5E-02	5.0E-03	200	13/13	top,z=14.5	-125	56	50	53

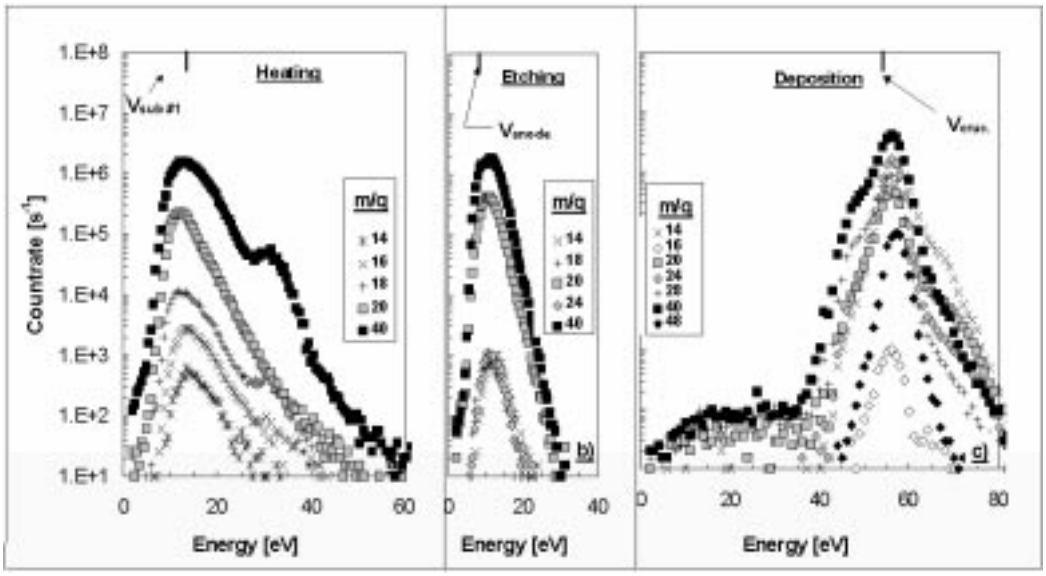

Figure 2: Energy spectra of various positive ions for standard heating: (a), etching (b) and TiN deposition process (c)
Slika 2: Energijski spektri raznih pozitivnih ionov med standardnimi postopki gretja (a), jedkanja (b) in depozicije TiN (c)

tensity of Ti ions increase the intensities of water and oxygen ions decrease for more than 3 decades, indicating the efficiency of the etching process.

As in case of the heating, the peak is close to the highest potential in the chamber. In this case the auxiliary anode is at the highest positive potential.

Energy spectra for standard TiN deposition

The energy spectrum for standard deposition **(Figure 2c)** differ significantly from spectra for heating and etching. The peak energy is much higher and is close to 56 eV, or about 2 V higher than the potential measured on the crucible.

The energy spectrum also show an interesting fact, the intensity of the double charge Ti^{++} ion (m/q = 24) is almost 20 times higher than intensity of the single charged Ti^{+} ion with m/q = 48 and even the intensity of the triple charged Ti^{3+} ion (m/q = 16) is quite high. (It will be shown latter that ions with m/q = 16 are Ti and not oxygen ions).

4 MASS SPECTRUM

The mass spectrum measured at the peak energy 55 eV during the TiN deposition is shown in **Figure 3**. The ion with the highest count rate in this spectrum is as already mentioned a double charged Ti^{++} ion (m/q = 24) with intensity even higher than the intensity of Ar. Ti peaks show a typical spectrum with five peaks corresponding to the Ti isotopes with masses 46, 47, 48, 49 and 50. This is clearly seen not only for the single charged Ti peak centered at m/q = 48 (relative abundance of this isotope is 73%), but also for multiple charged ions with m/q = 24 (Ti^{2+}), 16 (Ti^{3+}) and even 12 (Ti^{4+}), as it can be easily seen in the insert measured with higher

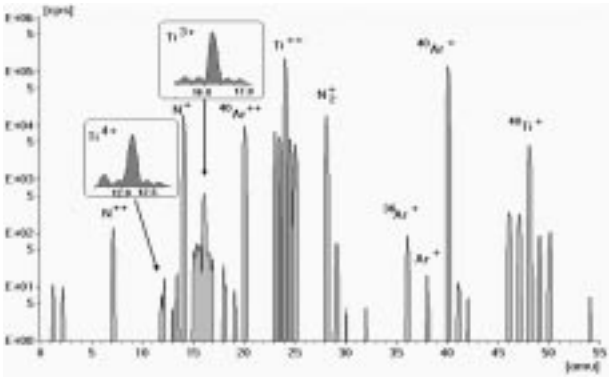

Figure 3: Mass spectrum during standard TiN deposition measured at the peak energy 55 eV. The inserts show the fine structure of the peaks corresponding to Ti^{3+} (m/q=16) and Ti^{4+} (m/q=12) ions
Slika 3: Masni spekter posnet med standardnim postopkom depozicije TiN pri energiji vrha 55 eV. Inserta kažeta fino strukturo vrhov Ti^{3+} (m/q=16) Ti^{4+} (m/q=12)

resolution. The small shift of mass scales in inserts for 0.1 - 0.2 a.m.u. is related to the calibration of the mass spectrometer. The fine structure of peaks around 12 and 16 a.m.u. clearly indicates that these peaks correspond mostly to the multiple charged Ti ions and not to $^{12}C^{+}$ and $^{16}O^{+}$ ions, as one may expect.

5 EFFECT OF PROCESS PARAMETERS ON THE ENERGY SPECTRA

Up to now all the measurements were performed under standard conditions. To understand the effects of different parameters on the energy spectra and on the chemical and physical properties of deposited films measurements under different conditions should be performed. In the next section we will see the effect of ar-

gon pressure and arc current on the energy spectra of positive ions.

Effect of Ar pressure

Pressure has the most noticeable effect on the energy spectra, and of course on the rate of evaporation. In our experiment only the argon pressure was varied from 1-2x10^{-3} mbar, while nitrogen pressure was kept constant at 0.5x10^{-3} mbar. All other parameters were as for standard process.

It is clear from spectra in **Figure 4** that with increasing Ar pressure the peak energy and peak width decrease. Even more, for Ar pressures close to the lowest working pressure (p_{Ar} = 1.0x10^{-3} mbar, **Figure 4c**), a weak secondary peaks centered around 25 eV appear.

It was already mentioned that under standard conditions the intensity of the double charged Ti ions is for about one order of magnitude higher than for the single charged ions. At lower pressure (p_{Ar} = 1.0x10^{-3} mbar, **Figure 4c**) the difference amounts to only a few times difference, but at higher pressure (p_{Ar} = 2.0x10^{-3} mbar, **Figure 4a**) the difference is higher.

An important parameter for triode ion plating is the deposition rate, which is in turn proportional to the nitrogen consumption rate. Our measurements show that the nitrogen consumption rate normalized to standard conditions decreases with increasing pressure from 200% at 1.0x10^{-3} mbar to 10% at 2.0x10^{-3} mbar.

Effect of Arc current

In these set of experiments the effect of arc current (by all other standard parameters) on energy spectra and of course on the deposition kinetics was studied. It is reasonable to expetct that with increasing arc current also the reaction rate increases. Measurements shows that normalized nitrogen consumption rate varies from 30% at I_{arc} = 190 A to over 200% at I_{arc} = 220 A. It is worth to note that nitrogen consumption rate drops to zero for arc currents below 175 A indicating very low deposition rate.

Energy spectra in **Figure 5** behave in a similar way as those in **Figure 4**. Increasing the deposition rate (increasing the arc current) the spectra become wider with higher peak energy. Contrary to observations in the previous section, the ratio between single and double charged Ti does not depend on the reaction kinetics. It depends only on the pressure.

6 DISCUSSION

From the form of the mass spectrum in **Figure 3** with some 20 times higher Ti^{++} than Ti^{+} and even with high Ti^{3+} and Ti^{4+} peaks is evident, that the studied triode ion plating system has in TiN deposition mode an extremely high ionization efficiency. This can be attributed to the good confinement of plasma electrons by combined action of magnetic and electric field. A weak mirror magnetic vessel formed by the arrangement of the electrode and coils confines at least some of the electrons on spiral paths oscillating between top and bottom of the magnetic mirror. Their Larmor radius[4] for a typical measured energy (1 eV) and magnetic field (7 mT) is less than 1 mm. Even the low energy Ar ions (1eV, 10mT) have Larmor radius ($r_L \approx$ 10 cm) smaller than the dimensions of the vessel. Of course ions are not magnetized because the collision frequency is much higher than their cyclotron frequency.

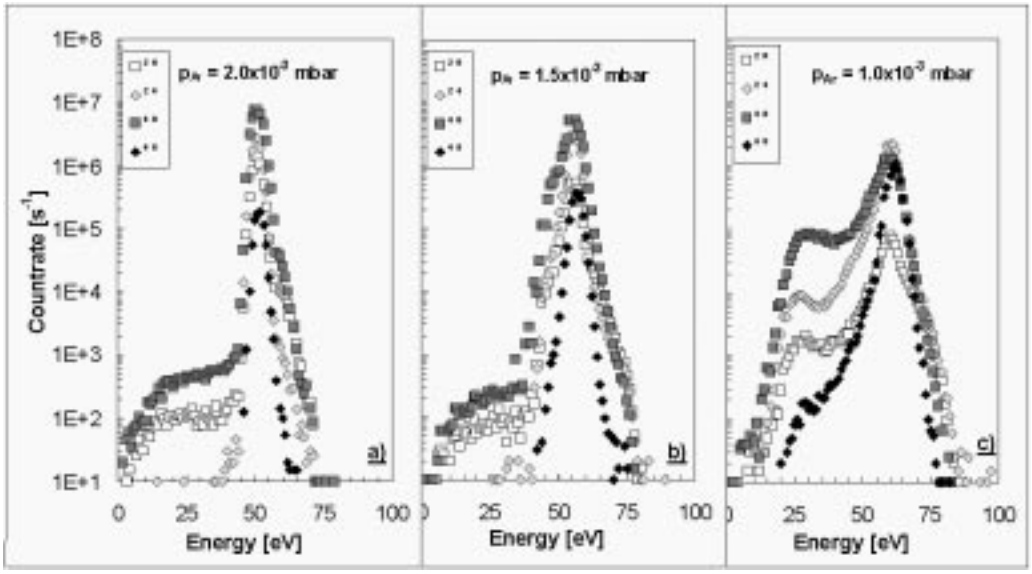

Figure 4: Energy spectra of Ti (m/q=24, 48) and Ar (m/q=20, 40) single and double charged ions during TiN deposition for different Ar pressures; other conditions are standard one **(Table 1)**: a) p_{Ar}=1.0x10^{-3} mbar, b) p_{Ar}=1.5x10^{-3} mbar, standard conditions, c) p_{Ar}=2.0x10^{-3} mbar

Slika 4: Energijski spektri enkrat in dvakrat nabitih ionov Ti (m/q=24, 48) in Ar (m/q=20, 40) med depozicijo TiN pri različnih tlakih Ar. Ostali pogoji so standardni **(Tabela 1)**: a) p_{Ar}=1.0x10^{-3} mbar, b) p_{Ar}=1.5x10^{-3} mbar, standardni tlak, c) p_{Ar}=2.0x10^{-3} mbar

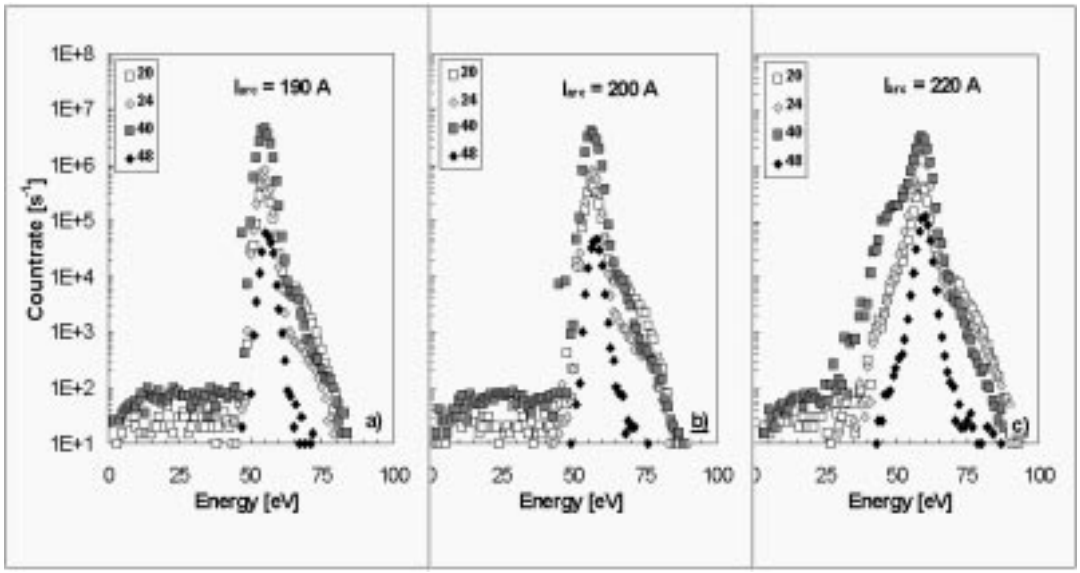

Figure 5: Energy spectra of Ti (m/q=24, 48) and Ar (m/q=20, 40) single and double charged ions during TiN deposition for different arc currents; other conditions are standard one **(Table 1)**: a) I_{Arc}=190 A, b) I_{Arc}=200, standard conditions, c) I_{Arc}=220 A

Slika 5: Energijski spektri enkrat in dvakrat nabitih ionov Ti (m/q=24, 48) in Ar (m/q=20, 40) med depozicijo TiN pri različnih tokovih loka. Ostali pogoji so standardni **(Tabela 1)**: I_{arc}=190 A, b) I_{arc}=200 A, standardni tok loka, c) I_{arc}=220 A

Unfortunately, the effect of magnetic field on the probability for multiple ionization of Ti ions during the deposition can not be shown. To obtain a reasonable rate of Ti evaporation the LV arc has to be focused onto the crucible by a magnetic field. The current through both coils has to be in the range from 13-16 A (5.6-6.8 mT). The effect of this relatively small change in field is confounded by the effect of pressure variations and variations in the thermal conductance of titanium in the crucible. Our results[5] on the effect of magnetic filed on the energy spectra during heating and etching step, when the coil current is changed in wide range from 1 to 20 A (0.5 - 8.5 mT), confirm the above conclusion on good magnetic confinement of the plasma. Moreover, the comparison with results from the similar triode ion plating system (BAI 640) but with different geometry[3,6,7], also confirm the above conclusion.

Energy spectra at all three modes are relatively narrow at least under standard conditions. This is attributed to the very uniform plasma potential in the vessel. Langmuir probe measurements[5] show that plasma potential is close to the voltage measured on the crucible during deposition, on the auxiliary electrode during etching, or to the voltage measured on the floating substrates during the heating step.

7 CONCLUSIONS

Energy and mass resolved plasma spectroscopy in combination with Langmuir plasma probe measurements is an efficient tool for plasma characterization. Our results show that the LV arc in combination with the arrangements of electrodes and coils in a way to form a weak mirror magnetic vessel very efficiently ionized the gas and evaporated metal species. The majority (≈95%) of the Ti ion flux consist of the double charged Ti^{++} ions accelerated toward the substrate with energies from 90 to 120 eV. The rest (≈5%) of Ti ions have energies from 45 - 60 eV (Ti^{+}) and about 0.1% even have energies over 135 eV. To assure the optimum growth conditions obviously the additional optimization of the process, for instance biasing, the substrates is necessary.

8 REFERENCES

[1] E. Mol and E. Bergmann, *Surf. Coat. Technolog.*, 37 (1989) 483-509

[2] E. Bergmann, *Surf. Coat. Technolog.*, 57 (1993) 133-137

[3] M. Nesladek, C. Quaeyhaegens, S. Wouters, L. M. Stals, E. Bergmann, G. Rettinghaus, *Surf. Coat. Technol.*, 68/69 (1994) 339

[4] A. Grill, Cold Plasma in Materials and Fabrication, IEEE Press NY 1994, p 133

[5] M. Maček, B. Navinšek, P. Panjan, S. Kadlec, *33rd conference MIDEM'97*, Gozd Martuljek, Slovenia, September 24-26 1997, 241-245

[6] M. Maček, B. Navinšek, P. Panjan, S. Kadlec, S. Wouters, C. Quaeyhaegens, L. M. Stals, *submitted to Surf. Coat. Technology*

[7] S. Kadlec, M. Maček, S. Wouters, B. Navinšek, P. Panjan, C. Quaeyhaegens, L. M. Stals, *Proceedings 1998 Int. Congress on Plasma Physics*, Prague, K-78, Czech Republic, June 29-July 3, 1998