

# Correlation between Emission Spectra, Mass Spectrometry and Surface Processes in Ar/N<sub>2</sub>, Reactive Magnetron Discharge with Titanium Target<sup>1</sup>

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**Abstract** – In the present paper new experimental results are presented on reactive magnetron discharge. Plasma parameters, in a pulsed operated regime, are measured by mass spectrometry as partial pressures of molecular nitrogen ions, titanium and argon ions. Relative variations of nitrogen molecules, titanium and argon atoms in some excited state are measured by emission spectra. The results are related to the total variation of the discharge voltage. A clear picture can be obtained of the dynamic system and hysteresis phenomena observed within reactive magnetron discharge.

## 1. Introduction

Magnetron sputtering is one of the most frequently tool for the deposition of high quality functional coatings [1]. For some applications and high-rate deposition, the thin film of the metallic compound is often performed in the "reactive" mode, where a metal target is exposed to a discharge in a rare gas with some fraction of reactive gas (e.g. oxygen or nitrogen) added. The performance of reactive sputtering is impeded by the effect of the target "poisoning", which means that a compound film is formed on the target, which results, in some cases, in a significantly reduced sputter yield and, thereby, reduced deposition rate. Another consequence of the target poisoning is a hysteresis loop, which might appear, e.g. in the I–V characteristic. These phenomena have been described taking into account the reactive gas balance and a saturate state of the reactive gas chemisorption on the surface of both the target and the other surrounding surfaces including the substrate [2]. In the present paper new experimental results are presented on reactive magnetron discharge produced in Ar/N<sub>2</sub> gas mixture with titanium target using pulsed system of operation between two states of constant discharge current intensity. Time evolution of some plasma parameters is correlated with hysteresis loop.

## 2. Experimental setup

The measurements were performed in a vacuum chamber depressurized by a turbo molecular pump to a pressure of  $1 \cdot 10^{-6}$  torr. A planar circular magnetron with a titanium target of 55 mm diameter [3], and an argon/nitrogen gas mixture were used. The argon flow was kept constant at 14 sccm, while the nitrogen flow was 0.36 sccm for a total gas pressure of 10 mtorr. Magnetron discharge was sustained by a programmable dc power supply, which provided a good control of the discharge current intensity. The current intensity was varied as a step function between two constant values. Accordingly, the time evolution of the discharge voltage was measured as an indicator of the time evolution of the discharge impedance, which depends on both the cathode surface properties and the properties of the plasma volume. The optical diagnosis of the argon/nitrogen plasma with titanium target was realized using a fast Ocean Optics spectrometer and an optical fiber, which collects the emitted light either by entire plasma volume or by part of it. With a quadrupole mass spectrometer Hiden Analytical there were registered the time evolutions of the argon and titanium ions and nitrogen molecular ion concentrations in the chamber volume.

## 3. Results and discussions

One of the typical characteristics of the reactive magnetron discharge is the hysteresis loop within the current voltage characteristic [4]. This was obtained by varying the discharge current intensity as saw tooth function between two values, which corresponds to, so called, compound regime and metallic one, respectively. By plotting the V–I characteristic corresponding to this kind of current intensity variation a hysteresis loop is obtained, as shown in Fig. 1. By using this representation one can see the main modes of operation of the reactive magnetron discharge. At low current intensities (lower as about 30 mA) a "compound" mode (CM) is present when surface of

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the target is covered with TiN compound. At higher values of the current intensity (more as about 140 mA) the discharge operates in "metallic" mode (MM) and the target surface is mainly metallic. Between these two extreme cases an "intermediary" mode (IM) is present in which part of the target surface is metallic and partly covered by compound due to competition between sputtering and forming of the compound at the cathode surface. Moreover, the balance of the competition behaves differently at increasing and decreasing of the discharge current intensity showing a memory effect of the system. In Fig. 1, the upper side of the curve (branch BCD) corresponds to the increasing of the discharge current intensity in which compound behavior prevails because of the low sputtering rate of the TiN. The lower side of the curve (branch DFG) corresponds to decreasing the discharge current intensity when metallic characteristic is dominant due to higher sputtering rate of Ti [5]. The different forms of the voltage evolution with respect to the discharge current clearly show the differences between the rates of the two processes: sputtering and forming of the compound. It is also clear that there are two different values of the discharge current intensity at which a negative slope of the I–V characteristic begins. These values correspond to appearance on the target surface of metallic area when the current intensity increases (point C,  $I \approx 100$  mA), and formation of the compound on the metallic area when the current intensity decreases (point F,  $I \approx 50$  mA). For higher values of the discharge current intensity (region DE) a net metallic area is present on the target. The form of hysteresis and its width depends on the rate of the current intensity variation [4] and argon/nitrogen partial pressure ratio. In Fig. 1 the variation rate was about 4.5 mA/second and the period of the saw-tooth signal was about 80 seconds.

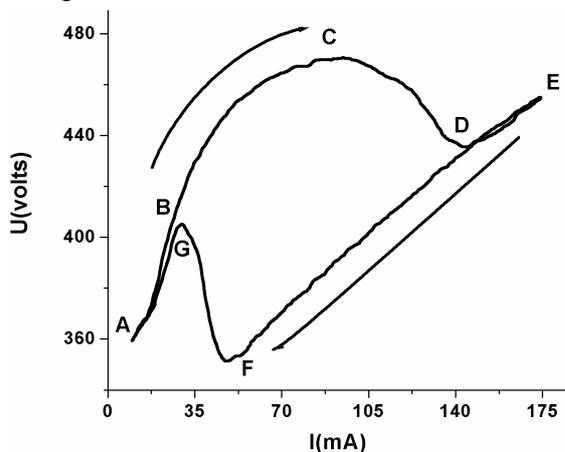


Fig. 1. Hysteresis effect in V–I characteristic, registered with a saw-tooth variation of the discharge current intensity (total variation time 80 seconds)

For the pulsed regime operation a square pulse was used with a transition between two constant va-

lues of the discharge current intensity in less than 0.1 seconds. The low value,  $I=20$  mA corresponds to the CM operation, while the higher value (denoted  $I_{max}$ ) is gradually increased up to the MM operation. Each current intensity value was kept constant for 40 seconds. The time dependence of the discharge voltage after each transition of the discharge between the  $I_{min}=20$  mA to different  $I_{max}$  is presented in Fig. 2.

The discharge voltage variation provides first information about the variation of the discharge impedance, which is determined by both parameters of the plasma volume and at the electrodes surface. The results show that the major role is played by phenomena occurring on the surface of the cathode. The discharge voltage has different temporal evolution with increasing of the discharge current compared with decreasing of the discharge current. These different evolutions provide information about the rate of the processes occurring at the cathode during the formation and sputtering of the compound on the target surface, respectively [6].

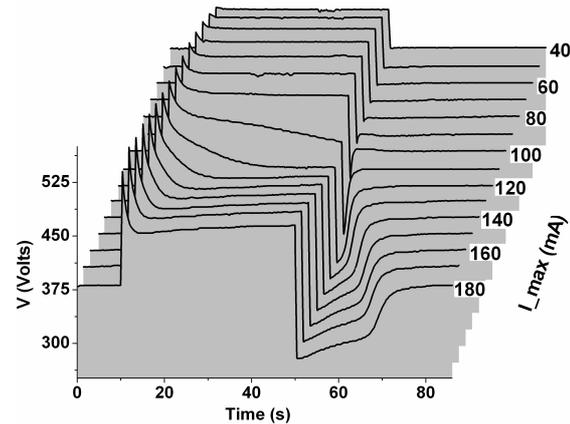


Fig. 2. Time evolution of the discharge voltage corresponding to the pulsed discharge current from  $I_{min}=20$  mA to different  $I_{max}$  values

As it can be seen from Fig. 2, when discharge current is changed from constant  $I_{min}=20$  mA gradually to  $I_{max}$  from 40 mA to 100 mA, discharge voltage follows, each time with constant value, which increases with discharge current intensity as the ABC branch on the hysteresis characteristic, presented in Fig. 1, is shown. This behavior shows that, after each transition between  $I_{min}$  and  $I_{max}$  and back, the discharge operates as the CM because the compound covers all the time the cathode of the magnetron discharge. But, situation is different when transition corresponds to  $I_{max}$  in the range from 100 mA to 140 mA. In this case the discharge voltage has both different time evolution and dependence on discharge current intensity. The first, discharge voltage at the maximum value of the discharge current is decreasing with increasing value of the step discharge current. It corresponds to the negative slope on the hysteresis

characteristic presented in Fig. 1, branch CD, when discharge operates as intermediary mode at transition from the CM to MM. In this regime, the competition between formation of the compound on the target surface and its sputtering evolves in favor of the latter. This observation is proved by the second fact presented in Fig. 2 that, after transition from  $I_{\min}=20$  mA to  $I_{\max}$ , the discharge voltage decreases in time which shows a transition to the metallic mode of operation with lower impedance of the discharge. The process is faster with increasing of the ion flux bombarding the target surface, which means increasing the  $I_{\max}$  value.

Moreover, at discharge reverts from  $I_{\max}$  in the range from 100 mA to 140 mA to  $I_{\min}=20$  mA the discharge potential increases in time in two steps. One step with a low rate which last longer for higher initial  $I_{\max}$  value and a second step with higher rate which seems to be almost constant. These results correspond to the lower branch DFG of hysteresis curve from Fig. 1 and shows transition from MM to the CM of operation when competition between sputtering and formation of the compounds is in favor of the second process.

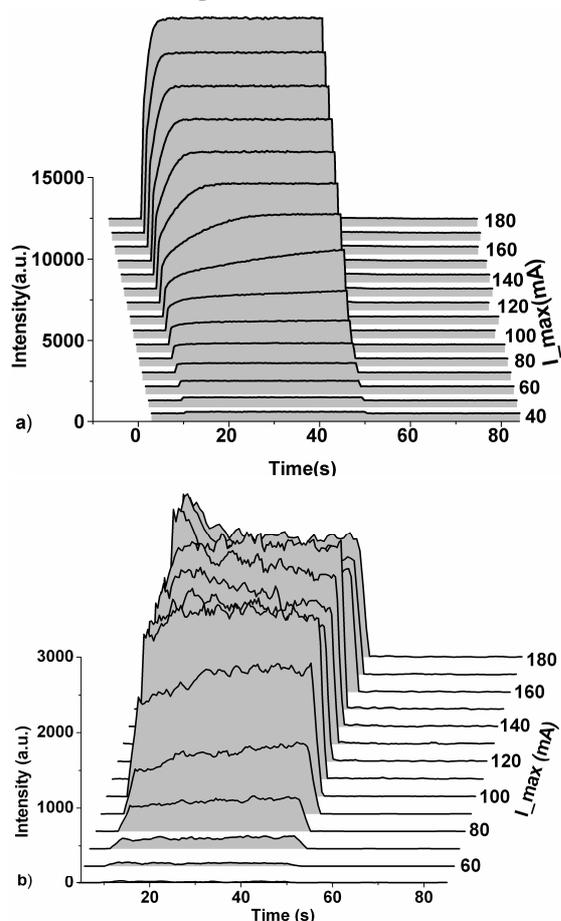


Fig. 3. Time evolution of  $\text{Ti}^+$  spectral line (503.9 nm) (a) and  $\text{Ti}^+$  partial pressure (b), corresponding to the discharge current for pulses from  $I_{\min}=20$  mA to different  $I_{\max}$  values

Additional confirmations of proposed scenarios have been obtained by time evolution of the  $\text{Ti}^+$  (503.9 nm),  $\text{Ar}^+$  (420.06 nm), and  $\text{N}_2^+$  (356.39 nm) emission lines, and time evolution of the partial pressure of the corresponding ions measured with mass spectrometry. Thus, titanium spectral line evolution (Fig. 3, a) clearly shows the presence of the three modes of operation in the reactive magnetron. At low current intensities, below 100 mA (point C on Fig. 1), the time evolution of the spectral line is almost rectangular, following time evolution of the discharge current intensity but, it becomes different above this limit. These changes show that starting with this value of the discharge current intensity more titanium ions atoms are present within the discharge and their number increases with both in time, for a constant discharge current, and the  $I_{\max}$  value. Starting with this value of the discharge current "cleaning" from the compound may take place and metallic area is expanding. Changes on the target surface are expressed in the time evolution of the Ti spectral line and appearance of a saturation after a certain duration which shortens with the increase of the  $I_{\max}$  [6] because sputtering of the compound takes place in a shorter time with higher discharge current intensity.

The mass spectrometry measurements (Fig. 3, b) show also that titanium partial pressure has an important increase above  $I_{\max}=100$  mA. For higher discharge current intensities the equilibrium value of the titanium ion partial pressure does not increase significantly, and follows the evolution of the discharge voltage (see Fig. 2).

At low current values, the time evolution of the  $\text{Ar}^+$  spectral lines is in good correlation with the discharge current intensity, while at high current values this evolution depends mainly of the processes occurring in plasma volume. From mass spectrometry measurements (Fig. 4, b), we can see that the partial pressure of the  $\text{Ar}^+$  increases with increasing discharge current up to 100 mA, than the partial pressure decreases with increasing the discharge current intensity. This is due to the fact that at higher intensity of the discharge current more Ti atoms may appear within the discharge and their lower ionization potential leads to reduction of the number of argon ions.

The important quantity of titanium sputtered atoms from the target at higher discharge current intensity has an important influence on the nitrogen emission spectral line, because titanium acts like a getter for nitrogen at the discharge chamber walls. As shown in Fig. 5, a, evolution of the  $\text{N}_2^+$  spectral line (358.39 nm) for  $I_{\max}$  greater than 100 mA, has a different form, meaning that at transition to low current ( $I_{\min}=20$  mA) the evolution does not follow the square form anymore. A certain period of time is necessary to reach the equilibrium. This period increases with the increase of  $I_{\max}$  value, and is in good correlation with the period for equilibrium in the voltage evolution. These periods are better showed in

mass spectrometry evolution of the  $N_2^+$ . The number of the  $N_2^+$  ions can be detected by mass spectrometry at low discharge current intensity only after the equilibrium is reached and the surfaces (including the target) are saturated with nitrogen. Otherwise, all nitrogen molecules are reacting and gathered by fresh metallic deposition of titanium thin layer all over the discharge chamber wall. An interesting behavior occurs in this case for the evolution at  $I_{max}$  too. For  $I_{max}$  below 100 mA the  $N_2^+$  partial pressure increases with increasing of the discharge current intensity. When metallic surface is present ( $I_{max} > 100$  mA) the nitrogen partial pressure begins to decrease, and a certain duration in which equilibrium is reached is also present. The value of this duration decreases with increasing current intensity, the same evolution as the one observed in voltage discharge behavior. Decreasing of partial pressure at high values of the discharge current intensity has at least three causes. Two of them are related to the target surface and to the fact that the important quantities of titanium sputtered and deposit on the chamber surfaces acts like a getter for the nitrogen. In the discharge volume titanium is excited and ionized and its lower ionization potential makes it a good competitor for nitrogen ionization. In the third place is the fact that at high discharge current intensities the dissociation rate of reactive gas becomes important, and so the  $N^+$  ion (mass 14) can be observed [4].

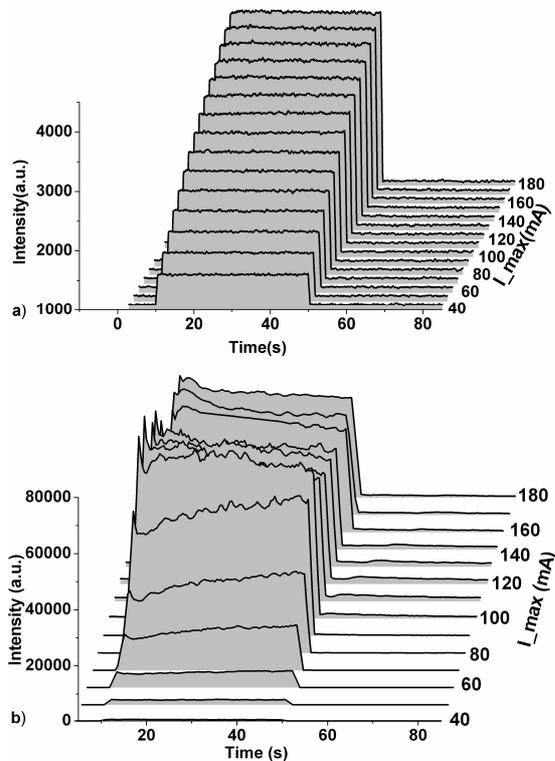


Fig. 4. Time evolution of  $Ar^+$  spectral line (420.06 nm) (a) and  $Ar^+$  partial pressure (b), corresponding to the discharge current for pulses from  $I_{min}=20$  mA to different  $I_{max}$  values

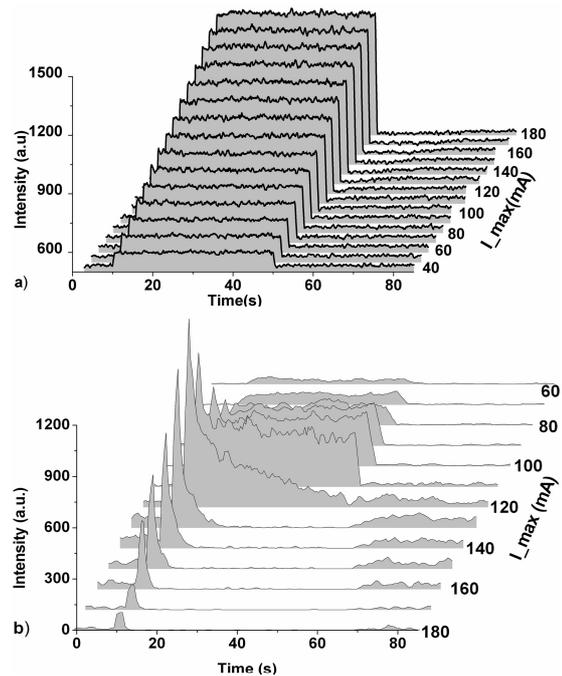


Fig. 5. Time evolution of  $N_2^+$  spectral line (358.39 nm) (a) and  $N_2^+$  partial pressure (b), corresponding to the discharge current for pulses from  $I_{min}=20$  mA to different  $I_{max}$  values

#### 4. Conclusions

Hysteresis behavior can be explained also by studying a pulse regime operation, if total duration between compound and metallic operating regime is comparable. The results obtained by mass spectrometry and OES provide additional information beside the ones obtained from impedance behavior. In this way a clear picture can be obtained, regarding the processes that occur at target surface, but also in the discharge volume and chamber walls.

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