I-V characteristics of magnetron with hot target sputtered in three-component gas mixture

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Abstract. The discharge current-voltage characteristics of a dc magnetron with a single cold titanium target and a single hot titanium target in Ar + N₂ + O₂ environment were studied. Two series of experiments, in which the flow rates of nitrogen Q_N₂ and oxygen Q_O₂ played different roles, were performed. In the first series, O₂ was introduced into a mixture of Ar + N₂ (Q_N₂ = const and Q_O₂ = var). In the second one, N₂ was introduced into a mixture of Ar + O₂ (Q_N₂ = const and Q_O₂ = var). It was found that the I-V characteristics of the studied sputtering instruments measured in the current density range of 10–200 mA/cm² differ significantly. The I-V characteristics of a magnetron with a cold target can have one maximum or jump. The I-V characteristics of a magnetron with a hot target have two maxima and one minimum in one case, and in the other case, there is only one maximum.

1. Introduction
The synthesis of films in the Me – O – N system is performed in many of the world’s leading research centers. Transition Ti, Ta, W, Fe, Mo, Nb, and other metals are used as Me in these systems most often. Oxynitrides (figure 1, where the numbers in the sectors of the diagram indicate the share of publications about this system), the composition of which is expressed by the chemical formula MeO₁ₓN₁ᵧ, in many cases, form a continuous series of compounds with various concentrations of nitrogen and oxygen (including two-component oxides y = 0 and nitrides x = 0).

Figure 1. Publications about oxynitride films in 2010–2019.
By adjusting the ratio of oxygen and nitrogen it’s possible to obtain a film with given physical and chemical properties. MeO$_x$N$_y$ films are used [1–3]:
- in optoelectronics and microelectronics;
- in solar cells;
- to protect the surface from the impact of corrosive environment;
- as gas barriers;
- as decorative coatings for high-quality consumer goods, etc.

A wide variety of possible applications of oxynitride films has stimulated the development of methods for their deposition. The most popular methods are reactive sputtering [3, 4]. An increase in the growth rate, a change in the chemical composition and the crystal structure of the films were achieved using a magnetron with a single hot metal target [5–7], which can be heated up to the melting point and higher.

In order to efficiently use a hot target magnetron in the synthesis of oxide films, it is necessary to study in detail the characteristics of the discharge in an oxygen-containing environment. The purpose of this work was to study the discharge current-voltage characteristics of a magnetron with a hot titanium target operating in a gas mixture of Ar + N$_2$ + O$_2$.

2. Experimental details
A detailed description of the experimental conditions is given in [8]. In this work, we used 130 mm diameter balanced magnetrons with titanium targets of:
- 6 mm thick with typical cooling by running water (cold target);
- 1 mm thick cooled through fastening elements and a 1 mm vacuum gap from a copper water-cooled board (hot target).

The magnetron sputtering processes in a mixture of Ar + N$_2$ + O$_2$ with a partial pressure of argon of 2 mTorr, flow rates of nitrogen and oxygen up to 6 sccm, and a discharge current density of up to 200 mA/cm$^2$ were studied.

We focused on two groups of experiments. In each of them, the influence of one reactive gas on the process was studied, while the other played the role of a constant parameter.

3. Results and discussion
In a series of experiments, $Q_{N_2} =$ const and $Q_{O_2} =$ var, oxygen was introduced into the mixture of argon + nitrogen. It significantly influenced the discharge current-voltage characteristics of the magnetron with a cold target (figure 2, a). When analyzing the experimental results, we should take into account that in a three-component gas mixture, two stationary modes of the target operation are also possible: reactive and metallic.

![Figure 2](image_url)

**Figure 2.** The discharge I-V characteristics of a cold target magnetron (a) and TiI (398.4) line intensity (b) at $Q_{N_2} =$ 4 sccm and $Q_{O_2}$ (sccm): 1 – 0; 2 – 1; 3 – 2; 4 – 3

But, in contrast to the two-component environment, the reactive mode, which in this case is better to be called “oxynitride” one, should consist of two parts: with an increase in the discharge current, the oxynitride mode switches to the nitride mode, which is further replaced by the metallic one. This is
due to the different chemical activity of nitrogen and oxygen. Comparing the dependences of 2, 3, and 4 with the I-V characteristics \( I \) in figure 2, a we see that:

- each I-V characteristic has a maximum, which with increasing \( Q_{O_2} \) shifts to higher currents;
- in the initial sections of the I-V characteristics, to the left of the maxima, the target operates in the oxynitride mode, in which its surface is covered with an oxynitride film, and the environment contains both reactive gases (figure 3);
- a smooth increase in the discharge voltage in this area is associated with the extinction of excited argon atoms by the atoms of the reactive gases. Therefore, to maintain a given discharge current, an increase in voltage is required;
- the oxynitride mode is terminated at the points of the I-V characteristics corresponding to the maxima when the intensities of the OI (777) lines decrease to zero (figure 3, a). The target shifts to the nitride mode;
- the transition from this mode to the metal one takes place at current densities of 106, 117 and 131 mA/cm\(^2\) corresponding to oxygen flow rates of 1, 2 and 3 sccm (see figure 2, b). The transition points are determined from the abrupt decrease to zero of the intensity of the N\(_2\)I (391.4) nitrogen lines in figure 3, b.

An increase in nitrogen flow rate does not qualitatively change the I-V characteristics of the discharge. There is only a shift of the change points of the target operation mode to the region of higher currents.

The discharge I-V characteristics during hot target sputtering shown in figure 4, a have significant differences from the cold target I-V characteristics in figure 2, a:

- each of them contains two maxima and one minimum;
- with an increase in the oxygen flow rate, the I-V characteristics shift to the region of higher values of the current density and at the same time there is a significant increase in the discharge voltage;
- the I-V characteristics do not show obvious signs of a target operation mode change;
in the change of the intensity of the TiI (398.5) lines for each value of the oxygen flow rate in figure 4, b, two break points are observed. The first of them (at 53, 58 and 64 sccm) corresponds to the minimum of each I-V characteristic and reflects the transition of the target from the oxynitride mode to the nitride one. The second point at \( j \approx 86 \) mA/cm\(^2\) corresponds to the second maxima of the I-V characteristic and sets the target to transition from the nitride mode to the metal one.

Therefore, three extremums are the main features of the I-V characteristics of a hot target magnetron sputtered in Ar + N\(_2\) + O\(_2\). The first maximum is generated by the processes associated with oxygen, the second one: with nitrogen.

In another series of experiments, nitrogen was introduced into the mixture of argon + oxygen with \( Q_{O_2} = \) const and \( Q_{N_2} = \) var. The results of studying this process when the magnetron operates with a cold target are shown in figure 5. When \( Q_{N_2} = 0 \) the transition from the oxide mode to the metallic one is abrupt [8]. Figure 5 shows two such curves: the I-V characteristic 1 was measured at \( Q_{O_2} = 4 \) sccm, the dash-dotted line I-V characteristic: at \( Q_{O_2} = 5 \) sccm. Increasing the oxygen flow rate by 1 sccm resulted in an increase in the current density which changes the target operation mode for about 30 mA/cm\(^2\).

![Figure 5](image1.png)

Figure 5. The discharge I-V characteristics of a cold target magnetron at \( Q_{O_2} = 4 \) sccm and \( Q_{N_2} \) (sccm): 1–0; 2–1; 3–2; 4–3; 5–4.

The curves 2 ... 5 in figure 5 correspond to different flow rates of nitrogen additionally introduced into the gas environment. The presented results have a number of distinctive features:

- all I-V characteristics are measured in the discharge current range, in which the transition to the metallic mode is not observed. They reflect a single transition of the target from the oxynitride mode to the nitride one;
- nitrogen influences the mode change process insignificantly;
- the discharge voltage in the oxynitride mode of the target operation increases with increasing nitrogen flow rate. The appearance of this effect can be associated with the extinction of metastable argon atoms, which was initiated by the atoms and molecules of nitrogen and oxygen.

![Figure 6](image2.png)

Figure 6. The discharge I-V characteristics of a hot target magnetron at \( Q_{O_2}; a – 3 \) sccm and \( Q_{N_2} \) (sccm): 1–4, 2–5, 3–6 and b–10 sccm and \( Q_{N_2} \) (sccm): 1–1; 2–2; 3–3; 4–4.

Figure 6 shows the I-V characteristics of a magnetron with a hot target. In the experiments, it was found that when \( Q_{O_2} < Q_{N_2} \) (figure 6, a) the I-V characteristics have three extremums and are similar to the case when nitrogen is added to the Ar + O\(_2\) mixture (see figure 4, a). In the current density range of
0–120 mA/cm², as it can be seen from figure 6, a, a change in the target operation mode occurs twice. When \( Q_{O_2} > Q_{N_2} \) (figure 6, b) the process changes. If under this condition \( Q_{N_2} = 0 \), then the points of transition from the oxide mode to the metal one at \( Q_{O_2} \)-6, 10 and 12 sccm are 30.6, 38.9 and 50 mA/cm², respectively. These points correspond to the extrema on the corresponding I-V characteristics. When nitrogen is added to the Ar + O₂ mixture, the I-V characteristic in the current density range of 0–120 mA/cm² reflects only one transition of the target from the oxide mode to the nitride one. The value of \( Q_{N_2} \), as it can be seen from figure 6, b, slightly influences the sputtering process, which is typical for other values of \( Q_{O_2} \).

In conclusion, we draw attention to the fact that the flow rates of oxygen and nitrogen, being independent factors of the sputtering process, interact with each other. This property means that the influence of the flow rate of any gas on the sputtering process depends on the value that the flow rate of the other gas has. This can be seen, first, from figure 4, a, on which the second maxima of the I-V characteristic differ significantly: with an increase in the oxygen flow rate from 0 (curve 1) to 3 sccm (curve 4), the discharge voltage at the maximum increases from 436 V to 474 V. The second confirmation of this property is shown in figure 6, a. All I-V characteristics measured at a constant flow rate of oxygen and different flow rates of nitrogen also differ significantly. Moreover, as it can be seen from figure 6, a, an increase in \( Q_{N_2} \) leads to a decrease in the influence of \( Q_{O_2} \).

4. Conclusions

An experimental study of the discharge current-voltage characteristics of a titanium target magnetron in a mixture of three gases allowed establishing that there are important differences between the sputtering processes of hot and cold targets. These differences were found in two series of experiments, in which the flow rates of nitrogen \( Q_{N_2} \) and oxygen \( Q_{O_2} \) played different roles.

In the first series, oxygen was introduced into the Ar + N₂ mixture. In this case, at any flow rate of nitrogen, the I-V characteristics of the magnetron with a cold target had one maximum, which separated the regions of the oxynitride and nitride target operation modes. At the same time, in the current density range of 10–200 mA/cm², without a discharge voltage jump, the second transition from the nitride mode to the metal mode also took place. The I-V characteristics during hot target sputtering had two maxima and one minimum. There were no obvious signs of changes in the target operation modes. The values of \( Q_{N_2} \) and \( Q_{O_2} \), being independent factors of the sputtering process, interacted with each other. This property was discovered in the fact that the influence of a gas flow rate on the sputtering process depends on the flow rate value of another gas.

In the second series, nitrogen was introduced into the Ar + O₂ mixture. When sputtering a cold target in the current density range of 10–150 mA/cm², only one jump transition from the oxynitride to nitride mode was observed. The I-V characteristics of a magnetron with a hot target in the current density range of 10–120 mA/cm² had one maximum, in the vicinity of which the target transitioned from the oxynitride mode to the nitride mode and then to the metal one under a slight influence of nitrogen flow rate on these processes.

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