Reactive magnetron sputtering of hot titanium target in mixture of argon and nitrogen

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Abstract. The influence of nitrogen flow rate on the discharge I-V characteristics of a dc magnetron with a single hot titanium target is studied. The basic processes forming the discharge are determined. The discharge physical models are proposed.

1. Introduction
Nitride films (TiN [1], CrN [2], HfN [3], and others) still draw the interest related to the increase of the hardness and the chemical resistance of metals, cutting tools, molds, etc. In order to deposit these films, reactive magnetron sputtering was used more often than other methods [1]. An increase in the growth rate by an order of magnitude and more, a change in the chemical composition and crystal structure of the films were achieved using a magnetron with a single hot metal target [4, 5], which could be heated to the melting temperature and higher. In order to efficiently use a hot-target magnetron, a thorough study of the discharge characteristics in a reactive environment is required.

The purpose of this work is to study the discharge I-V characteristics of a hot titanium target magnetron operating in an Ar + N₂ gas mixture. The experimental I-V characteristics, first published in our work [6], were thoroughly analyzed in order to identify the physical processes that form the magnetron discharge during reactive sputtering.

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

The magnetron sputtering processes in the Ar + N₂ environment are studied at the argon partial pressure of 2 mTorr and the nitrogen flow rate of 4, 5 and 6 sccm.

3. Results and discussion
In the most general form, reactive sputtering in a single reactive gas environment is described by the 3D dependence of the discharge voltage \( U = f(j, Q_0) \) on the discharge current density \( j \) and the gas flow rate \( Q_0 \). The surface, described by the function \( U = f(j, Q_0) \) in the coordinate system \( U - j - Q_0 \), has a complex shape. Flat curves \( U_{j/Q_0 \text{const}} = f(j) \) in its cross sections by the \( U - Q_0 \) planes are the I-V characteristics of the discharge. According to them, boundaries of the target operating modes are set...
for the independent variable $j$. In order to identify these boundaries by the factor $Q_0$, it is necessary to mark out the sections $U_{in, \text{cont}} = f(Q_0)$ of the surface $U = f(j, Q_0)$ by the planes $U-j$. The flat curves in these sections are called discharge voltage-flux characteristics. Experimentally, both the I-V characteristics and voltage-flux characteristics can be measured independently. Our experience shows that it is not possible to match these results for the construction of the surface $U = f(j, Q_0)$ due to the high error (up to 10%) of measurements in the gas discharge.

It is known that during reactive sputtering of hot and cold targets, two stationary modes of operation are possible: reactive and metallic [7].

![Figure 1](image1.png)

**Figure 1.** The I-V characteristics of a titanium target magnetron: (a) – cold; (b) – hot.

In figure 1(a) the first of them corresponds to the left sections of the I-V characteristic obtained in our experiments, where the voltage is 8–15 V higher than during target sputtering in pure argon (the curve $Q_{N_2} = 0$ sccm). In reactive (nitride) mode, the target surface is coated by a film of titanium nitride (TiN). In this case, the discharge is formed due to its ion induced electron emission, which is about 8% less than that of titanium [8]. A difference between the corresponding discharge voltages has the same order of magnitude. At a current density of more than 160 mA/cm$^2$ and all nitrogen flow rates, the cold target enters the metallic mode. This is indicated by the voltage spikes in figure 1(a), which occur at nitrogen flow rate $Q_0 = 4, 5$ and 6 sccm at points $j_\alpha = 105, 127$ and 152 mA/cm$^2$, respectively.

Measurement results of the I-V characteristics for a hot target are shown in figure 1(b). Their features are as follows:

1) they all have a maximum;

2) on all the curves there are no obvious signs of a transition from the nitride mode to the metallic one. They were identified by the optical electron spectroscopy and measurement of total pressure. The transition of the target to the metallic mode corresponded to the disappearance of nitrogen lines from the discharge optical spectra, and the decrease in the total pressure to the level of the initially established argon partial pressure. Points, where operating modes change, compared with the cold target were shifted to lower current density: $j_\alpha = 48.6, 62.5$ and 76.4 mA/cm$^2$, which corresponded to nitrogen flow rate of 4, 5 and 6 sccm;

![Figure 2](image2.png)

**Figure 2.** The derivatives of the I-V characteristics of a magnetron with a hot titanium target. The I-V characteristics of magnetron operating in an Ar + N$_2$ mixture, has an extremum and two inflection points. To the left of the extremum in figure 1 $(dU/dj)_{Ar,N_2} > (dU/dj)_{Ar}$. 
3) the transition of the hot target to the metallic mode was accompanied by an increase in the discharge voltage. At the same time, as with a cold target magnetron, this transition entailed its decrease;

4) the observed result is also different, as in the metallic mode, the discharge voltage reaches values that are 80–90 V higher than during target sputtering in argon.

These features of the I-V characteristics allow us to assume, that reactive sputtering of a hot titanium target includes a number of processes. At low currents, the chemical reaction of nitride formation on the target surface and nitride sputtering by argon ions compete. If a chemical reaction prevails to the left of the first inflection point, then to the right of it, as the current density increases, the influence of sputtering increases and the surface of the target is cleared from the nitride film. In the reactive mode of the target, there is high probability of another process leading to an increase in the discharge voltage. When a gas of atoms and molecules able to intercept the acts of excitation and ionization is added to argon, the concentration of metastable argon atoms decreases. Therefore, in order to maintain a given discharge current, a higher voltage is required.

Competition of two processes ends at the extremum of the I-V characteristics. Then two other competing processes become significant. The first of them is possibly related to the decrease in the working gas density, which results in an increase of the discharge voltage. Significant (up to 50–60%) decrease in density, which is equivalent to a decrease in pressure, was found during cold target sputtering [9]. It is caused by gas heating near the target due to collisions between sputtered atoms and gas particles. Thermionic emission, which accompanies the heating of the target, competes with this process. Its increase leads to a decrease in the discharge voltage. Moreover, this issue becomes important at the second point of inflection of the I-V characteristics, and at the point of an extremum with \( dU(j)/dj = 0 \) it becomes dominant.

In order to validate our assumptions, a number of calculations were performed. The first pair of competing processes is universally accepted for magnetrons with cold targets [7]. Observations over the discharge emission spectra and the partial pressure of the reactive gas during the sputtering of hot targets suggest that these processes are also applicable for hot targets [10].

The main attention was paid to the second pair of processes initiated by heating the target. In the calculations, the temperature dependences of the titanium target temperature \( T_1 \) on the discharge current density \( j \) obtained by modeling are used [8]. These dependencies were expressed by the approximation formula

\[
T_1(j) \approx T_\infty - T_0 e^{-j/j_0}
\]  

(1)

with the parameters given in table 1.

| \( Q_0 \), sccm | \( T^*_n \), \( 10^3 \) K | \( T_0 \), \( 10^3 \) K | \( j_0 \), mA/cm\(^2\) |
|-------------|----------------|----------------|--------------|
| 4           | 78.5           |                |              |
| 5           | 2.50           | -1.98          | 82.4         |
| 6           |                | 86.8           |              |

Before presenting the calculation results, we introduce certain remarks. Reactive sputtering of the cold target has features similar to sputtering in an inert gas environment. This similarity arises when the target enters a stationary metallic mode during reactive sputtering. In this case, as it follows from figure 1(a), both I-V characteristics are identical.

Reactive sputtering of a hot target is an incomparably more complicated process. But it is possible to identify common features with sputtering in an inert gas. This similarity, as in the case of a cold target, occurs when during reactive sputtering the target goes into a stationary metallic mode. According to external features both cases are identical, as gas environment contains only argon.
(during reactive sputtering nitrogen is sorbed by a wall), and the target surface is a pure metal. But in the Ar + N₂ mixture, the discharge voltage is higher in this area, and the temperature of the target increases. Calculations using the Hertz-Knudsen equation [7] showed that in the metallic mode, the total flux of titanium atoms \( Q_{tot} \) increases significantly due to the flux of evaporated \( Q_{ev} \) atoms (Figure 3). Moreover, a three-fold difference between the total fluxes of titanium atoms during target sputtering in different gaseous environments (figure 4) may arise (inset in figure 4).

**Figure 3.** Total \( Q_{tot} \), sputtered \( Q_{sp} \) and evaporated \( Q_{ev} \) fluxes of Ti atoms during magnetron operation in Ar+N₂ mixture. Argon pressure of 2 mTorr and nitrogen flow rate in the range of 4–6 sccm.

**Figure 4.** Total titanium fluxes \( Q_{tot} \) during sputtering in Ar (1) and Ar + N₂ (2) with the argon pressure of 2 mTorr and nitrogen flow rate in the range of 4–6 sccm. Inset shows their ratio.

We assume that stronger gas rarefaction, which may occur due to the increase of particles’ flux emitted by a target, causes this difference. The flux is caused by sputtering and evaporation.

Additionally, it is found that the current density value, at which sputtered and evaporated fluxes are equal, weakly depends on the flow rate of nitrogen, and reaches approximately 60 mA/cm² (see figure 3 and 4). This value corresponds to the I-V characteristics in Figure 1, b, where the target is cleared of the nitride.

**Figure 5.** Total fluxes of particles \( Q_{tot} \).

**Figure 6.** Electron emission currents.

Figure 5 presents the final results of the calculation of total fluxes. At low current, as it follows from figure 5, when the target is in the nitride mode, the flux of \( Q_{tot} \) at any nitrogen flow rate is determined by nitride sputtering. After the transition to the metallic mode, which is in figure 5 for any \( Q_0 \) is shown by a surge, the process depends on sputtering and evaporation of titanium. The obtained flux
estimates showed that significant evaporation appears to the left of the maxima of the I-V characteristics (see figure 1(b)). It leads to a stronger heating of the gas near the target by sputtered and evaporated particles. The resulting rarefaction is accompanied by an increase in the discharge voltage with increasing current.

In order to study the influence of thermionic emission on the reactive sputtering, the Richardson-Dushman equation was used [7], where the value $T_i = f(j)$ was given by formula (1) taking into account table 1. Figure 6 shows the results of the calculations. The dashed line in Figure 6 reflects the change in ion-electron emission current. The combined lines consist of two parts. The parts shown by dots reflect the change in the current of thermionic emission in the nitride mode of target operation. Solid lines correspond to the changes in target operation mode and the stationary metallic mode.

The ion-electron and thermionic emission currents are equal when the value of $j \approx 89$ mA/cm$^2$, which insignificantly depends on the flow rate of nitrogen. The maxima of the I-V characteristics are located close to this value. The target temperature at this point reaches approximately 1920 K. This result validates our assumption that, in the metallic mode, gas rarefaction near the target and thermionic emission compete.

4. Conclusions
The study of the discharge I-V characteristics shows that there is an important difference between the processes of reactive sputtering of cold and hot titanium targets. The I-V characteristics of a magnetron with a hot target sputtered in Ar + N$_2$ have two inflection points and an extremum of the maximum type. The inflection points appear due to competition. Firstly, the chemical reaction of nitride formation on the target surface and the process of nitride sputtering by argon ions compete. The ratio of their rates depends on the discharge current density, and determines the target operation mode. Second, in the metallic mode, gas rarefaction near the target and thermionic emission compete. Due to the higher temperature of the target, as compared with sputtering in Ar, its evaporation makes a more significant contribution to gas rarefaction.

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