I-V characteristics of magnetron with hot titanium target sputtered in argon-oxygen mixture

E A Minzhulina, V I Shapovalov, N Aslan and D S Shestakov
Saint Petersburg Electrotechnical University "LETI", St. Petersburg, Russia
E-mail: vishapovalov@mail.ru

Abstract. The discharge current-voltage characteristics of a dc magnetron with a single hot titanium target in Ar + O\textsubscript{2} environment are studied. It was found that the I-V characteristics measured in the range of current densities of 10-200 mA/cm\textsuperscript{2} have three inflection points and a maximum. The competition of several processes can cause the discovered features. In the oxide target operating mode, these processes include the chemical reaction for the formation of oxide on the surface of the target and its sputtering by argon ions. In the metal mode, gas rarefaction near the target and thermionic emission compete.

1. Introduction
Transition metal oxide films are disordered wide-band semiconductors with a fundamental absorption edge in the near UV range. They have high dielectric permittivity and low absorption in the visible and near-IR ranges. Some of them show a chromogenic, ferroelectric, electret, photocatalytic, antibacterial, super-hydrophilic and anti-fog properties, and have a dielectric–metal phase transition when heated. The above features create wide opportunities for practical application [1–3].

Reactive magnetron sputtering is used for deposition of these films more often than other methods [4–6]. The increase in the growth rate, change in the chemical composition and crystal structure of the films were obtained by means of a magnetron with a single hot metal target [7–9], which can be heated up to a melting temperature and above.

For the effective use of a magnetron with a hot target in the synthesis of oxide films, it is necessary to study in detail the features of the discharge in the environment containing oxygen. The goal of this work was to study the discharge current-voltage characteristics of a magnetron with a hot titanium target operating in an Ar+O\textsubscript{2} mixture gas.

2. Experimental details
A detailed description of the experimental conditions is given in [9]. In this work, we used balanced magnetrons of 130 mm in diameter equipped with titanium targets:
- 6 mm thick with typical cooling by running water (cold target);
- 1 mm thick with cooling through fastening elements and a vacuum gap of 1 mm from the copper water-cooled board (hot target).

Magnetron sputtering processes in Ar + O\textsubscript{2} at argon partial pressure of 2 mTorr, oxygen flow rate of 4, 5 and 6 sccm, and discharge current density up to 200 mA/cm\textsuperscript{2} were studied.
3. Results and discussion
Cold titanium target sputtering in an oxygen-containing environment (see figure 1, a) has well-known characteristics of metal target reactive sputtering [10]. They include, first, two possible modes of target operation: metal and oxide. When the discharge current or flow rate of reactive gas changes, the conditions of transition from one mode to another can be achieved. Secondly, the hysteresis effect is observed during the experiments. Both of these features are shown in figure 1, a. It shows the I-V characteristics measured by increasing (solid lines) and decreasing (dashed lines) discharge current. Dependences corresponding to the same gas flow rate in figure 1 have the same markers. A sharp drop in the discharge voltage (more than 100 V) due to an increase in γ-emission (γTi = 0.127, γTiO2 = 0.078 [11]) is recorded in the I-V characteristics at the transition points of the target from oxide to metal mode. At these points, the current density is 83, 111 and 138 mA/cm² at oxygen flow rates of 4, 5 and 6 sccm, respectively. Reverse transitions from the metal to the oxide mode occur at lower current densities.

The discharge emission spectra measured at each point of the I-V characteristics confirm the changes occurring on the target surface. In the oxide mode, the lines of atomic titanium TiI are absent, and the intensity of the line of atomic oxygen OI increases in proportion to the discharge current (see figure 1, b). The transition of the target to the metal mode is accompanied by the appearance of the TiI lines in the spectrum and the disappearance of the OI line.

The I-V characteristics of the hot titanium target magnetron are shown in figure 2, a. They are characterized by:
- presence of maximums;

![Figure 1. The I-V characteristics of a magnetron (a) with a cold titanium target and line intensities TiI(398.5) (solid lines) and OI(777.4) (dashed lines) (b) at the oxygen flow rate (sccm): 1 – 0; 2 – 4, 3 – 5, 4 – 6.](image1)

![Figure 2. The I-V characteristics of a magnetron with a hot titanium target in a composition of Ar + O₂ (a) and intensity of TiI lines (398.5) (b) at the oxygen flow rate (sccm): 1 – 0; 2 – 4, 3 – 5, 4 – 6.](image2)
• absence of obvious signs of changing the target operation mode;
• at \( j < 25 \text{ mA/cm}^2 \), the targets operate in oxide mode in all cases, and the discharge voltage is 50-80 V higher than in the case of target sputtering in an environment of pure argon (curve \( I \));
• the transition of the hot target to the metal mode is accompanied by an increase in the discharge voltage. While a similar transition of the cold target leads to its decrease.

The values of the discharge current density at which the transition to the metal mode occurred were determined by the discharge emission spectra (see figure 2, b). Lines TiI(398.5), as shown in figure 2, b, appeared at current densities of 25.0, 27.8 and 30.6 mA/cm\( ^2 \), which correspond to oxygen flow rate \( Q_0 = 4, 5 \) and \( 6 \) sccm.

![Figure 3](image)

**Figure 3.** The derivatives of the I-V characteristics of a magnetron with cold (a) and hot (b) titanium targets sputtered at the oxygen flow rate (sccm): \( I - 0; 2 - 4; 3 - 5; 4 - 6. \)

The difference between the processes of reactive sputtering of a cold target and a hot target is clearly demonstrated by the \( dU/dj \) derivatives shown in figure 3. The monotone derivatives in Fig. 3, a are broken only at the points of a change mode. As noted above, this rise is caused by an increase in the ion-electron emission coefficient \( \gamma \). A sharp change in \( \gamma \) indicates a very fast transition of the target to the metallic mode. This transition is a process with positive feedback, which starts when equality between the target oxidation rate and oxide sputtering by argon ions is achieved.

The reactive sputtering process of a hot target is more complicated, as confirmed by the derivatives in figure 3, b. They show that the I-V characteristics in figure 2, a have extremes and inflection points. The derivatives in figure 3, b show that to the left of the maximum, each I-V characteristic in figure 2, a has two points of inflection. They are generated by two pairs of processes. If the first point is only marked in the region of 10-15 mA/cm\( ^2 \), then the second one in the region of 22-30 mA/cm\( ^2 \) is quite obvious. In addition, in the discussed I-V characteristics, in the range of 30-40 mA/cm\( ^2 \), third inflection points are observed. Their nature is still unclear.

At low currents, the chemical reaction of oxide formation on the target surface and its sputtering by argon ions compete. If to the left of the first inflection point the first process prevails, 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 oxide film. This process ends at the points indicated above. Then two other processes begin to compete: gas rarefaction near the target and thermionic emission. Here, as the discharge current density increases, the first of them is accompanied by an increase in the discharge voltage, and the second - by a decrease. Moreover, at the inflection point of the I-V characteristics, the second process becomes significant, and at the extremum point with \( dU(j)/dj = 0 \), it becomes dominant. We show further the validity of the assumptions made. But initially we will pay attention to the fact that the oxygen flow rate influences the discharge power (figure 4, a) and, therefore, the heating of the target (figure 4, b).

The temperature change in figure 4, b with reliability R describes the dependence

\[
T_t = T_\infty - T_0 e^{-j/j_0}
\]

(1)

with the parameters given in table. 1. Expression (1) is obtained by modeling a thermal process in a hot target magnetron [8].
Table 1. Parameters of expression (1) for $T_i$.

| $Q_0$, sccm | $T_{\alpha}$, K | $T_0$, K | $j_0$, mA/cm$^2$ | $R$  |
|-------------|----------------|----------|-----------------|------|
| 4           | 2.39           | -1.75    | 76.0            | 0.999|
| 5           | 2.40           | -1.77    | 72.3            | 0.997|
| 6           | 2.28           | -1.72    | 57.4            | 0.998|

Figure 5, a shows the total particle fluxes consisting of the sputtered and evaporated components. If the first of them is proportional to the ion current, then the second, calculated by the Hertz-Knudsen equation [10] taking into account (1), is an exponential function. As figure 5, a shows, at low current, when the target is in the oxide mode, the flow of $Q_{\text{tot}}$ at any oxygen flow rate is determined only by the oxide sputtering. When switching to the metal mode for any $Q_0$, the value of $Q_{\text{tot}}$ increases abruptly by about twenty times. The process begins to depend on sputtering and evaporation of titanium.

The obtained flux estimates showed that significant evaporation arises to the left of the I-V characteristics maximums. It leads to a stronger heating of the gas near the target by sputtered and evaporated particles. The resulting rarefaction with increasing current is accompanied by an increase in the discharge voltage.

At reactive sputtering of a hot target according to our assumption the competitor to gas dilution is thermionic emission. The Richardson-Dushman equation was used to estimate this phenomenon [7]. Figure 5, b shows the results of calculations. The dashed line reflects the change in the current of ion-electron emission. The combined lines 1, 2 and 3 consist of two parts. Point lines specify the change in the current of thermionic emission in the oxide mode of the target. The discontinuous sections of the...
solid lines correspond to the change in the state of the target surface, and then the smooth growth – to the metal stationary mode.

The equality of the currents of ion-electron and thermionic emission insignificantly depends on the oxygen flow rate. It corresponds to the value \( j \approx 94 \text{ mA/cm}^2 \). The temperature of the target at this point has reached approximately 1880 K. This result confirms that in the metallic mode of target operation, thermionic emission competes with gas rarefaction near the target.

When studying the dependences \( U_{j=const}=f(Q_0) \), which we call the I-V characteristics, it was found that for small values of the oxygen flow rate, the \( Q_0 \) the targets operate in a metallic mode. As \( Q_0 \) increases, the target transits to the oxide mode. Conditions for changing the target operation mode are given in table 2, which shows that in order to change the operating mode of a hot target, the oxygen flow rate is required to approximately double.

| \( j \), mA/cm\(^2\) | \( Q_{O_2}, \text{ sccm} \) | \( U, \text{ V} \) | \( Q_{O_2}, \text{ sccm} \) | \( U, \text{ V} \) |
|----------------------|------------------|---------|------------------|---------|
| 27                   | 2.0              | 374     | 3.8              | 440     |
| 55                   | 4.5              | 407     | 11.4             | 441     |
| 82                   | 7.5              | 408     | 13.8             | 488     |

4. Conclusion

The study of the discharge I-V characteristics allowed to establish that there is an important difference between the reactive sputtering processes of cold and hot titanium targets: the I-V characteristics of a magnetron with a hot target sputtered in an \( \text{Ar} + \text{O}_2 \) environment has three inflection points and an extremum of the maximum type. The inflection points appear due to competition, firstly, the chemical reaction of oxide formation on the target surface with the process of its sputtering by argon ions. The ratio of their rates depending on the discharge current density determines the target operation mode. Secondly, in the metal mode, gas rarefaction near the target and thermionic emission compete. Due to the higher temperature of the target, as compared with sputtering in an \( \text{Ar} \) environment, its evaporation makes a more significant contribution to gas rarefaction.

References

[1] Shapovalov V I, Karzin V V and Bondarenko A S 2017 Phys. Lett. A. 381 472–5
[2] Vahl A, Dittmann J, Jetter J et al. 2019 Nanotechnol. 30 235603
[3] Radjehi L, Djelloul A, Lamri S et al. 2019 Sur. Engin. 35 520–6
[4] Zhu M, Li F, Zhou G et al. 2019 Vacuum 164 293–9
[5] Cheng Y T, Qiu W Q, Zhou K S et al. 2019 Ceram. Intern. 45 8175–80
[6] Acosta M, Méndez R A, Riech I et al. 2019 Superlatt. Microstr. 127 123–7
[7] Shapovalov V I and Minzhulina E A 2019 Vacuum 161 324–7
[8] Kozin A A and Shapovalov V I 2019 Sur. Coat. Technol. 359 451–8
[9] Shapovalov V I, Minzhulina E A and Smirnov V V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 387 012069
[10] Goncharov A O, Minzhulina E A and Shapovalov V I 2018 IOP Conf. Ser.: Mater. Sci. Eng. 387 012020
[11] Depla D, Mahieu S and De Gryse R 2009 Thin Solid Films 517 2825–39