East European Journal of Physics. **3.** 606-612 (2023)
DOI:10.26565/2312-4334-2023-3-72 ISSN 2312-4334

THE EFFECT OF PLASMA ACTIVATION OF REACTIVE GAS IN REACTIVE MAGNETRON SPUTTERING[†]

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Received July, 11, 2023; revised August 5, 2023; accepted August 10

The effect of plasma activation of reactive gas on the process of reactive magnetron synthesis of oxide coatings was theoretically and experimentally investigated using a radio-frequency inductively coupled plasma source, which creates a flow of activated reactive gas directed towards the surface on which the oxide coating is deposited. The reactive gas passes through a dense inductively coupled plasma located inside the plasma source, while argon is supplied through a separate channel near the magnetron. A theoretical model has been built allowing the calculation of spatial distributions of fluxes of metal atoms and molecules of activated reaction gas, as well as the stoichiometry area of the synthesized coatings. Calculations were performed on the example of aluminum oxide. It was found that the plasma activation of the reactive gas allows to increase the sticking coefficient of oxygen to the surface of the growing coating from values less than 0.1 for non-activated molecular oxygen to 0.9 when 500 W of RF power is introduced into the inductive discharge. In order to verify the developed model, experiments were conducted on depositing an aluminum oxide film on glass substrates located at different distances from the magnetron target, followed by measuring the distribution of film transparency along the substrate length and comparing it with the calculated distribution. A comparison of the calculation results with the experimental data shows a good agreement in the entire studied range of parameters. Based on the generalization of the obtained results, an empirical rule was formulated that the power ratio of the magnetron discharge and the plasma activator should be approximately 8:1.
Keywords: *Reactive magnetron synthesis, Inductively coupled plasma, Plasma activation of reactive gas, Mathematical simulation*
PACS: 52.77.Dq

INTRODUCTION

Reactive magnetron sputtering is one of the promising methods for the synthesis of high-quality coatings of metal oxides or nitrides on the surface of various products for mechanical engineering, microelectronics, optics, and also for medical applications. A significant disadvantage of the reactive magnetron sputtering is the interaction of the reactive gas not only with the growing film but also with the surface of the magnetron target. Because of this, the target is covered with oxide film causing a decrease in the sputtering rate and the appearance of process instability. The main challenge of reactive magnetron sputtering is the preferential delivery of reactive gas to the surface of the growing film keeping the magnetron target non-oxidized.

It is known that when alumina coatings are deposited by reactive magnetron synthesis, one of the main problems is the low sticking coefficient of molecular oxygen to the aluminum surface. In particular, in [1], the sticking coefficient of oxygen molecules to an atomically pure aluminum surface in ultrahigh vacuum was experimentally measured, while it was found that the probability of an oxygen molecule in the ground state sticking to the aluminum surface at room temperature is about 2%. In [2], similar results were obtained using mathematical modeling by the molecular dynamics method. The results of [3, 4] show that even in conditions typical for industrial technologies (not perfect vacuum, limited surface cleanliness), the sticking coefficient of molecular oxygen to the surface of a growing film in the process of reactive magnetron synthesis does not exceed several percent and the ratio of the flows of oxygen and aluminum required to obtain a stoichiometric film is at least 17.

Since in the reactive magnetron synthesis of Al_2O_3 it is necessary to achieve a high sticking coefficient of oxygen to the almost completely oxidized surface of the growing film, the described results of fundamental studies of molecular oxygen sticking to the atomically clean surface of aluminum can be applied to the description of the synthesis of stoichiometric films of aluminum oxide only indirectly. Therefore, for the practical use of scientific data, it is necessary to build a mathematical model based on the results of systematic measurements of the stoichiometric composition of the synthesized coatings at different ratios of metal and reactive gas flows. As we showed earlier [5], an extremely important role is played not only by the value of the reactive gas flow, but also by the oxygen state (vibrational excitation and dissociation degree of the molecules), and plasma activation of the reactive gas flow can increase the oxygen sticking coefficient dramatically.

Attempts to use plasma activation of reactive gas are known, moreover, in almost any magnetron sputtering system (especially when using an unbalanced magnetron), gas activation occurs in the magnetron plasma, but the effect of such activation is usually small, and to this day there is no clear understanding of the mechanisms of plasma activation and precise "recipes" for the organization of technological processes.

Plasma is a powerful tool, but its effect on gas is quite complex: ionization, excitation, dissociation, and the relationship between these processes strongly depends on the type and pressure of the gas, the density and temperature of

[†] ***Cite as:*** S.V. Dudin, S.D. Yakovin, A.V. Zykov, East Eur. J. Phys. 3, 606 (2023), https://doi.org/10.26565/2312-4334-2023-3-72

electrons, and the properties of the surfaces limiting the plasma. It is very difficult to separate these effects, so here we use the term "plasma activation", under which we understand the complex effect of plasma on a neutral gas, which increases its reactive properties. The effectiveness of plasma activation in reactive magnetron synthesis can be quantified through an increase in the sticking coefficient of the reactive gas.

It is well known that additional activation of the reactive gas significantly improves gas utilization, thus reducing the required gas flow rate that allows the target sputtering in metallic mode. To increase the degree of activation of reactive gas particles, magnetron sputtering technology with additional ionization was used. In particular, this is described in [6]. The process of film growth during reactive deposition consists of two stages. The first is the condensation of the material sputtered from the target. The second is the reaction of the film material with the reactive gas. It was shown that an increase in the plasma density near the substrate by means of an additional inductively coupled discharge makes it possible to increase the activity of the gas and the sticking coefficient of its molecules to the growing film. However, this approach puts RF power not only into the reactive gas but also into the sputtering gas (which takes most of the gas mixture) that greatly reduces the efficiency of the system. In addition, this power is deposited into a large volume of plasma, which also leads to its inefficient use.

In this paper, we explore a different approach. The reactive gas passes through a dense inductively coupled plasma localized inside a dedicated plasma source, while argon is fed through a separate channel near the magnetron. As a result of the concentration of high RF power in a small volume, a dense plasma is created there, which makes it possible to achieve a higher degree of activation of the reactive gas. As a result, a directed flow of activated reactive gas is formed, which, if the process is properly organized, can be delivered directly to the surface of the growing film. Taking into account the complexity of choosing the optimal geometry of the system a mathematical model has been developed and experimentally verified that is described below.

EXPERIMENTAL RESULTS

The process of reactive magnetron sputtering was studied using the multifunctional Cluster Ion-Plasma System (CIPS) [7], which consists of compatible sources of fluxes of metal atoms, ions, and chemically active particles for a complex effect on the growing film. In the current research, the unbalanced magnetron was used in pair with the gas-activating plasma source. The layout of the system may be found in [7]. The RF inductively coupled plasma source is designed to create a flow of activated reactive gas particles, as well as a flow of slow ions and electrons. It can be also used to clean the surface of processed parts prior to coating deposition. The ICP source is located inside the vacuum chamber and can be moved, which allows choosing the optimal ratio between the distances from the sample to the magnetron and to the plasma source. The plasma in such a source is concentrated in a chamber made of a ceramic tube (Fig. 1).

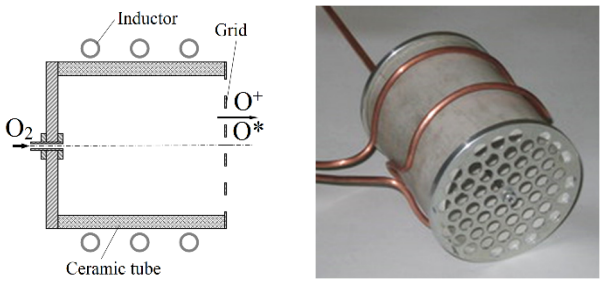

Figure 1. ICP source for reactive gas activation

At the outlet of the source, a metal grid is installed, which limits the plasma and ensures a pressure difference between the source and the technological chamber. An RF generator with a frequency of 13.56 MHz and a power of up to 1 kW is connected to the inductor coil through a matching circuit. Fig. 2 presents a photo of the simultaneous operation of the magnetron and the plasma source. Details of the gas activation in plasma are discussed in [8].

When studying the transparency of oxide films depending on stoichiometry, an interesting fact was found: a non-stoichiometric film is more transparent to long-wave light with the greatest transparency in the infrared range. This phenomenon is illustrated in Fig. 3.

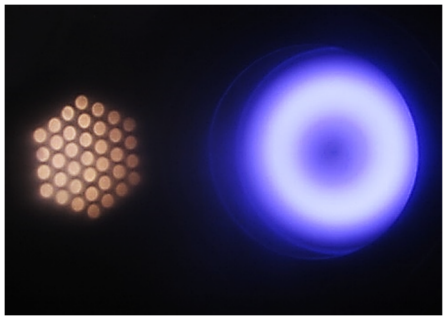

Figure 2. Photograph of the simultaneous operation of the magnetron and the plasma source.

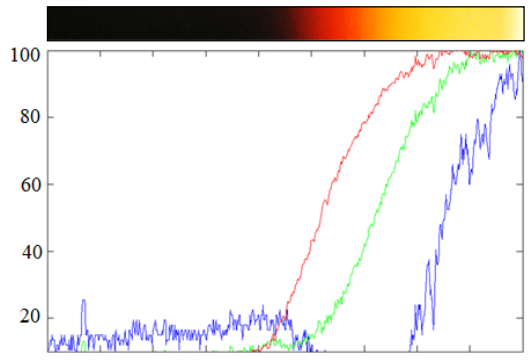

Figure 3. Distribution of the transparency of the alumina film along the sample for radiation with different wavelengths: 650 nm (red line), 450 nm (blue line), 550 nm (green line). On the right edge of the sample, the film is completely stoichiometric

THEORETICAL MODEL

To improve the understanding of the process of plasma activation of the reactive gas during reactive magnetron synthesis of oxide coatings, a mathematical model was built, which is described below.

The dependence of the current density of argon ions on the target surface from the radius is given by the following piecewise linear approximation:

$$J_{Ar}(r) := \left(\frac{R2 - R1}{2} - \left| r - \frac{R1 + R2}{2} \right| \right), \tag{1}$$

where $R1 = 2$ cm and $R2 = 7$ cm are the inner and outer radii of the erosion area of the magnetron target. The normalization constant for this dependence was determined by calculating the integral current of argon ions on the target, which is equal to the magnetron discharge current measured in the experiment:

$$I_{Ar\_norm} := \int_{R1}^{R2} J_{Ar}(r) \cdot 2 \cdot \pi \cdot r dr . \tag{2}$$

The flux density of sputtered aluminum atoms at a point with coordinates r, z through a surface located at an angle αs to the axis of the magnetron is determined by the following expression:

$$j_A(r,z) := S \cdot \frac{1}{I_{Ar\_norm}} \cdot \int_{R1}^{R2} \int_0^{\pi} \frac{4r'}{\pi} \cdot J_{Ar}(r') \cdot \frac{\cos(\alpha_S)}{2} \times$$
$$\times \frac{z^2 + r^2 + r'^2 + 2rr'\cos(\varphi) + \left(\frac{z}{\cos(\alpha_S)} \right)^2 - r'^2 \cdot \sin(\varphi)^2 - \left(-r - r' \cdot \cos(\varphi) - z \cdot \tan(\alpha_S) \right)^2}{\left(z^2 + r^2 + r'^2 + 2rr'\cos(\varphi) \right)^2} d\varphi dr \tag{3}$$

In this expression, the sputtering coefficient S is defined as a function of the discharge voltage U:

$$S := 0.4 \cdot \frac{U}{530} \tag{4}$$

Fig. 4 shows the calculated distributions of the aluminum film deposition rate at different distances from the magnetron. The diagram of the relative location of the magnetron target, the oxygen plasma activator, and the substrate is shown in Fig. 5. All calculations and experiments were performed with the magnetron current of 7.8 A, magnetron voltage of 520 V, and oxygen flow rate of 20 sccm.

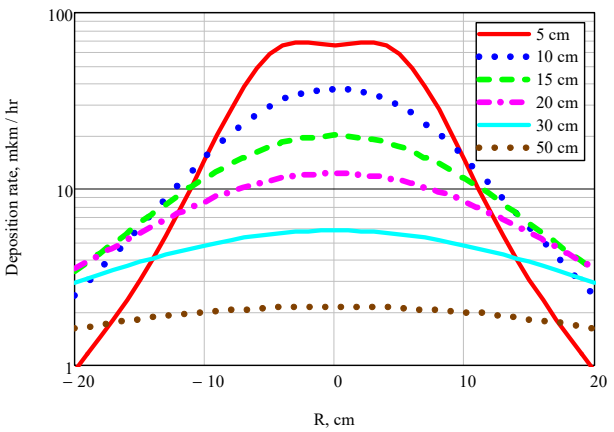

Figure 4. Calculated distributions of the aluminum film deposition rate in μm/h at different distances from the magnetron. The curves correspond to the following distances from the magnetron target (from top to bottom): 5, 10, 15, 20, 30, 50 cm

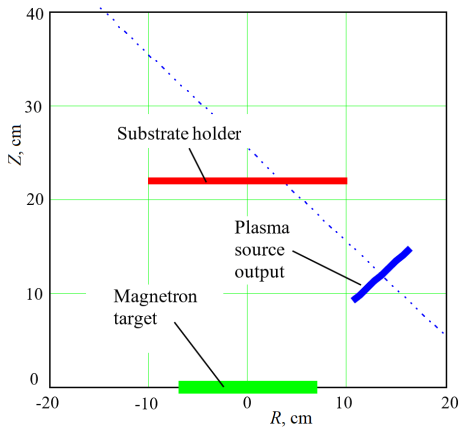

Figure 5. Schematic of the relative location of the magnetron target, the oxygen plasma activator, and the substrate. The dotted line shows the axis of the plasma activator. Coordinates are in cm

The molecular oxygen flux density at the point with coordinates r, z (the coordinate origin is in the center of the outlet of the plasma source) through the surface located at an angle β_s to the axis of the reactive gas activator is determined by an expression similar to (3):

$$j_{O2}(r,z) := \int_0^{R_{O2}} \int_0^{\pi} \frac{4r'}{\pi} \cdot J_{O2} \cdot \frac{\cos(\beta_S)}{2} \times \\ \times \frac{z^2 + r^2 + r'^2 + 2rr'\cos(\varphi) + \left(\frac{z}{\cos(\beta_S)}\right)^2 - r'^2 \cdot \sin(\varphi)^2 - \left(-r - r' \cdot \cos(\varphi) - z \cdot \tan(\beta_S)\right)^2}{\left(z^2 + r^2 + r'^2 + 2rr'\cos(\varphi)\right)^2} d\varphi dr \tag{5}$$

In this expression, R_{O2} = 4 cm is the radius of the plasma source, $J_{O2} := 1/\pi \cdot {R_{O2}}^2$.

To convert the coordinates to the system with the origin in the center of the magnetron target, the following expression may be applied:

$$j'_{O2}(r,z) := j_{O2}\left[(r - x_{O2}) \cdot \cos(\alpha_{O2}) + (z - y_{O2}) \cdot \sin(\alpha_{O2}) - (r - x_{O2}) \cdot \sin(\alpha_{O2}) + (z - y_{O2}) \cdot \cos(\alpha_{O2})\right] \tag{6}$$

In addition, it is necessary to take into account the isotropic flow j_{O2ost} of non-activated oxygen with the partial pressure p_{O2} from the chamber to the substrate:

$$j_{O2ost} := \frac{1}{4} \cdot e \cdot p_{O2} \cdot 3.5 \cdot 10^{16} \cdot \sqrt{\frac{8 \cdot T}{\pi \cdot M}} \tag{7}$$

The calculated spatial distributions of aluminum and oxygen flux density on the substrate, which is perpendicular to the magnetron axis, are shown in Fig. 6.

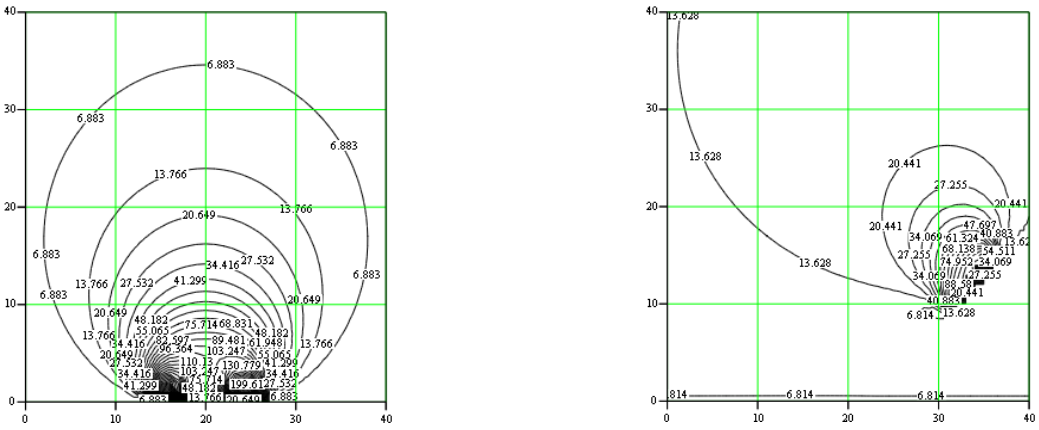

Figure 6. Calculated spatial distributions of aluminum (left) and oxygen (right) flux density on a substrate perpendicular to the magnetron axis (the coordinate scale is the same as in Fig. 5).

Now we can write the stoichiometric ratio

$$\xi := \frac{4}{3} \cdot \frac{I_{O2} \cdot K \cdot j'_{O2} + j_{O2ost}}{I_{Ar} \cdot j_A} \tag{8}$$

Here, *K* is the sticking coefficient of activated oxygen to the surface of the growing film. The expression (7) Takes into account the fact that the oxygen comes to the film surface from two sources: the directed flow of activated oxygen from the plasma source and the isotropic flow of the residual oxygen from the chamber, which is accounted for using the partial pressure p_{O2}.

In order to compare the results of calculations with experimental data on the dependence of film transparency on process parameters, it is necessary to know the dependence of transparency on film stoichiometry. This dependence was taken from [9]. Fig. 7 shows the experimental values of transparency compared to the analytical approximation.

It should be noted that the film transparency depends not only on its stoichiometry but also on its thickness. In the described model, the absorption of light is considered to be proportional to the thickness of the coating, which was calculated at each spatial point, based on the local flow of aluminum. Examples of calculated distributions of coating thickness along samples located at different distances from the magnetron symmetrically and perpendicularly to its axis are shown in Fig. 8.

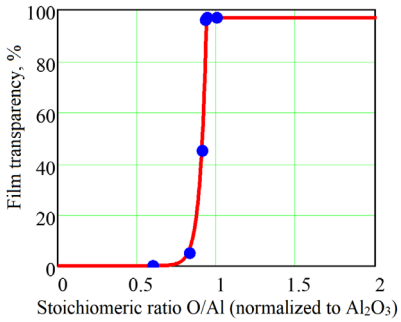

Figure 7. Experimental values of transparency (points) compared to analytical approximation (curve) depending on the stoichiometric ratio of oxygen and aluminum flows (taking into account the sticking coefficient)

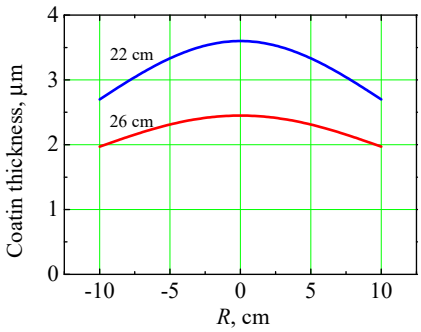

Figure 8. Calculated oxide coating thickness distribution along the 20 cm long substrate at different distances from the magnetron target

Thus, using the above expressions, we can calculate the stoichiometric ratio and transparency of the film at any point of the technological chamber at any size and relative location of the magnetron, the substrate, and the plasma activator of the reactive gas, and finally, at arbitrary process parameters. Fig. 9 shows the calculated spatial distributions of the stoichiometric ratio and transparency of the film in the process chamber. It can be seen that near the magnetron, where the flow of aluminum is high, it is impossible to obtain a stoichiometric film, at the same time there is a rather large region of stoichiometry, in which the samples should be placed during technological processes.

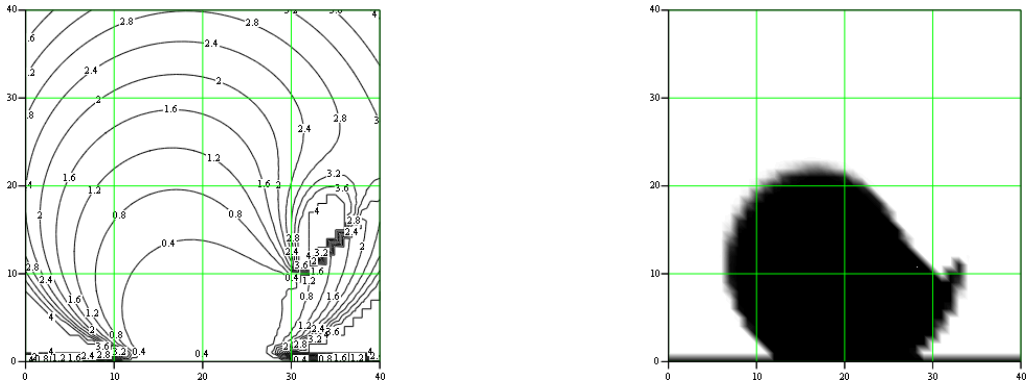

Figure 9. Spatial distributions of the stoichiometric ratio (left) and film transparency (right) in the technological chamber

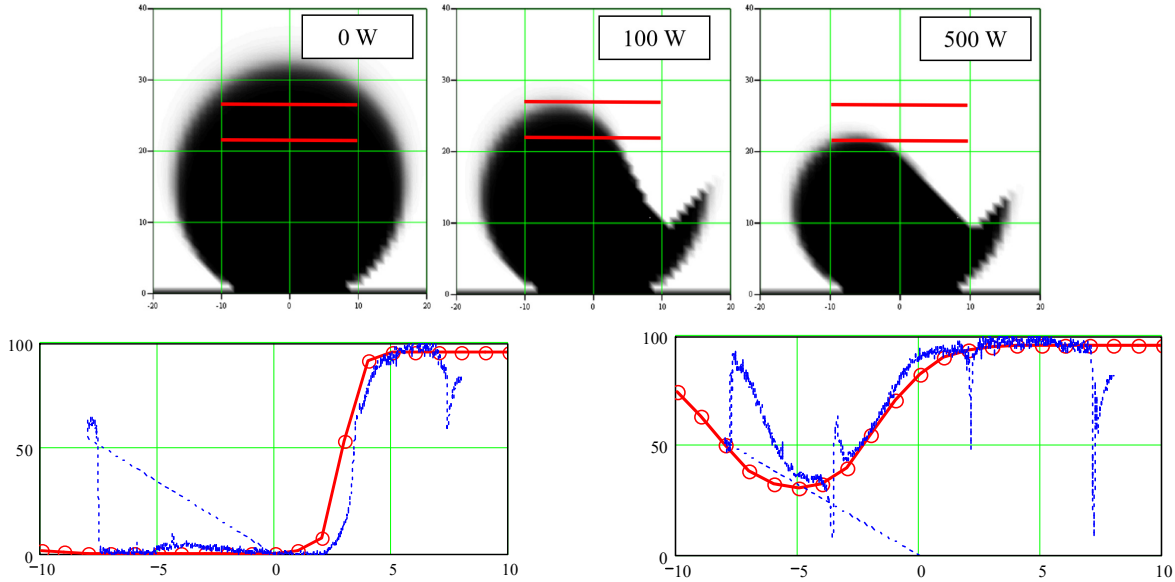

Figure 10. Comparison of experimental data on the spatial distribution of the coating transparency with the simulation results. In the upper figures, the calculated transparency is shown by grayscale. Two positions of the substrates are shown in red: 22 cm and 26 cm from the magnetron target. The lower pictures compare theoretical (red) and experimental (blue) transparency cource along the sample for the distance of 22 cm (left) and 26 cm (right)

To verify the developed model, experiments were carried out on depositing an aluminum oxide film to glass substrates located at different distances from the magnetron target, followed by measuring the distribution of film transparency (at 600 nm wavelength) along the length of the substrate and comparing it with the calculated distribution. All the parameters were input into the model according to the experimental conditions, excluding the sticking coefficient for oxygen, which is predominantly unknown. Then, the sticking coefficient was iteratively fit to achieve the maximum possible accordance between the calculation result and the experimental data. The results of calculations, experiments, and their comparison are shown in Fig. 10.

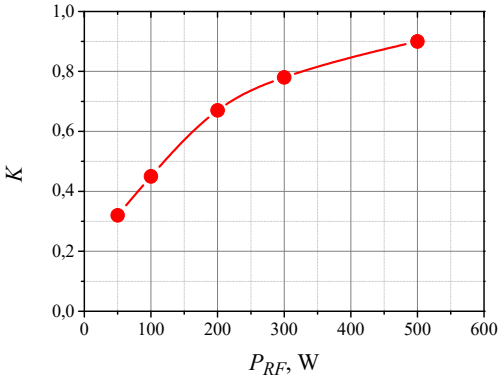

Figure 11. Dependence of the oxygen sticking coefficient on RF power supplied to the plasma activator

The obtained results allow us to find a very important principle of the process of plasma activation of reactive gas, namely the dependence of the oxygen sticking coefficient on the RF power supplied to the plasma activator. The found dependence is shown in Fig. 11. It is quite obvious that the sticking coefficient increases with increasing RF power input into the gas-activator plasma source and approaches almost unity at a power of 500 W or more. Thus, the further increase of RF power does not make sense, which is very important in view of the high price of powerful RF generators. To generalize the obtained results, it is possible to formulate the following empirical rule: the power ratio of the magnetron discharge and the plasma activator should be approximately 8:1.

CONCLUSION

In this paper, we discussed the possibility of improvement of the technology of reactive magnetron sputtering by addition to the sputtering system of a dedicated plasma source activating the reactive gas being passed through the dense plasma inside the source. The source creates a flow of activated reactive gas directed towards the surface on which the oxide coating is deposited. It has been shown that when alumina coatings are deposited by reactive magnetron synthesis, the problem of the low sticking coefficient of molecular oxygen to the aluminum surface can be solved if sufficient RF power is input to the source. This possibility of plasma activation of reactive gas in the process of reactive magnetron synthesis of oxide coatings was theoretically and experimentally investigated. The theoretical model has been built that allows the calculation of spatial distributions of flows of metal and reaction gas, as well as the stoichiometry area of the synthesized coatings. Calculations were performed on the example of aluminum oxide. It was found that the plasma activation of the reactive gas allows to increase significantly the sticking coefficient of oxygen to the surface of the growing coating. In our experiments, the sticking coefficient changed from values less than 0.1 without additional gas activation to 0.9 when 500 W of RF power was introduced into the inductive discharge.

The developed model has been experimentally verified. In the experiments, an aluminum oxide film was deposited on glass substrates located at different distances from the magnetron target at different levels of RF power input. The resulting distribution of film transparency along the substrate was measured and compared with the simulation output. A comparison of the calculation results with the experimental data shows a good agreement in the entire studied range of parameters. Analyzing the obtained results, we formulated an empirical rule giving the way of estimation of the additional RF power required to reach the oxygen sticking coefficient close to unity. According to this rule, the optimal power ratio of the magnetron discharge and the plasma activator should be approximately 8:1.

Acknowledgement

This work was supported by the National Research Foundation of Ukraine in the framework of the project 2021.01/0204.

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ВПЛИВ ПЛАЗМОВОЇ АКТИВАЦІЇ РЕАКТИВНОГО ГАЗУ ПРИ РЕАКТИВНОМУ МАГНЕТРОННОМУ РОЗПИЛЕННІ

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Теоретично та експериментально досліджено вплив плазмової активації реактивного газу на процес реактивного магнетронного синтезу оксидних покриттів з використанням ВЧ індукційного джерела плазми, яке створює потік активованого реактивного газу, спрямований у напрямку поверхні, на яку наноситься оксидне покриття. Реактивний газ проходить через щільну індуктивно зв'язану плазму, розташовану всередині джерела плазми, тоді як аргон подається через окремий канал поблизу магнетрона. Побудовано теоретичну модель, яка дозволяє розрахувати просторові розподіли потоків атомів металу та молекул активованого реакційного газу, а також розподіл стехіометрії синтезованих покриттів. Виконано розрахунки на прикладі оксиду алюмінію. Виявлено, що плазмова активація реактивного газу дозволяє збільшити коефіцієнт прилипання кисню до поверхні покриття, що зростає, від значень, менших за 0,1 для неактивованого молекулярного кисню, до 0,9 при введенні в індукційний розряд ВЧ потужності 500 Вт. Для перевірки розробленої моделі були проведені експерименти з нанесення плівки оксиду алюмінію на скляні підкладки, розташовані на різних відстанях від мішені магнетрона, з подальшим вимірюванням розподілу прозорості плівки по довжині підкладки та порівнянням його з розрахунковим розподілом. Порівняння результатів розрахунків з експериментальними даними демонструє добре узгодження в усьому дослідженому діапазоні параметрів. На підставі узагальнення отриманих результатів було сформульоване емпіричне правило, що співвідношення потужностей магнетронного розряду та плазмового активатора має бути приблизно 8:1.

Ключові слова: *реактивний магнетронний синтез, індуктивно зв'язана плазма, плазмова активація реактивного газу, математичне моделювання*