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INFLUENCE OF GAS PRESSURE ON THE GROWTH OF CLUSTERS IN MAGNETRON DISCHARGE

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Based on the hybrid model, a magnetron discharge in a cylindrical chamber filled with argon was modeled. The obtained results were used to study the influence of gas pressure on the sputtering of the copper cathode, the diffusion of copper atoms in the discharge chamber, and the process of cluster formation. It is shown that the number of copper atoms in the discharge chamber, which is determined by their flow from the cathode, diffusion, and the processes of cluster formation and growth, depends non-monotonically on the gas pressure and reaches a maximum value at $p \sim 1.75$ Torr. The simulation results also show that the total number of dimers and clusters in the chamber increases with increasing gas pressure at $p < 1.75$ Torr. However, with a further increase in pressure, the number of dimers remains nearly unchanged, while the number of clusters consisting of three or more copper atoms decreases.

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INTRODUCTION

The formation of nanoparticles in magnetron plasma is an important and promising area of research in the field of nanotechnology [1]. This method is actively used to create nanoparticles with specified sizes and compositions, which can be deposited on substrates or used in other high-tech applications. One of the key advantages of magnetron sputtering is the ability to precisely control the size and composition of particles, which is achieved by using electrodes made of different materials or alloys [2, 3]. However, the process remains inefficient due to low productivity: a significant part of the nanoparticles settles on the walls of the chamber or returns to the cathode, and only a small number reaches the substrate. Optimization of the process parameters is critically important, as it allows solving the problem of the efficiency of nanoparticle transport and increasing the productivity of their formation.

The study of the process of generating nanoparticles in magnetron plasma has been carried out in a number of works [4, 5], however, a self-consistent model that would take into account the mutual influence of the parameters of the magnetron discharge and clusters on the plasma has not been developed.

The aim of this work was to model the magnetron discharge, the formation of clusters of metal atoms (e.g. copper or molybdenum) sputtered from the cathode during its bombardment by ions, and their diffusion in the magnetron discharge chamber in the frame of self-consistent model.

1. MODEL AND SIMULATION METHOD

Consider a magnetron discharge that is ignited in a cylindrical chamber with radius R=0.03 m. The distance between the cathode and the anode is L=0.03 m, the radius of the cathode is r_c=0.025 m, and the radius of the anode is r_a=0.03 m. The voltage between the electrodes is U=300 V. Argon is used as the buffer gas, and it is assumed that the cathode is made from copper. The pressure of the buffer gas varies within P=0.5…3 Torr.

To simulate the magnetron discharge, a hybrid model is used [6,7], according to which all plasma electrons are divided into two groups: fast and slow. Fast electrons appear in the chamber as a result of emission from the cathode when it is bombarded by ions. These electrons have sufficient energy to ionize or excite argon atoms. Their total energy, which is equal to the sum of kinetic and potential energy, exceeds a certain value ε_{th}, which for argon gas is 11.5 eV. On the other hand, the total energy of slow electrons is less than ε_{th}.

To simulate the motion of fast electrons and elementary processes involving them, the "particles in cells" model and the Monte Carlo method (PIC/MCC) are used. The study of macro electrons trajectories begins from the moment of their injection and continues until the moment of disappearance. The disappearance can occur in two ways: 1) by transition to the group of so-called slow electrons; 2) by absorption of electrons by electrodes. The number of macro electrons injected from the cathode is determined by the ion flux to the cathode and the secondary ion-electron emission coefficient. The equations used to describe the motion of macro electrons between their collisions with atoms are (1) and (2):

$$m_e \frac{d\vec{v}}{dt} = e\vec{E} + e\left[\vec{v} \times \vec{B}\right], \quad (1)$$

$$\frac{d\vec{r}}{dt} = \vec{v}, \quad (2)$$

where e, $\vec{v}$, $\vec{r}$ is the charge, velocity vector and radius vector of the electron, respectively; $\vec{E}$ and $\vec{B}$ are the electric and magnetic field strengths. The electric field has radial and azimuthal components and is calculated from the Poisson equation in the hydrodynamic model.

The maximum value of the magnetic field is B=0.03 T, and its distribution in the discharge chamber is determined by an approximation of the experimental data obtained in the [8].

According to the Monte Carlo method, the probability of collision of electrons with argon atoms over time Δt is calculated and compared with a random number R belonging to the interval [0, 1]:

$$P_{coll} = 1 - \exp\left(-\Delta t \sum \sigma_{col}(\varepsilon) n_a\right),$$

where n_a is the concentration of argon atoms, $\sigma_{col}(\varepsilon)$ is the cross section of different types of electron collisions with energy ε. In the model, we take into account the excitation and ionization of argon atoms by electron impact, as well as elastic collisions of electrons with atoms. We neglect the collisions of electrons with copper atoms, which may be acceptable in the case of a slight sputtering of the electrode. The concentration of fast electrons n_e^h is determined by the "particles in cells" method [9].

To simulate slow electrons and ions, a hydrodynamic model is used, which includes the continuity equation and Poisson's equation. The continuity equations for ions and slow electrons have the form (3) and (4):

$$\frac{\partial n_e}{\partial t} + \nabla\left(n_e \vec{v_e}\right) = S, \quad (3)$$

$$\frac{\partial n_i}{\partial t} + \nabla\left(n_i \vec{v_i}\right) = S, \quad (4)$$

where n_e, n_i are the densities, $\vec{v_e}$, $\vec{v_i}$ are the velocities of slow electrons and ions, respectively, and S is the ionization rate, which is calculated in the kinetic part using the Monte Carlo method [9]. Here, we consider the case when the density of argon ions is essentially larger than that of copper ions.

The drift-diffusion approximation was used to describe the ion and slow electron fluxes (5) and (6):

$$\Phi_e = n_e \vec{v_e} = -\mu_e n_e \vec{E} - D_e \nabla n_e, \quad \mu_e = \frac{\frac{e}{m_e \nu_{ea}}}{1 + \frac{\omega_c}{\nu_{ea}}}, \quad (5)$$

$$\Phi_i = n_i \vec{v_i} = \mu_i n_i \vec{E} - D_i \nabla n_i, \quad \mu_i = \frac{e}{m_i \nu_{ia}}, \quad (6)$$

where μ_e, μ_i are the motilities of electrons and ions, respectively; ω_c is the cyclotron frequency of rotation of electrons around the magnetic field lines; ν_{ea}, ν_{ea} are the frequencies of collisions of electrons and ions with neutral atoms; D_e, D_i are the diffusion coefficients of electrons and ions.

Poisson's equation in a cylindrical coordinate system looks like this (7):

$$\frac{\partial^2 \varphi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial \varphi}{\partial r}\right) = -\frac{e}{\varepsilon_0}\left(n_i - n_e - n_e^h\right). \quad (7)$$

To model the formation of clusters and their spatial distribution in the cylindrical chamber, the diffusion equations for copper atoms and clusters are used (8):

$$\frac{\partial N_n}{\partial t} - \frac{\partial}{\partial z}\left(D_n \frac{\partial N_n}{\partial z}\right) - \frac{1}{r}\frac{\partial}{\partial r}\left(r D_n \frac{\partial N_n}{\partial r}\right) = S_n, \quad (8)$$

where D_n, N_n are the diffusion coefficient and the concentration of clusters containing n atoms. In our model, the maximum cluster size $n_{\max} = 30$. In the case of $n=1$ equation (8) describes the diffusion of copper atoms, and at $n=2$ one describes the diffusion of dimers. The diffusion coefficient is determined according to the formula [10] $D_n = D_0 / n^{2/3}$, $D_0 = \frac{3}{8\sqrt{2\pi} r_w^2 n_a}\sqrt{\frac{kT}{m}}$,

where T, m are the temperature and mass of the buffer gas atoms, r_w is the Wigner-Seitz radius [10]. The term on the right-hand side of equation (8) describes the change in concentration due to particle transformations during collisions. For clusters of size n $(n>2)$ we have (9)

$$S_n = k_{n-1} N_1 N_{n-1} - k_n N_1 N_n - \left(\nu_n N_n - \nu_{n+1} N_{n+1}\right), \quad (9)$$

where the coefficient k_n determines the rate of adhesion of copper atoms to a cluster of size n, ν_n is the frequency of atom evaporation from this cluster. To determine these constants, we will use the liquid drop model for the cluster. According to this model, we assume that the cluster melts and loses its crystalline structure. The radius of such cluster is determined by the formula $r(n)=r_w n^{1/3}$, and the constant of atom adhesion to the cluster surface is $k_n = k_0 n^{2/3}$, $k_0 = \sqrt{\frac{2T}{\pi m}}\pi r_w^2$.

The total binding energy of atoms in a cluster is determined by the formula (10)

$$\mathrm{E}(n) = \varepsilon_0 n - A \cdot n^{2/3}, \quad (10)$$

where ε_0 is the sublimation energy of the macroscopic system per atom, A is specific surface energy of the cluster. The second term on the right-hand side of formula (10) includes the surface energy, which can be expressed in terms of the surface tension of the macroscopic system. The binding energy of an atom in a liquid cluster [11]

$$\varepsilon_n = \frac{d\mathrm{E}(n)}{dn} = \varepsilon_0 - \frac{\Delta\varepsilon}{n^{1/3}}, \quad \Delta\varepsilon = \frac{2}{3}A.$$

The evaporation rate ν_n can be expressed in terms of the rate constant of atomic adhesion based on the principle of detailed equilibrium (11)

$$\nu_n = k_n N_{sat}(T) \exp\left(-\frac{\varepsilon_{n+1} - \varepsilon_0}{kT}\right), \quad (11)$$

where $N_{sat}(T)$ is the concentration of atoms of saturated metal vapour at temperature T.

For dimmers we have

$S_2 = K N_1^2 n_a + \nu_3 N_3 - k_2 N_2 N_1 - \nu_2 N_2$, where for copper atoms the rate constant of the three-particle process is $K=3\cdot10^{-33}$ cm$^{-6}\cdot$s^{-1} [11].

The term in the right-hand side of equation (8) for metal atoms (at $n=1$) is

$$S_1 = \sum_{n=2}^{n_{\max}} n S_n.$$

The numerical integration of equations (1), (2) is carried out using the Boris algorithm [12]. The particle-

in-cell (PIC) method is used to determine the concentration of fast electrons. The solution to the system of equations (3)–(7) is found by the finite difference method. The exponential scheme of Sharfetter and Hummel [13] is used to discretize the fluxes of electrons and ions.

2. RESULTS AND DISCUSSION

Fig. 1 presents the spatial distributions of the electric field potential and ion density at gas pressure of 1 Torr in the discharge chamber. As can be seen from Fig. 1,b a region of increased density of ions is formed in the chamber at some distance from the cathode, which is due to the ionization of neutral argon atoms by fast electrons.

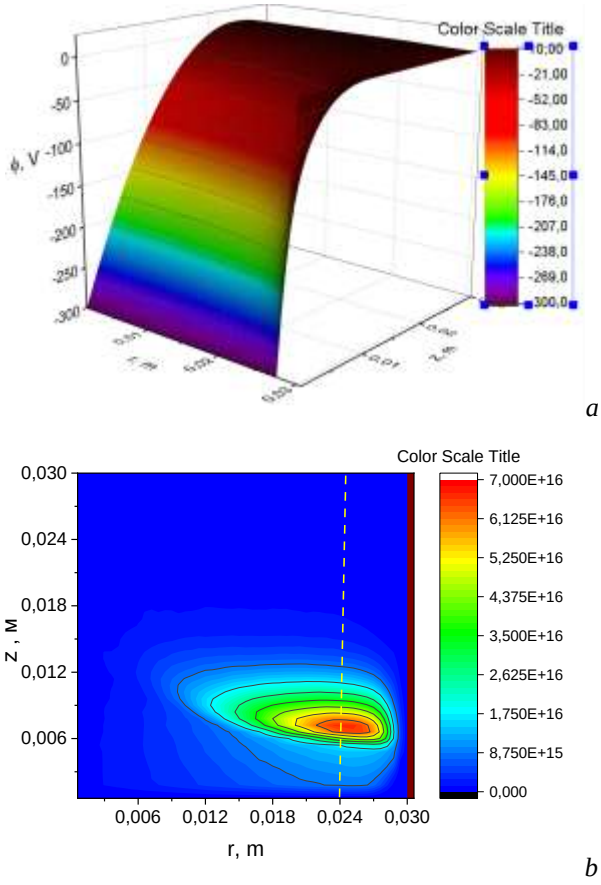

Fig. 1. Spatial distributions of electric field potential (a) and ion density (b) at gas pressure p=1 Torr

The spatial distributions of the ion density, total electron density (slow and fast electrons), fast electron density, and electric field potential along the dotted line in Fig. 1,b, which passes through the region of maximum ionization parallel to the axial axis, are shown in Fig. 2.

The figure shows that a charged region is formed near the cathode, in which a sharp change in potential occurs, and therefore a large electric field is observed. The ionization region is located at the boundary of the near-cathode layer. Ions are accelerated by the field in the near-cathode layer, bombard the cathode, knocking out electrons and copper atoms. The cathode scattering coefficient depends on the ion energy and is determined on the basis of experimental data [14].

Fig. 3 shows the radial distributions of ion fluxes to the cathode and copper atom fluxes from the cathode for different gas pressures. It should be noted that the ion fluxes to the cathode are not uniform over its surface, their maximum values are opposite the ionization region. With increasing gas pressure, the ion fluxes increase, which is associated with an increase in the ion density in the discharge.

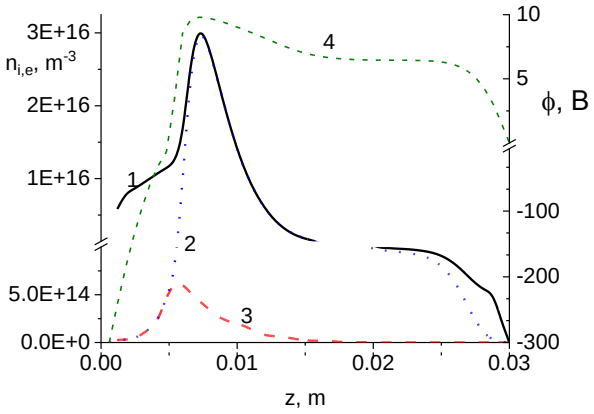

Fig. 2. Axial spatial distributions at r=0.024 m the density of ions (curve 1), electrons (curve 2), fast electrons (curve 3) and the potential of the self-consistent electric field (curve 4)

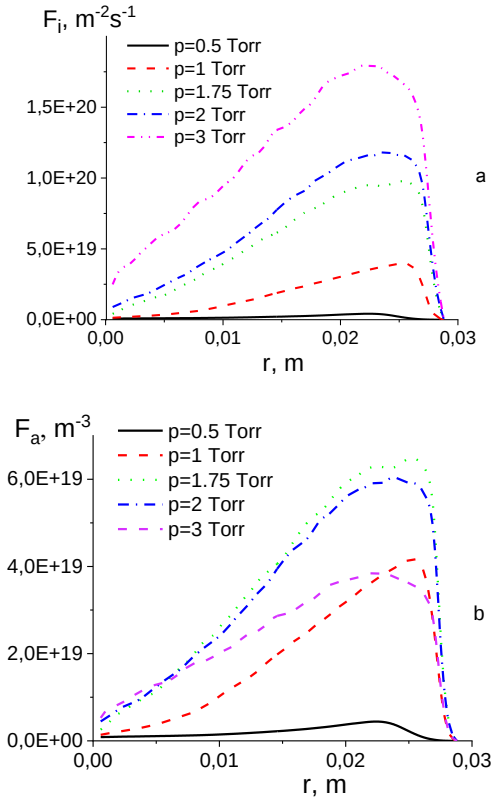

Fig. 3. Radial distributions of ion fluxes to the cathode surface (a) and copper atom fluxes from the cathode (b) at different argon pressures in the chamber

The fluxes of copper atoms from the cathode are also non-uniform in radius, but their intensity depends on the pressure non-monotonically. With increasing gas pressure to p^*~1.75 Torr, the sputtering of the cathode

increases, and with a further increase in pressure, it decreases. This is due to a decrease in the energy of ions bombarding the cathode and, as a result, a decrease in the sputtering coefficient with increasing pressure.

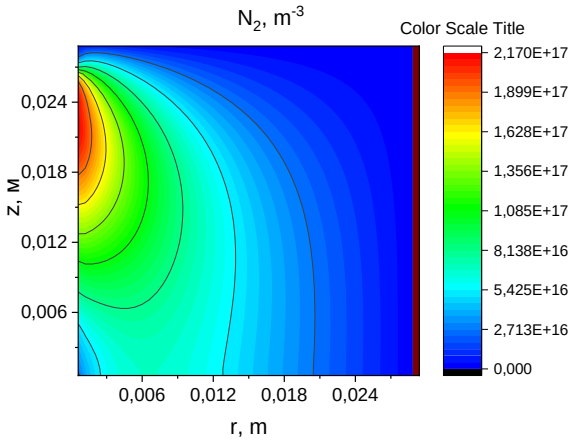

Fig. 4. Spatial distribution of dimers at p=1.75 Torr

The total number of copper atoms N_{Cu} in the chamber is determined from the condition of equality of their flux from the cathode and losses for cluster formation, as well as losses due to diffusion to the walls. The dependence N_{Cu} on the gas pressure is shown in Fig. 5. The decrease in the number of copper atoms in the chamber with increasing pressure from p=1.75 Torr to p=3 Torr can be explained by a decrease in their flux from the cathode. However, with increasing pressure from p=0.5 to p=1.75 Torr, the flux of atoms from the cathode increases, but N_{Cu} has a minimum in this area at p=1 Torr.

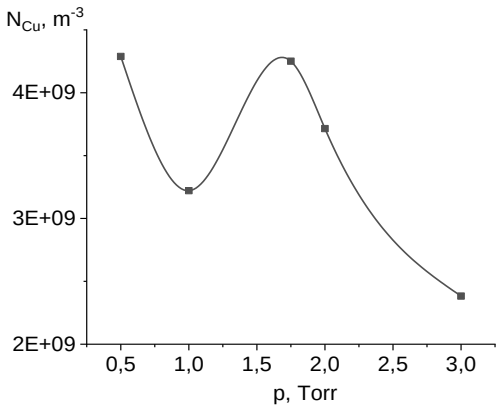

Fig. 5. Number of copper atoms in the chamber as a function of argon pressure

After the start of the injection of copper atoms into the magnetron discharge chamber, the processes of nucleation, diffusion and growth of clusters occur [15], and after some time, stationary spatial distributions of their concentrations are established. Fig. 4 shows the spatial distribution of dimers at a gas pressure p*~1.75 Torr. The maximum concentration of dimers is observed near the cathode opposite the ionization region in the discharge. Due to diffusion in the cylindrical chamber, dimers spread mainly in the radial direction to the axis of the chamber, as a result of which a near-cathode region is formed where their concentration is increased.

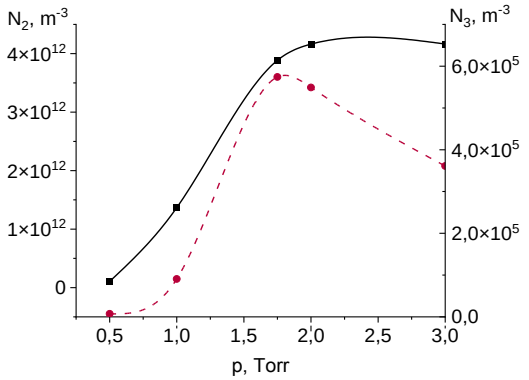

Fig. 6. The number of dimers (solid curve) and clusters (dashed curve) in the chamber as a function of argon pressure

Fig. 6 show the dependences of the total number of dimers and clusters *(n=3)* on the gas pressure. The number of dimers N_2 increases with increasing pressure to p^*, and with further increasing pressure remains unchanged. The number of clusters N_3 also increases with increasing pressure in the range $p \in [0.5…1.75]$ Torr, but decreases with further increasing pressure.

CONCLUSIONS

Based on the hybrid model, we have developed a code for modelling magnetron discharge and the formation of metal clusters, in particular copper and molybdenum, in a cylindrical chamber filled with argon at pressures $p \in [0.5…3]$ Torr. The results of the simulation were used to study the effect of gas pressure on the sputtering of a copper cathode, the diffusion of copper atoms in the discharge chamber, and the process of cluster formation. It was shown that the magnitude of the flow of atoms from the cathode depends on the gas pressure non-monotonically. This is explained by the fact that the sputtering of the cathode depends not only on the flow of ions to it, but also on the ion energy, which increases with decreasing gas pressure. The number of copper atoms in the discharge chamber, which is determined by their flow from the cathode, diffusion, and the processes of cluster formation and growth, also depends non-monotonically on the gas pressure and reaches a maximum value at $p^* \approx 1.75$ Torr. The simulation results show that the total number of dimers in the chamber increases with increasing gas pressure to the value p^*, and remains unchanged with further increasing pressure. The total number of clusters consisting of three or more copper atoms increases with increasing pressure to a value of p^*, and then decreases.

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ВПЛИВ ТИСКУ ГАЗУ НА РІСТ КЛАСТЕРІВ У МАГНЕТРОННОМУ РОЗРЯДІ

А.С. Бібік, О.І. Демешко, О.Ю. Кравченко, І.Б. Денисенко, А.М. Веклич

На основі гібридної моделі промодельований магнетронний розряд у циліндричній камері, яка заповнена аргоном. Отримані результати використано для дослідження впливу тиску газу на розпилення мідного катода, дифузію атомів міді в розрядній камері та процес утворення кластерів. Показано, що кількість атомів міді в розрядній камері, яка визначається їх потоком з катода, дифузією, процесами утворення і росту кластерів, немонотонно залежить від тиску газу і досягає максимального значення при $p \sim 1{,}75$ Торр. Результати моделювання також показують, що загальна кількість димерів і кластерів у камері збільшується зі збільшенням тиску газу до значення $p < 1{,}75$ Торр. Однак при подальшому підвищенні тиску кількість димерів залишається незмінною, а кількість кластерів, що складаються з трьох і більше атомів міді, зменшується.