Numerical study of nitrogen bulk dissociation in DC magnetron discharge in Ar+N\textsubscript{2} mixture

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Abstract. The effect of the composition of the gas feed mixture on the dissociation rate constant of molecular nitrogen is examined by numerical solving the Boltzmann equation written in a two-term approximation for conditions corresponding to nitride aluminum films deposition. By solving of macroscopic balance equations in volume occupied with plasmas of stationary low-pressure glow discharge in a nitrogen-argon mixture the atomic nitrogen density was determined. It’s shown that there is a maximum of atomic nitrogen density at certain stoichiometry of gas feed mixture.

1. Introduction

The development of radio devices, communication and data transmission systems is determined primarily by expanding their frequency range towards microwave frequencies in the range from units to several tens of gigahertz and is associated with improving existing ones and creating new functional elements that perform frequency selection and signal generation. Modern technical solutions in this field are based on the use of a combination of basic research results and technological achievements in the field of microsystem technology, piezoelectronics, materials science and nanotechnology [1]. Aluminium nitride films are used in various microelectronic devices, including piezoelectric resonators and filters [2]. The main method of manufacturing such films is the method of reactive magnetron sputtering of an aluminum target in a buffer gas containing molecular nitrogen [3-4].

For the synthesis of high-quality films, it is necessary to take into account the main factors affecting the stoichiometry of aluminum and nitrogen directly on the surface of the substrate, because this affects on the electrophysical properties of the material. Since the surface kinetics of particles on the substrate is largely determined by particle flows from the plasma volume, information about the density of atomic nitrogen in the discharge volume becomes important.

In this work, the effect of stoichiometry of the feed gas composition on the density of atomic nitrogen in the volume of the magnetron sputtering system is estimated.

2. Task definition

To determine the concentration of nitrogen, we used an elementary kinetic approach – we considered a closed system of balance equations for neutral plasma particles, which involves the processes of their income and losses in a specific volume.
The primary source of nitrogen atoms in the gas discharge plasma is dissociation of molecules $N_2$ electron impact. At low pressures, the energy distribution of electrons differs from Maxwell’s, so they usually resort to a numerical solution of the Boltzmann equation, which for one’s turn gives the quantitative values of all basic electron kinetic coefficients. The gas pumping out is the main loss channel for neutral plasma particles from the deposition chamber.

Electron concentration and value of reduced field are defined a priori as external parameters.

3. Theory

For not very strong electric fields, the electron energy distribution function (EEDF) is usually represented as a two-way approximation ($f \approx f_0 + \theta \cdot \tilde{f}_1$, $\theta$ - decomposition parameter). Symmetric part of the distribution function $f_0$ note here that it is recorded as:

$$f_0(\varepsilon) = \frac{2 \varepsilon^2}{3m_e \sqrt{\varepsilon}} \frac{\partial}{\partial \varepsilon} \left( \varepsilon^{3/2} \frac{\partial f_0}{\partial \varepsilon} \right) + S^{el} + S^{in},$$

(1)

here $f_0(\varepsilon)$ – is distribution function in energy space ($f_0(\varepsilon) = e^{\varepsilon V}$); $E$ – is strength of electric field; $m_e$ – is mass of electron; $v_m(\varepsilon)$ – is total frequency of elastic collisions. $S^{el}$, $S^{in}$ – integrals of elastic and inelastic collisions, the expressions for which are well known (see for example, [5]). In (1) it is neglected electron diffusion in coordinate space.

Knowledge of EEDF makes it possible to find all kinetic coefficients, including rate constants of electron impact processes, which are determined by the following formula:

$$k = \int_0^\infty \sqrt{\frac{2\varepsilon}{m_e}} \sigma(\varepsilon) f_0 d\varepsilon,$$

(2)

where $\sigma$ is collision process cross section.

The finite-difference method proposed by Rockwood [6] was used for numerical solution of equation (1). To find the stationary solution we used the relaxation count method, in which Euler’s scheme for approximation of time derivative (left side of equation) was applied.

In the calculations, we used a set of sections for argon and nitrogen from the Morgan database of LXcat project [7]. In this set of sections, the process of dissociating nitrogen into neutral fragments is explicitly absent. It is connected with the fact, that ionization cross-section of $N_2$ used in this set (as well as others) includes as well the channel of dissociative ionization. For this reason, after obtaining EEDF, the dissociation rate constant was calculated by using the detached dissociation cross-section of $N_2$ into neutral fragments recommended in [8].

The density of atomic nitrogen is balanced due to the generation of particles in the process of dissociating $N_2$ and leaving them from the volume as a result of pumping. So the equation of the atomic nitrogen balance can be written as:

$$2k_{dis}n_{N_2} = \frac{n_{N_2}}{\tau},$$

(3)

where $k_{dis}$ is dissociation rate constant, $\tau$ is gas pumping time.

The molecular nitrogen balance equation includes the decrease due to dissociation and pumping of gas and the inflow due to the discharge of the working mixture:

$$k_{dis}n_{N_2} + \frac{n_{N_2}}{\tau} = \frac{n_{N_2}^0}{\tau}.$$

(4)
In (4) \(n_{N_2}^0\) is the initial density of N\(_2\) determined by the partial pressure in the absence of discharge. Excluding \(n_{N_2}\) from the last two expressions we find that:

\[
n_N = \frac{2k_{dis}n_e n_{N_2}^0}{k_{dis} n_e + 1/\tau} \tag{5}
\]

Thus, knowing the dissociation rate constant, electron density and gas pumping time, the volume density of atomic nitrogen in the discharge chamber can be found.

4. RESULTS

According to [9], where Langmuir probe measurements were made in titanium magnetron sputtering system, in the supra-cathode region the electron temperature has values equal to 2-2.2 eV at a pressure of 0.7 Pa and discharge power of up to 100 W. Since the same plasma-forming gas are used for nitride titanium manufacturing as for nitride aluminum films, we believe that electron temperatures measured in [9] should be close to those in the case of aluminum sputtering in typical magnetron discharge. Preliminary calculations show that the temperature 2.2 eV is obtained at the given value of the field \(E/N = 5 \cdot 10^{-16} \text{ V} \cdot \text{cm}^2\). We choose this value as fixed parameter for calculations of EEDF.

Calculation was made for pressure \(p = 0.7\) Pa and vacuum chamber volume \(V = 0.1\) m\(^3\). The gas flow rate was set in the range \(Q = 10-20\) sccm. Electron density was taken equal to \(n_e = 10^{10}\) cm\(^{-3}\), which corresponds to the results of probe measurements [9].

The gas pumping time is elementary determined by the values of pressure, chamber volume and feed gas flow rate.

Figure 1 shows EEDF curves for three values of nitrogen partial fraction \(\delta_{N_2}\). It can be seen that all other things being equal, an increase in nitrogen content leads to a narrowing of the distribution curve, i.e. a population of high-energy electrons is decreased. This is quite natural, since nitrogen has low-threshold processes of vibration excitation. Thus, with an increase in nitrogen concentration, the specific contribution of these processes to the balance of inelastic electron losses increases (figure 2). This is also confirmed by the dependence of the electron temperature (figure 3) from \(\delta_{N_2}\), which monotonically decreases with the gas feed mixture contains more N\(_2\).

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**Figure 1.** EEDF at different nitrogen fraction in working mixture Ar+N\(_2\) \((E/N = 5 \cdot 10^{-16} \text{ V} \cdot \text{cm}^2)\).

**Figure 2.** Fraction of electron inelastic loss in Ar+N\(_2\) \((E/N = 5 \cdot 10^{-16} \text{ V} \cdot \text{cm}^2)\).
Figure 3. Electron temperature in Ar+N$_2$ plasma (E/N = 5·10$^{-16}$ V·cm$^2$).

Figure 4. Atomic nitrogen density ($n_e = 10^{10}$ cm$^{-3}$).

Figure 4 shows the atomic nitrogen density curves depending on the stoichiometry of the feed gas. A maximum of 60% nitrogen is clearly observed. In addition, it can be seen that an increase in gas flow leads to a decrease in N density.

5. Discussions

The nitrogen dissociation rate constant may not be monotonically dependent on the value $\delta_{N_2}$. On the one hand, increasing the fraction of buffer gas (argon) stimulates reactions with high thresholds, since the average electron energy will increase. On the other hand, a reducing of the nitrogen content in the feed mixture leads to a proportional decrease the overall dissociation rate. These two concurrent factors may be responsible for the presence of maximum on the curves of figure 4.

Conclusions

Using the macroscopic balance equations and the dissociation rate constant values, the density of atomic nitrogen in plasma Ar + N$_2$ was determined for the operating conditions of the magnetron sputtering system. It is shown that at a given reduced electric field and electron concentration, a maximum concentration of N in discharge chamber is observed at a certain stoichiometry of the composition of the feed gas. In the future, it is planned to improve the model by adding processes of atomic nitrogen sticking to the surface of the substrate and cathode.

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