Mechanisms of Cl_2 Molecules Dissociation in a Gas Discharge Plasma in Mixtures with Ar, O_2. N_2

A. M. Efremov and Kwang-Ho Kwon

Abstract— **The influence of argon, oxygen, and nit rogen admixtures on the dissociation of Cl_2 molec ules in a glow discharge low-temperature plasma under the constant pressure conditions was investi gated. For Cl_2/Ar and Cl_2/O_2 mixtures, the conce ntration of chlorine atoms was observed to be a practically constant at argon or oxygen concentra tions up to 50%. This invariability is a most pro bably explained by relative increase in rate of Cl $_2$ direct electron impact dissociation due to the ch anges in electrophysical parameters of plasma suc h as EEDF, electron drift rate and mean energy. For all the considered mixtures, the contribution of stepwise dissociation involving active species fr om gas additives (metastable atoms and molecules, vibrationally excited molecules) was found to be negligible.**

Index Terms – **Chlorine, Dissociation, Electron impact, rate constant.**

I. INTRODUCTION

Plasmas in chlorine mixtures with inert and molecular gases are widely used in microelectronics technology for a "dry" etching of a large scale of materials [1-4]. To explain or to predict some etching effects we usually need the information concerning the kinetic mechanisms of formation and decay and volume densities of active particles involved to the etching process. Therefore, this work was aimed at the examination of the chlorine dissociation process in the mixtures with argon, oxygen, and nitrogen within a wide range of concentrations. The choice of the molecular additives has been made based on the fact that formation of intermediate chlorine oxides is possible in the presence of oxygen [5], and nitrogen gives vibrationally exited molecules therefore their collisions with chlorine molecules can result in dissociation of the latter [6].

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II. EXPERIMENTS AND MODELING

We conducted experiments in a cylindrical glass flow-type reactor. The gas temperature was measured using two thermocouples of different diameter; the reduced electric field strength was found from Langmuir probe measurements. The concentrations of chlorine molecules and atoms in the discharge were determined using absorption spectroscopic technique and optical emission actinometry. The overall pressure of plasma mixture throughout the experiments was 100 Pa, and input power was about 0.5 W/cm^3 In order to determine the rate constants of electron impact processes and characteristics of the charged component of plasma, we used mathematical simulation of the discharge by solving the Boltzmann kinetic equation in combination with rate equations for the formation and decay of neutral and charged species in quasisteady-state approximation [7]:

$$R_{ION} = R_{DA} + D_e N_e \quad (1)$$

$$R_{ION} = K_{ii}\, N_e\, \beta^2 + D_+ \beta \quad (2)$$

$$R_{DA} = K_{ii}\, N_e\, \beta^2 \quad (3)$$

where R_{ION} and R_{DA} are the total rates of ionization and dissociative attachment, D_e and D_+ are the diffusion decay frequencies for electrons and positive ions, N_e is an electron density in plasma volume, β is the relative

concentration of negative ions ($\beta = N_-/N_e$), K_{ii} is a ion-ion recombination rate constant. The values R_{ION} and R_{DA} may be found as follows:

$$R_{ION} = K_{ION}^{I}(1-\alpha)(1-\gamma)N_0 + K_{ION}^{II}(1-\gamma)2\alpha N_0 + K_{ION}^{III}\gamma N_0 \quad (4)$$

$$R_{DA} = K_{DA}^{I}(1-\alpha)(1-\gamma)N_0 + K_{DA}^{III}\gamma N_0 \quad (5)$$

where K_{ION} and K_{DA} are the rate constants of ionization and dissociative attachment for Cl_2 molecules (I), chlorine atoms (II) and additive gases (III), α is Cl_2 molecules dissociation degree, γ is a relative contence of additive gas in initial mixture, N_0 is a total density of neutral particles.

III. Results and Discussion

Figure 1 represents variation of the concentration of chlorine atoms and molecules in the mixures of varying composition, which indicates that for Cl_2/Ar and Cl_2/O_2 mixtures. The concentration of chlorine atoms remains constant as the concentration of a gaseous additive increases up to 50%, and the behavior of this value within the entire concentration range of gaseous additives does not correlate with the character of the variation in concentration of molecular chlorine. In the chlorine–nitrogen plasmas, the concentration of the atoms within the entire range of composition variation decreases monotonically; nevertheless, the relative trend of the dependence also does not correlate with the variation of the concentration of initial Cl_2 molecules. The observed effects can be caused by increasing the rate of bulk generation of chlorine atoms or decreasing the probability of their heterogeneous recombination upon dilution of chlorine with an inert or molecular additive.

In the bulk, chlorine atoms are known to be formed by dissociative electron impact excitation of lower electronic states of Cl_2 molecules [1, 7, 8]. For the pure chlorine plasma, the contribution of the dissociative attachment to this process does not exceed 5% in the pressure range of 20–400 Pa. The calculations of rate constants for the corresponding processes show that this conclusion holds for the plasmas in chlorine

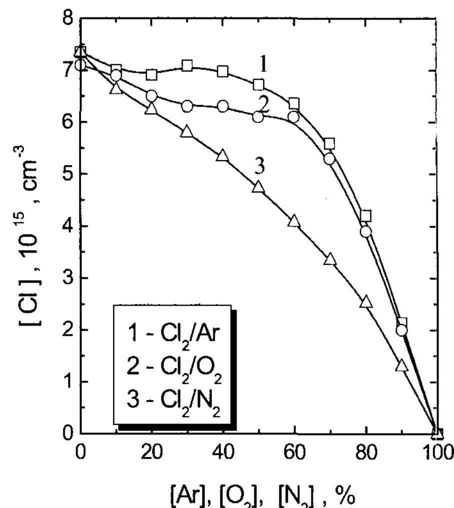


Fig.1. Chlorine atoms density as a function of initial gas mixture composition.

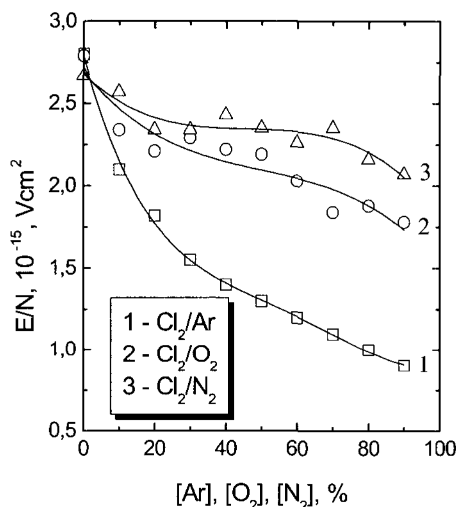


Fig.2. Reduced electric field strength as a function of initial gas mixture composition.

mixtures with any of the above-mentioned gases. Thus, it is reasonable to consider the influence of the gaseous additives on the features of direct dissociation of Cl_2 molecules. Figure 2 shows that the addition of these gases to chlorine decreases the reduced electric field E/N. For the mixtures of chlorine with nitrogen and oxygen, the rate constant of Cl_2 dissociation by direct electron impact is not very sensitive to this parameter (6.5×10^{-9} – 5.9×10^{-9} cm^3/s and 5.07×10^{-9} – 3.3×10^{-9} cm^3/s, respectively, for varying concentration of added gas from 3 to 97%), because the threshold energy of the process (~ 4 eV) is less than the mean electron energy in the discharge (8 - 12 eV). A certain increase in the electron concentration

with decreasing reduced electrical field does not compensate the decrease in concentration of chlorine molecules in the mixtures, and the rate of dissociation decreases over the entire range of mixture composition. The calculations show that, for the mixture of chlorine with argon, the character of change in drift velocity and in mean electron energy does not correlate with variation of reduced electric field. This is obvious, because the inert gas is "transparent" for electrons with energies below the first excitation potential. The rise of mean electron energy and of the proportion of fast electrons in the energy distribution function (fig.3) as a result of chlorine dilution with argon increases the rate coefficient of direct dissociation of Cl_2 molecules (4.5×10^{-9} – 8.9×10^{-9} cm^3/s). In this case, dissociation rate decreases by less than half upon tenfold dilution. Moreover, the dependence of the dissociation rate on argon content is nonmonotonic with a maximum at 20–30% concentration of the inert gas (fig.4) Thus, for Cl_2/Ar plasma, a relative increase in the rate of direct dissociation due to change in electrophysical parameters of discharge can be one of the factors responsible for the experimentally observed invariability of concentration of chlorine atoms within the range of argon concentration up to 50–60%.

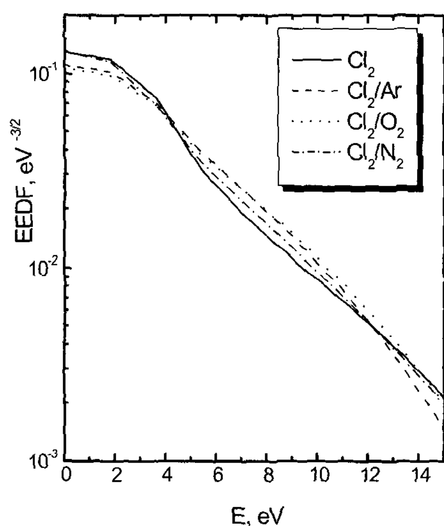
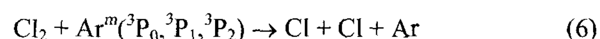


Fig.3. Electron energy distribution function in pure chlorine and in binary mixtures with an equal ratio of both components.

In the analysis of the influence of argon on the rate of chlorine dissociation, it is usually assumed that chlorine molecules can dissociate in collisions with metastable argon atoms $Ar^m(^3P_0,^3P_1,^3P_2)$:



$$Cl_2 + Ar^m(^3P_0,^3P_1,^3P_2) \rightarrow Cl + Cl + Ar \quad (6)$$

Table 1. Rate coefficients for Ar metastable atoms relaxation.

Process	Rate Coefficient
$Ar^m + Cl_2 \rightarrow Ar + Cl_2^*$	$(2-5)\times10^{-10}$ cm^3/sec
$Ar^m + e \rightarrow Ar + e$	$(5-7)\times10^{-10}$ cm^3/sec
$Ar^m + Ar \rightarrow Ar + Ar$	$(2-5)\times10^{-15}$ cm^3/sec
$Ar^m + Cl \rightarrow Ar + Cl^*$	$(1-7)\times10^{-15}$ cm^3/sec
$Ar^m_{(g)} \rightarrow Ar^m_{(s)} \rightarrow Ar_{(s)}$	~ 100 sec^{-1}

Detailed mathematical simulation of chlorine–argon plasmas, including the solution of the balance equations for metastable atoms [9] (table 1), shows that these processes cannot quantitatively assure the experimentally observed increase in chlorine atom concentration of up to 90% argon concentration in the mixture. The contribution of any other secondary bulk processes in the mixture under examination is even less, and we must conclude that the change in generation rate of chlorine atoms in the mixtures of chlorine with argon is solely due to the variation of the features of the direct process.

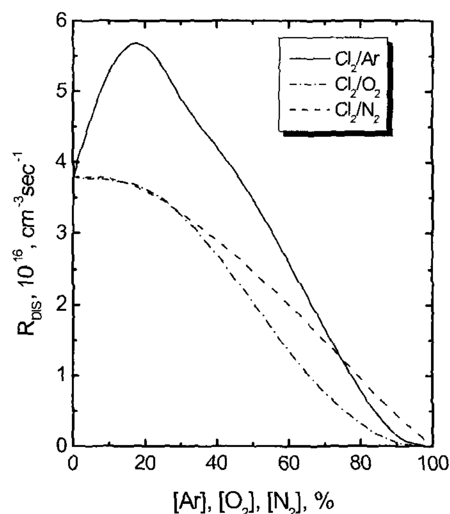


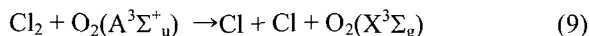
Fig.4. The rate of Cl_2 direct electron impact dissociation as a function of initial gas mixture composition.

Analyzing the processes of formation of chlorine atoms in the mixtures of chlorine with oxygen, note that the change in dissociation rate by variation of electrical parameters of plasma does not explain the observed effects. In our opinion, the most significant secondary

processes are, for example:

$$O_2 + Cl \rightarrow O + ClO \quad (7)$$

$$Cl_2 + O \rightarrow Cl + ClO \quad (8)$$



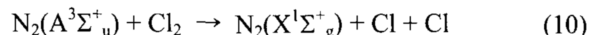
$$Cl_2 + O_2(A^3\Sigma^+_u) \rightarrow Cl + Cl + O_2(X^3\Sigma_g) \quad (9)$$

Reaction (7) is unlikely process because of its threshold energy of about 0.6 eV, which is rather high for "heavy" particles. Reaction (8) is energetically favored, and its rate is determined by the dissociation rate of oxygen molecules. The further electron impact dissociation of ClO molecules affording regeneration of oxygen atoms and their participation in reaction (8) is also possible. The results of calculations show that, at up to 70% oxygen concentration in the mixture, the rate of dissociation of O_2 molecules is at least two orders of magnitude less than the rate of direct electron impact dissociation of chlorine molecules. Thus, even assuming that all oxygen atoms produced in the discharge will be consumed for chlorine dissociation via reaction (8), the contribution of this process to the generation of chlorine atoms cannot exceed 10% of that of the direct process in the entire range of the mixture composition. The same results were observed concerning the contribution of reaction (9) both in the frame of "upper evaluation" and exact calculations using the kinetic scheme for $O_2(A^3\Sigma^+_u)$ formation and decay [10] (table 2) Consequently, the secondary processes in the bulk of chlorine–oxygen plasma do not explain the experimentally observed dependence of chlorine atom concentration on the mixture composition.

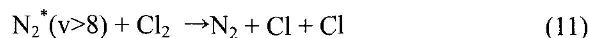
Table 2. Rate coefficients for oxygen metastable molecules relaxation.

Process	Rate Coefficient
$O_2(A^3\Sigma^+_u) + Cl_2 \rightarrow O_2(X^3\Sigma_g) + Cl_2^*$	2×10^{-12} cm^3/sec
$O_2(A^3\Sigma^+_u) + O_2(X^3\Sigma_g) \rightarrow O_2(X^3\Sigma_g) + O_2^*$	5×10^{-12} cm^3/sec
$O_2(A^3\Sigma^+_u) + Cl \rightarrow O_2(X^3\Sigma_g) + Cl^*$	7×10^{-13} cm^3/sec
$O_2(A^3\Sigma^+_u)_{(g)} \rightarrow O_2(A^3\Sigma^+_u)_{(s)} \rightarrow O_2(X^3\Sigma_g)_{(s)}$	~ 50 sec^{-1}

Analyzing the secondary processes in a Cl_2/N_2 plasma, it is necessary to take into account the possibility of stepwise dissociation of Cl_2 molecules upon their interaction with vibrationally excited N_2 molecules and metastable particles $N_2(A^3\Sigma^+_u)$:



$$N_2(A^3\Sigma^+_u) + Cl_2 \rightarrow N_2(X^1\Sigma^+_g) + Cl + Cl \quad (10)$$



$$N_2^*(v>8) + Cl_2 \rightarrow N_2 + Cl + Cl \quad (11)$$

Table 3. Rate coefficients for nytrogen metastable molecules relaxation

Process	Rate Coefficient
$N_2(A^3\Sigma^+_u) + Cl_2 \rightarrow N_2(X^1\Sigma_g^+) + Cl_2^*$	$(2\text{-}4)\times10^{-12}$ cm^3/sec
$N_2(A^3\Sigma^+_u) + N_2(X^1\Sigma_g^+) \rightarrow N_2(X^1\Sigma_g^+) + N_2^*$	6×10^{-12} cm^3/sec
$N_2(A^3\Sigma^+_u) + Cl \rightarrow N_2(X^1\Sigma_g^+) + Cl^*$	8×10^{-13} cm^3/sec
$N_2(A^3\Sigma^+_u)_{(g)} \rightarrow N_2(A^3\Sigma^+_u)_{(s)} \rightarrow N_2(X^3\Sigma_g^+)_{(s)}$	~ 60 sec^{-1}

Reaction (10) is energetically favored because $N_2(A^3\Sigma^+_u)$ molecule is featured by a long life-time (~12 sec) and a free energy more than 6.8 eV. Calculation have shown that the maximal contribution of reaction (10) in chlorine atoms generation rate in plasma volume is less than 10% even for a N_2 content more than 80%. This conclusion is suggested both by the "upper evaluation" and exact modeling using the kinetic scheme for $N_2(A^3\Sigma^+_u)$ molecules formation and decay [10] (table 3). As for reaction (11) it is obviously that only N_2 molecules on high vibrational levels (v>8) can participate in the process of stepwise dissociation. The results of calculations show that the concentration of excited molecules with energies exceeding the bond energy of Cl_2 is 1.7×10^{11} - 1.6×10^{12} cm^{-3} at the nitrogen content in a mixture varying from 10 to 90%. Consequently, the rate of this process can vary from 8.8×10^{14} to 1.7×10^{15} cm^{-3}s^{-1} over the identical composition range. The comparison of these data with the rate of direct electron impact dissociation of chlorine molecules shows that the contribution of stepwise dissociation in comparison with the direct mechanism cannot exceed 6%, and this process does not explain the experimentally observed dependence of chlorine atom

concentration on the mixture composition.

IV. CONCLUSION

In summary, the presented data suggest that, of all the considered mixtures, only the Cl_2–Ar case has a qualitative explanation of the increase in concentration of chlorine atoms, by relative increase of the rate of direct dissociation due to variation of electrophysical parameters of plasma. For the mixtures of chlorine with oxygen, the cause of the observed effect seems to consist in the influence of gaseous additives on the probability of heterogeneous decay of chlorine atoms.

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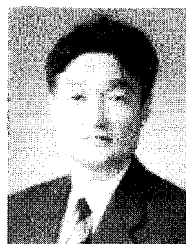

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