VOLUME AND SURFACE CHEMISTRY IN INDUCTIVELY COUPLED Ar/Cl_2 PLASMA

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Abstract

Parameters of Cl_2/Ar plasma in inductive coupled plasma (ICP) reactor were investigated aimed to understand mechanism of Ar addition influence on electro-physical plasma properties and active species kinetics. It was found that addition of Ar to chlorine under constant total pressure condition leads to noticeable changes in electron gas parameters due to "transparency" effect. Direct electron impact dissociation of Cl_2 molecules was found as main source of chlorine atoms while the contributions of dissociative attachment and stepwise dissociation involving Ar metastable atoms seem to be insufficient.

Introduction

Chlorine chemistry-based etching is widely used in microelectronic technology. Among well-known applications of chlorine plasma it is possible to underline two important trends. First trend includes improvement of etching characteristics of materials, which can be etched in fluorine-containing plasmas. Nearest examples are high-anisotropic etching of Si and SiGe alloys. Second trend is connected with etching of materials, which form low-volatile fluorides and thus fluorine-containing plasma can't be used. In this field, chlorine and chlorine-containing plasmas are considered as single possible environment for the etching of such materials as A^3B^5 semiconductors (GaAs, GaSb, GaP), metals (Al, Cu, Pt, W, Mo, Nb) and ferroelectrics (SBT, BST).

Primary aims of Ar addition to chlorine plasma were stabilization of discharge in low-pressure region and reducing of chlorine content in wasted gases aimed to pumping equipment defense and environmental protection. Nevertheless first applications of Cl_2/Ar mixtures for etching purposes showed that dilution of Cl_2 by Ar up to 50-60% under the constant general pressure conditions not only do not leads to etching rate reducing, but sometimes causes etching rate increasing. This effect is stable for observation for various etching systems such as bulk plasma reactors as well as RIE and ICP reactors [1 - 4].

It is evidently clear that any successful applications Cl_2/Ar plasma in industry are impossible without detailed analysis of the influence of input process parameters (pressure, power density, gas mixing ratio) on plasma electro-physical properties, kinetic dependencies of active species generation and decay and on mass content and fluxes of neutral and charged particles. There are some works devoted to this problem [5 - 8] but they are either describe the

effects in high-pressure discharges or contain only experimental data without kinetics analysis. This work is devoted to the investigations of the effects of Cl_2/Ar mixing ratio and input power density on volume chemistry of neutral and charged particles in Cl_2/Ar inductive coupled plasma.

Experimental and modeling

Experiments were performed in ICP reactor with excitation RF (13.56 MHz) discharges under such conditions as: input power density 0.05 - 0.1 W/cm^3, total pressure of Cl_2/Ar mixture 15 mTorr and total gas flow rate of 12 sccm. Plasma parameters such as electron temperature, electron density and ion current density were measured by single langmuire probe technique. Relative volume densities neutral particles (chlorine molecules, chlorine and argon atoms) were controlled by optical emission spectroscopy (OES) using characteristic emission maximums such as Cl_2(256.4 nm), Cl_2(307.6 nm), Cl(452.6 nm), Cl(725.4 nm), Ar(415.8 nm) and Ar(750.4 nm).

Plasma modeling algorithm was represented by 0-Dimensional plasma model operating with a terms of average plasma parameters. Electron gas subsystem was described by stationary Boltzmann kinetic equation without taking into account electron-electron collisions and second-order impacts (energy transmission from heavy particles to electrons). As output parameter from Boltzmann equation we obtained electron energy distribution function (EEDF), which allow to calculate such characteristics of electron gas as mean electron energy and drift rate, reduced diffusion coefficient and mobility, rate coefficient of electron impact processes. Subsystems of charged and neutral particles were described by mass and movement continuity equations [7, 9] in quasi-stationary approximation:

$$n_0 n_e\left(k_i^{Cl_2} y^{Cl_2} + k_i^{Cl} y^{Cl} + k_i^{Ar} y^{Ar}\right) = n_0 n_e k_{da}^{Cl_2} y^{Cl_2} + \frac{D_e}{\lambda^2} n_e \qquad (1)$$

$$n_0 n_e\left(k_i^{Cl_2} y^{Cl_2} + k_i^{Cl} y^{Cl} + k_i^{Ar} y^{Ar}\right) = k_{ii} n_+ n_- + \frac{D_+}{\lambda^2} n_+ \qquad (2)$$

$$n_0 n_e k_{da}^{Cl_2} y^{Cl_2} = k_{ii} n_+ n_- \qquad (3)$$

$$R_F = R_D + \frac{D}{\lambda^2} y^{Cl_2} n_0 + \frac{y^{Cl_2} n_0}{\tau_{res}} \qquad (4)$$

where n_0 – total density of neutral particles determined by gas pressure and temperature, n_e – electron density, n_+ - total density of positive ions (Cl_2^+ , Cl^+ and Ar^+), n_- - density of negative ions (Cl^-), y – mole fractions of neutral ground state particles in plasma volume, D – diffusion coefficient, k – rate coefficients, R_F and R_D – total formation and decay rates of chlorine atoms and molecules in chemical reactions, τ_{res} – residence time. In balance equation for negative ions (3) we did not take account heterogeneous decay of these species. This conclusion is based on the presence of double electric layer and negative charges on the reactor walls. Therefore we propose that decay of negative ions is limited only by ion-ion recombination in plasma volume

as well as quasi-neutrality equation may be applied for average volume densities of charged particles.

Results and discussion

Analysis of possible effects of Ar addition to chlorine plasma according to data of [5, 6] for high-pressure (100 Pa) DC discharge shows at least three channels which are able to influence on volume kinetic and thus on plasma mass content. First expected channel is connected with increasing of Cl_2 direct electron impact dissociation rate due to well-known "transparency" effect (increasing of high-energy electrons fraction in EEDF and growth of electron mean energy). Second expected channel may be caused by appearance of additional mechanism of Cl_2 molecules dissociation due to the interaction with argon metastable atoms. Such a process is wholly possible since the average energy of argon metastable atoms $Ar(^3P_0,^3P_1,^3P_2)$ 11.8 eV is sufficiently more than Cl_2 dissociation threshold. Last expected channel assumes strong influence of Ar addition on volume densities of electrons and negative ions due to changes of efficiency of dissociative attachment process.

Fig. 1 and Tab. 1 illustrate variations of electron energy distribution function and electron temperature during Ar addition under constant pressure and input power density conditions. Note that our experimental and modelling data concerning electron temperature are in good agreement with Modeling results show that the addition of Ar to Cl_2 leads to sufficient deformation of EEDF especially in high-energy "tail" region. Therefore, rate coefficients of most important electron impact processes such as dissociation and ionization are sensitive to changes of Cl_2/Ar mixing ratio. Comparison of rate coefficients shows that although dissociative attachment is threshold-less process, rate coefficient of dissociative attachment is sufficiently less than rate coefficient of direct electron impact dissociation of Cl_2 molecules. The reason is sufficient differences in cross-sections of corresponding processes. This conclusion is in good agreement with published results [6, 7] concerning DC discharge in Cl_2/Ar mixture. Calculations showed that stepwise dissociation of Cl_2 molecules during the interaction with metastable Ar atoms is not effective due to low volume density of $Ar(^3P_0,^3P_1,^3P_2)$. The reason is connected with differences between threshold energies as well as cross-sections of corresponding processes.

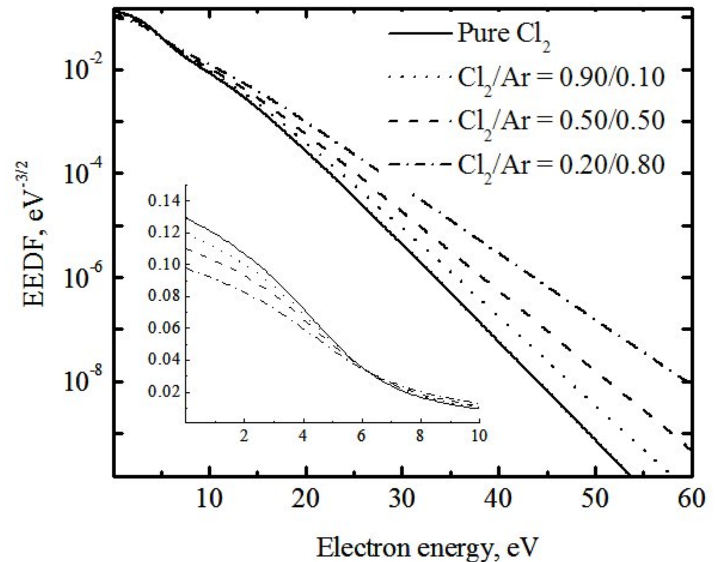

Fig.1 Electron energy distribution function in chlorine-argon plasma

Table 1

Electron temperature in Cl_2/Ar mixture plasma

$Ar/(Ar+Cl_2)$, %	0	20	50	80
<ε>, eV (experiment)	4.20±0.3	4.68±0.3	5.10±0.3	6.52±0.3
<ε>, eV (modeling)	4.26	4.71	5.15	6.48

Therefore direct electron impact dissociation may be considered as main source of chlorine atoms. Increasing of Ar mixing ratio leads to decreasing of Cl_2 dissociation rate but the tendency of decreasing is not so rapid as it expected from dilution effect. The same conclusion may be applied to volume density and flux of chlorine atoms.

As for balance of electrons, under low-pressure conditions decay of these particles are determined by diffusion while any variations of dissociative attachment efficiency do not influence on electron balance in plasma volume. Addition of Ar leads to increasing of electron diffusion coefficient due to increasing of electron temperature. Therefore behavior of electron density as function of Ar content is characterized by weak tendency to decreasing. Absolute values of electron density correspond to the scope of 10^{10} cm^{-3} performing typical values for ICP systems [8] with similar levels input power density. Relative density of negative ions (n_- / n_e) decreases during Ar addition while absolute values of this parameter do not exceed 20.

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