Available online at www.sciencedirect.com
ScienceDirect
Vacuum 81 (2007) 669–675
VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY
www.elsevier.com/locate/vacuum

Applicability of self-consistent global model for characterization of inductively coupled Cl_2 plasma

A.M. Efremov[a], Gwan-Ha Kim[b], Jong-Gyu Kim[b], A.V. Bogomolov[a], Chang-Il Kim[b,*]

[a]Department of Electronic Devices and Materials Technology, State University of Chemistry and Technology, 7 F. Engels st., 15300 Ivanovo, Russia
[b]School of Electrical and Electronic Engineering, Chung-Ang University, 221, Huksuk-Dong, Dongjak-Gu, Seoul 156-756, South Korea

Received 2 May 2006; received in revised form 5 September 2006; accepted 21 September 2006

Abstract

Investigations of the influence of gas pressure and input power on the Cl_2 plasma parameters in the inductively coupled plasma system were carried out. The investigations combined plasma diagnostics by Langmuir probe with plasma modeling represented by the self-consistent global model with Maxwellian approximation for the electron energy distribution function. From the experiments, it was found that the increase of gas pressure in the range of 0.27–3.33 Pa for 400–700 W of input power results in a decrease in both electron temperature (3.3–2.0 eV) and density ($6.5\times10^{16}-3.0\times10^{16}\,m^{-3}$ for 400 W and 1.2×10^{17}–$6.7\times10^{16}\,m^{-3}$ for 700 W). For the given range of experimental conditions, the model showed an outstanding agreement with the experiments and provided the data on kinetics of plasma active species, their densities and fluxes.

Keywords: Cl_2 inductive plasma; Modeling; Electron temperature; Dissociation; Ionization; Rate coefficient; Density

1. Introduction

Pure chlorine as well as its mixtures with various gases are frequently used in the microelectronic technology for "dry" patterning of microstructures with different types of coatings and substrates. Particularly, Cl_2-containing plasma is preferable environment for the etching of A^3B^5 group semiconductors and some metals (Al, Cu, Pt, Au, W, etc.), which form extremely low-volatile fluorides being etched in the fluorine-containing gases [1–3]. The task of optimization and improvements of the existing etch processes require deep understanding of the etch mechanism that is impossible without the knowledge of plasma parameters and active particles kinetics.

Plasma modeling is a powerful tool to analyze the kinetics of plasma reactions as well as the influence of input parameters (gas pressure, flow rate and input power) on the electron gas characteristics and volume densities of active species. The simplest modeling algorithm is given by the global (0-dimensional) model operating with volume-averaged plasma parameters. The basic concepts of global model for low-pressure electronegative plasmas were already described in several works [4–8]. Also, the works of Ullal et al. [9], Yonemura et al. [10], Efremov et al. [11,12] and Malyshev and Donnelly with co-authors [13–16] combined the experimental investigations and 0-dimensional modeling of Cl_2 inductively coupled plasma (ICP) to obtain and verify the data on electron energy distribution, electron temperature and densities of active species. Analyzing these works, it can be seen that at least three questions are still open. First, the majority of models cover only part of subsystems to be described as well as require the plasma diagnostics data as input parameters, so that the modeling results appear to be strongly dependent on the accuracy of the experiment. Secondly, there are disagreements about the applicability of the global model with Maxwellian approximation for the electron energy distribution function (EEDF) for characterization of the Cl_2 ICP typically for systems with ranges of pressure (~0.13–2.66 Pa) and input power density (~10^4–10^5 W/m^3). And thirdly, although the local subjects of the Cl_2 plasma chemistry are rather clear, the most of existing data cannot be combined and compared directly because of the

*Corresponding author. Fax: +82 2 8129 651.
E-mail address: cikim@cau.ac.kr (C.-I. Kim).

0042-207X/$ - see front matter
doi:10.1016/j.vacuum.2006.09.017

different experimental conditions and approaches used for data analysis. As a result, the plasma parameters, the densities of active species as well as the etch effects for a given reactor with a given range of operating conditions are hard to be evaluated without the experiments.

The aim of present work was to investigate the influence of input process parameters on the properties of inductively coupled Cl_2 plasma as well as evaluate the applicability of the global (0-dimensional) self-consistent model for the plasma chemistry analysis. As the model adequacy criteria, the data of plasma diagnostics by Langmuir probe (LP) were used.

2. Experimental and modeling details

2.1. Experimental setup

Experiments were carried out in planar ICP reactor used and described in our previous works [17,18]. The reactor chamber made from stainless steel had a shape of cylinder with an inner radius (R) of 0.15 m. On the top of the chamber, the 24 mm-thick horizontal quartz window separated the working zone and the four-turn copper coil connected to a RF (13.56 MHz) power supply. On the bottom of the chamber, the electrode used as the substrate holder was located. The bottom electrode made from the anodized Al was connected to another 13.56 MHz RF generator to control the DC bias voltage. The axial size of the working zone (L), i.e. the distance between quartz window and bottom electrode, was 0.14 m. The experiments were performed in the non-bias mode (i.e. with no RF power applied to the bottom electrode) under such input parameters as: gas pressure of 0.27–3.33 Pa, gas flow rate of 20 sccm, and input ICP power of 400–700 W that corresponds to power density of $(4–7) \times 10^4\ \mathrm{W/m^3}$.

Plasma diagnostics was performed by LP measurements. As in our previous works [11,12,17,18], the LP diagnostics were realized with a single, cylindrical, and RF-compensated probe (ESPION, Hiden Analytical). The probe was installed through the chamber wall-side view port, placed at 4 cm above the bottom electrode and centered in the radial direction. For the treatment of I–V curves aimed at obtaining plasma parameters, we used the software supplied by the equipment manufacturer.

2.2. Model description

A global (0-dimensional) self-consistent model with a quasi-stationary approximation for the volume kinetics [4,11,12] was applied to investigate the influence of input plasma parameters on both densities and fluxes of active species. The list of processes taken into account by the model is specified in Table 1. The rate coefficients for electron impact reactions (R1–R9, R11) were calculated as

$$k = \left(\frac{2e}{m_e}\right)^{1/2} \int_{\varepsilon^{th}}^{\infty} F_M(\varepsilon)\sigma(\varepsilon)\sqrt{\varepsilon}\,\mathrm{d}\varepsilon, \tag{1}$$

Table 1
Set of reactions for Cl_2 plasma modelling

N	Scheme	Rate coefficient, threshold energy
R1	$Cl_2 + e \rightarrow Cl_2^+ + 2e$	11.5 eV
R2	$Cl_2 + e \rightarrow Cl^- + Cl^+$	12.0 eV
R3	$Cl_2 + e \rightarrow Cl_2^- \rightarrow Cl + Cl^-$	—
R4	$Cl_2 + e \rightarrow Cl_2^*(B^3\Pi) \rightarrow Cl + Cl + e$	3.0 eV
R5	$Cl_2 + e \rightarrow Cl_2^*(2^1\Pi) + e$	5.25 eV
R6	$Cl_2 + e \rightarrow Cl_2^*(2^1\Sigma) + e$	8.25 eV
R7	$Cl2 + e \rightarrow Cl^*_{2(v)} + e$	0.07 eV
R8	$Cl + e \rightarrow Cl^+ + 2e$	13.5 eV
R9	$Cl + e \rightarrow Cl^*(4s-5d) + e$	8.9–12.4 eV[a]
R10	$Cl^- + n_+\ (Cl_2^+, Cl^+) \rightarrow n + Cl$	$5.0 \times 10^{-14}\ \mathrm{m^3/s}$
R11	$Cl^- + e \rightarrow Cl + 2e$	3.4 eV
R12	$Cl_{(g)} + Cl_{(s)} \rightarrow Cl_{2\ (s)} \rightarrow Cl_{2\ (g)}$	$\gamma_{Cl} D/\Lambda^2$
R13	$n_+\ (Cl_2^+, Cl^+) \rightarrow$ wall	$2\upsilon(Rh_L + Lh_R)/RL$
R14	$n_e \rightarrow$ wall	D_e/Λ^2

[a]Process R9 summarizes six electronic excitation pathways for the Cl atoms for the states of ^{3}D, ^{4}D, ^{4}P, ^{4}S, ^{5}D and ^{5}P with the range of threshold energies of 8.9–12.4 eV.

where $F_M(\varepsilon)$ is the Maxwellian EEDF, ε^{th} is the threshold energy, and $\sigma(\varepsilon)$ is the process cross-section. The set of cross-sections for Cl_2 and Cl was taken from Refs. [19,20].

Volume densities of ground-state neutral particles (Cl, Cl_2) were derived from the set of the steady-state balance equations:

$$n_{Cl_2} = n_0(T_0/T) - 0.5n_{Cl}, \tag{2}$$

$$(2k_4 + k_3)n_e n_{Cl_2} = (k_{12} + 1/\tau_R)n_{Cl}, \tag{3}$$

where n is the volume-averaged density of corresponding particles in plasma, k is the rate coefficients for the processes specified in Table 1, τ_R is the residence time, and T is the gas temperature. Eq. (2) is the mass balance equation for Cl_2 molecules assuming the total gas pressure to be constant before and after turning the plasma on, the lower-case index "0" relates to the state of the non-ionized gas, when the plasma is turned off. In Eq. (3), we neglected the volume three-body recombination of Cl atoms as well as assumed that the heterogeneous decay of these species follows the Eley–Redeal kinetics with $k_{12} = \gamma_{Cl} D/\Lambda^2$ [11,12,16]. Since different types of materials exist inside the reactor chamber, the effective recombination probability was estimated as $\gamma_{Cl} = \sum \gamma_i S_i/S$ [9], where $S = 2\pi R(R+L)$ and where S_i and γ_i are the partial surface areas and recombination probabilities for a given type of material. According to Ref. [21], we used $\gamma_i \sim 0.2$ for stainless steel, $\gamma_i \sim 10^{-3}$ for quartz, and $\gamma_i \sim 0.05$ for Al_2O_3. The effective diffusion coefficient for Cl atoms was calculated as $D^{-1} = D_f^{-1} + D_{in}^{-1}$, where $D_f = (\Lambda/3)(8k_B T/\pi m_{Cl})^{1/2}$ is the free diffusion coefficient and D_{in} is the inter-diffusion coefficient determined by the Chapman–Enskog equation together with Blanc's law [11]. The effective diffusion length Λ was estimated as $\Lambda^{-2} = (2.405/R)^2 + (\pi/L)^2$ [4,5]. The subsystem of charged particles (Cl^-, Cl_2^+,