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Characterization of a capacitively coupled RF plasma for SiO_2 deposition: numerical and experimental results

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Abstract

A fluid model including an electron beam of hot electrons is presented and used to describe the transport of charged particles in a 13.56-MHz O_2 plasma. An increase in the electron density when the RF power increases is observed from Langmuir probe measurements. The calculated evolution of the electron number density shows a reasonable agreement if the secondary emission coefficient is chosen equal to 10^{-4} on a steel (316L) electrode. The values of the plasma potential increase with increasing RF power from 30 to 35 V at 0.5–0.6 Torr, in the range 100–300 W. Surprisingly, the electron temperature decreases with increasing applied RF power. No clear explanation for this behavior is available yet.

Keywords: Plasma modeling; Langmuir probes; Radiofrequency; Oxygen plasma

1. Introduction

Capacitively coupled radiofrequency glow discharges (CCRF) are widely used in surface treatment processes. Plasmas of this kind, created in the vapor of a metalorganic compound mixed with oxygen, are studied to improve the deposition of plasma polymers or oxide thin films depending on the ratio of partial pressures of gases. For example, SiO_x thin films can be deposited in an O_2/hexamethyldisiloxane (HMDSO) plasma. The O_2/HMDSO ratio can be varied from 0 to 30, leading to different properties and characteristics of the SiO_x layers [1–4]. Though such processes have been studied for many years, they are not completely understood and the scaling-up of the reactors still remains difficult to achieve. Indeed, most of the studies dealing with O_2/HMDSO CCRF plasmas are performed in laboratory-scale devices, and the complexity of such plasmas does not allow an easy way to suggest appropriate designs of large volume reactors. Resorting to process modeling is often the cheapest way to overcome this problem.

Regarding the O_2/HMDSO CCRF discharges used for SiO_x deposition on metallic surfaces, the behavior of the charged particles is a key point to describe. Owing to the complexity of the HMDSO molecule and consequently to the O_2/HMDSO plasma, it has been assumed that the main part of the charged particle kinetics is governed by O_2, for high O_2/HMDSO ratios (>10). Thus, a pure O_2 plasma is first modeled. The adopted kinetic description of the electrons is made by considering separately two electron groups. The transport of the charged particles is described by solving the first three moments of the Boltzmann's equation, which are coupled with the Poisson's equation for the electric field. To obtain reliable results, the ionization rates must be chosen carefully.

On the other hand, the experimental analysis of the plasma is required to get reliable data about the species that govern the discharge behavior. In particular, the knowledge of parameters such as the electron number density or the electron energy distribution function is required to describe accurately the ionization rates. This paper is thus organized as follows. The fluid model and the set of equations describing

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the charged particle behavior as well as the boundary conditions and the numerical method are first presented. The experimental arrangement is next described. The results obtained from the numerical modeling and the experiments are discussed in the last part of this paper.

2. Fluid model

The time-dependent numerical model in one dimension of space used in this work is based on the solution of the first three moments of the Boltzmann's equation, describing the transport of charged particles. These equations are coupled with the Poisson's equation for the electric field and are written under the following conditions:

(1) The heat flux is negligible.
(2) The local field approximation applies.
(3) Two groups of electrons are considered [5–8]. The first group described as a monoenergetic beam consists of the "fast" electrons emitted by each electrode under ion bombardment. This term can be very important in the sustainment mechanism of the plasma since one electrode can have a metallic part in the industrial process which is a continuous flow system. Within the experimental setup used for this work, the value of secondary emission coefficient is rather small. Indeed, a batch reactor is used and oxidation of the steel electrodes (316L) occurs. The value of gamma is not known exactly, but it is expected to be lower than 10^{-3}. Indeed, in an oxygen plasma, for oxygen ions impinging a copper surface, γ varies from 10^{-7} for a clean surface to 10^{-6} for an oxidized surface [9]. The second group is composed of the "bulk" electrons, issued from ionization by the fast electrons in the negative glow (NG).
(4) The electrons created by ionization in the cathode-fall (CF) region belong to the monoenergetic beam provided that the local electric field strength is sufficiently large to give them a high energy which is consistent with the beam energy. If this condition is not fulfilled, the created electrons join the bulk population.
(5) The electrons created by ionization in the NG belong to the bulk electrons.
(6) The bulk electron distribution function is Maxwellian.

Considering the above-mentioned conditions, the sets of equations for each kind of particle are written as follows. For the fast electrons, a continuity and an energy equations are solved:

$$\begin{cases} \dfrac{\partial n_\mathrm{f}}{\partial t} + \dfrac{\partial (n_\mathrm{f} u_\mathrm{f})}{\partial x} = S_\mathrm{f}^n - P_\mathrm{f}^n \\ \dfrac{\partial (n_\mathrm{f} m \varepsilon_\mathrm{f})}{\partial t} + \dfrac{\partial (n_\mathrm{f} m u_\mathrm{f} \varepsilon_\mathrm{f})}{\partial x} - n_\mathrm{f} q u_\mathrm{f} E = S_\mathrm{f}^\varepsilon - P_\mathrm{f}^\varepsilon \end{cases} \quad (1)$$

The transport of the bulk electrons is described by a continuity equation, a momentum-transfer equation and an energy equation:

$$\begin{cases} \frac{\partial n_\mathrm{e}}{\partial t} + \frac{\partial (n_\mathrm{e} u_\mathrm{e})}{\partial x} = S_\mathrm{e}^n - P_\mathrm{e}^n \\ \frac{\partial (n_\mathrm{e} m u_\mathrm{e})}{\partial t} + \frac{\partial (n_\mathrm{e} m u_\mathrm{e} u_\mathrm{e})}{\partial x} + \frac{\partial (P)}{\partial x} - n_\mathrm{e} q E = S_\mathrm{e}^u - P_\mathrm{e}^u \\ \frac{\partial (n_\mathrm{e} m \varepsilon)}{\partial t} + \frac{\partial (n_\mathrm{e} m u_\mathrm{e} \varepsilon)}{\partial x} + \frac{\partial (P u_\mathrm{e})}{\partial x} - n_\mathrm{e} q u_\mathrm{e} E = S_\mathrm{e}^\varepsilon - P_\mathrm{e}^\varepsilon \end{cases} \quad (2)$$

The transport equations for the positive ions O_2^+ and O^+ consist of a continuity equation and a mobility equation:

$$\begin{cases} \frac{\partial n_\mathrm{p}}{\partial t} + \frac{\partial (n_\mathrm{p} u_\mathrm{p})}{\partial x} = \mathrm{SDI}_{\mathrm{O_2(resp.O)}} - P_\mathrm{p} \\ n_\mathrm{p} u_\mathrm{p} = n_\mathrm{p} w_\mathrm{p} - \frac{\partial (n_\mathrm{p} D_\mathrm{p})}{\partial x} \end{cases} \quad (3)$$

The oxygen being an electronegative gas, the negative ions O_2^- and O^- must be considered and their transport equations are:

$$\begin{cases} \frac{\partial n_\mathrm{n}}{\partial t} + \frac{\partial (n_\mathrm{n} u_\mathrm{n})}{\partial x} = S_\mathrm{n} - P_\mathrm{n} \\ n_\mathrm{n} u_\mathrm{n} = n_\mathrm{n} w_\mathrm{n} - \frac{\partial (n_\mathrm{n} D_\mathrm{n})}{\partial x} \end{cases} \quad (4)$$

S and P are the source and loss terms. All the previous equations are coupled with the Poisson's equation for the electric field:

$$\frac{\partial E}{\partial x} = \frac{|e|}{\varepsilon_0}\left(n_\mathrm{p} - n_\mathrm{e} - n_\mathrm{f} - n_\mathrm{n}\right) \quad (5)$$

The subscripts "f", "e", "p" and "n" refer to the fast electrons (beam), the bulk electrons, the positive ions and the negative ions respectively. n, u, ε, w and D are the density, the average velocity, the energy, the drift velocity and the diffusion rate, respectively. For the bulk electrons, the source term for the continuity equation is:

$$S_\mathrm{e}^n = \mathrm{SDI} + C_\mathrm{e} + P_\mathrm{f}$$

where C_e is the balance term in bulk electrons issued from the chemistry involving O_2 and O (Table 1) and SDI is the sum of the ionization source of O_2 and O. SDI_{O_2} (respectively SDI_O) is:

$$\mathrm{SDI}_{O_2} = N \times n_\mathrm{e} \times \frac{\int v f(v) \sigma(v) \mathrm{d}v}{\int f(v) \mathrm{d}v}$$

where N and $\sigma(v)$ are the density and the ionization cross section for O_2 (respectively O) [10]. The simplified

Table 1
Set of reactions used in the model describing the oxygen chemistry

Reaction	Rate
$O_2+e^-\rightarrow O+O^-$	$K_1=7.74\times10^{-12}$ cm^3 s^{-1}
$O^-+O_2\rightarrow O_2^-+O$	$K_2=1.00\times10^{-30}$ cm^3 s^{-1}
$O^-+O\rightarrow e^-+O_2$	$K_3=1.40\times10^{-10}$ cm^3 s^{-1}
$O_2^-+O\rightarrow O^-+O_2$	$K_4=3.30\times10^{-10}$ cm^3 s^{-1}
$e^-+O_2^+\rightarrow 2O$	$K_5=2.10\times10^{-7}$ cm^3 s^{-1}
$O^-+O_2^+\rightarrow O+O_2$	$K_6=9.60\times10^{-8}$ cm^3 s^{-1}
$O_2^-+O_2^+\rightarrow 2O_2$	$K_7=4.20\times10^{-7}$ cm^3 s^{-1}
$e^-+O_2\rightarrow e^-+O+O$	$K_8=3.91\times10^{-11}$ cm^3 s^{-1}
$e^-+O_2+O_2\rightarrow O_2+O_2^-$	$K_9=1.82\times10^{-31}$ cm^6 s^{-1}