Computational Study of Sheath Structure in Chemically Active Plasmas

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Abstract. Results of computer simulations describing an interaction between a low-temperature multi-component plasma and an immersed metal substrate are presented. For this purpose, computer model of volume processes in a DC glow discharge in Ar–O₂ mixture and a particle model of plasma-solid interaction were created. The interaction is studied not only in case when a constant value of voltage bias on the immersed substrate is kept, but also when sinusoidal voltage bias is applied. A pressure dependence of the sheath region in electronegative plasma is shown, too.

1 Introduction

A sheath, a plasma region between bulk plasma and a solid surface, is primarily responsible for the properties of films arising on the surface during plasma-chemical technologies. Many fundamental issues, such as the role of the charged plasma species or main plasma parameters still remain unresolved [1]. Detailed description of physico-chemical processes taking place during the interaction of plasma with a material surface is rather difficult, especially at higher pressures and/or in chemically active plasmas, and thus a combination of experimental and computational approaches seems to be very convenient. Standard methods of plasma diagnostics do not allow obtaining information about the detailed composition of plasma in the vicinity of immersed substrates. Specialized models are therefore necessary to solve this problem.

Two basic approaches are common in the computer modelling of plasma-solid interaction: the particle simulation technique [2] and the fluid modelling [3]. The particle codes usually give deeper insight into problems studied while the fluid modelling is less time consuming. The second argument for the particle approach is that a fluid modelling is better suited for the study of plasma not far from the equilibrium, the interaction with immersed substrates not being the case.

The structure and properties of the discharges in oxygen/argon mixture have been intensively studied for a very long period in our Prague laboratory. The measurements were performed in a positive column of the DC glow discharge, as this part of discharge is often used in various plasma technologies. The plasma consisted of oxygen both pure and in mixtures with argon. The experimental set-up

is described elsewhere [4]. For the study of plasma properties, various kinds of diagnostics were used. The results suggested that most of plasma parameters, as electron density, axial electric field, etc. are influenced by the concentration of oxygen in the mixture [5]. For example, in [4] it was shown by the optical diagnostics that the intensity of the emitted line of atomic oxygen decreases profoundly with increasing oxygen content.

In the paper, we concentrated on computer modelling of both the processes in the sheath in low-temperature multicomponent plasma in DC or low-frequency glow discharge and the chemical processes in the bulk plasma. Particle simulations were used for the modelling of interaction between low-temperature multicomponent plasma [6] (multicomponent means that we use more than one type of both positive and negative ions for the plasma description) and the immersed substrates. Another technique of computational physics, the macroscopic kinetic approach, was chosen for the study of chemical processes in the chemically active plasma. All the simulations are based on the experimental data obtained for the mixture of oxygen with inert gases. The following simulations consider a glow discharge in Ar–O₂ mixture, from which the measured data are used for our calculations.

2 Computer experiment

Our main goal was to study properties of a low-temperature chemically active plasma during the interaction between such type of plasma and immersed substrates with help of computer modelling. For this purpose, two computer models based on various techniques of computational physics were created.

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2.1 Model of the volume processes

The model simulates the processes in a DC glow discharge in the Ar–O₂ mixture and is based on a macroscopic kinetic approach, i.e. on the solution of continuity equations for all species introduced into the model. The kinetic scheme of the model contains more than 100 reactions between 15 neutral, charged and excited species for pure oxygen (electrons, O, O₂, O₃, O[−], O₂[−], O₃[−], O₄[−], O⁺, O₂⁺, O₃⁺, O₄⁺, O(¹D), O₂(¹Δ_g), O₂(¹Σ_g⁺)), 12 reaction between 5 neutral, charged, and excited species for pure argon (electrons, Ar, Ar⁺, Ar*, Ar₂⁺), and 14 reactions between argon and oxygen gases. The chemical reactions and the corresponding rate constants were obtained from both the literature [7]–[13] and our own calculations. Some rate constants depending on electron energy distribution function (EEDF) were calculated using the computer program ELENDF [14] which simulates the EEDF in the dependence on discharge parameters. Phelps' cross sections [15] and some others [9], [16] were used as input data for the program ELENDF.

2.2 Model of plasma-solid interactions

We prepared a two dimensional computer model for the simulation of plasma-solid interactions in the multicomponent plasma. This model is based on a self-consistent particle simulation technique and combines molecular dynamics and Monte Carlo methods. The simulations of the plasma-solid interaction were performed for a cylindrical probe.

The computer model used the undisturbed plasma consisting of the following charged species: electrons, Ar⁺, O₂⁺, O⁺, O[−], and O₂[−]. They were chosen according to our previous model. It was supposed that both electrons and all kinds of ions have the Maxwell velocity distributions with corresponding temperatures in the undisturbed plasma.

For simulations of motion of charged particles, Newton's equations of motion were used and solved by the second order velocity Verlet algorithm. Every movement of the particles was influenced by the self-consistent electric field created by all the other charged particles and by the substrate bias. The input data for the Poisson equation were prepared by the standard Particle-In-Cell technique in the Cloud-In-Cell modification [17]. Poisson equation was solved by Conjugate Gradients method [18].

A scattering of the charged particles by neutrals was handled stochastically by the Monte Carlo method. The set of possible interactions consists of elastic collisions for all kinds of particles, of excitation and ionization of Ar, O, and O₂ by electrons, and of the charge transfer between Ar atoms and Ar⁺ ions.

The probe with radius of 10^{−4} m was located in the middle of the working area, a square area with the size of 10^{−2} m. In order to use the PIC method we divided this area into a rectangular mesh 1000 × 1000. The probe was approximated by a linear interpolation on the rectangular mesh. The undisturbed plasma was considered to

be around this working area. Electron secondary emission and escapes of charged particles from the probe were not included.

Different time steps for electrons and heavier particles were used for speeding-up the calculations in static regime. The time steps were $\Delta t_e = 10^{-12}$ s for electrons and $\Delta t_i = 10^{-9}$ s for ions. However, this artificial procedure cannot be used for simulations of the dynamic properties of plasma. Parallel programming with help of MPI [19] was used in this case and the whole computing process was performed on three processors with the time step held between 10^{−11} and 10^{−12} s. Other parameters used were the temperature of electrons $T_e = 2$ eV, temperature of ions and neutrals $T_i = 300$ K, voltage bias $U = +10$ volts.

3 Results and discussion

The first part of the results is from the computer model of volume processes in a DC glow discharge in the Ar–O₂ mixture. As the results, the concentrations of neutral, excited, and charged species were obtained for various discharge parameters. For example, for our experimental conditions ($E/N = 60$ Td, pressure $p = 133$ Pa and the initial O₂ to Ar concentration ratio 50:50), the following concentrations of main species were found [in cm^{−3}]:

Neutral and excited species:

Ar:	1.59×10^{16}	O ₂ :	9.35×10^{15}
O:	9.71×10^{15}	O ₂ (¹ Δ _g):	1.75×10^{15}
O ₂ (¹ Σ _g ⁺):	6.21×10^{13}	O ₃ :	4.65×10^{11}
Ar*:	1.25×10^8	...	

Charged species – positive:

O ₂ ⁺ :	6.97×10^9	Ar ⁺ :	5.58×10^9
O ⁺ :	1.32×10^9	Ar ₂ ⁺ :	3.62×10^6
O ₄ ⁺ :	3.11×10^5	...	

Charged species – negative:

e [−] :	1.22×10^{10}	O [−] :	1.57×10^9
O ₂ [−] :	9.48×10^7	O ₃ [−] :	2.71×10^6

As we can see, the most important charged particles dominating in the sheath formation should be e[−], Ar⁺, O₂⁺, O⁺, O[−], and O₂[−] in this kind of plasma. Based on these results, we decided that the charged particles mentioned were used for the following model of interaction between the multicomponent plasma and immersed substrates. In addition, we show the calculated concentrations of these charged particles obtained for various ratios between O₂ and Ar gases (Fig. 1). As we can see at the beginning of the graph, when oxygen gas is added into the argon plasma, it causes rapid fall of argon ions concentration in the simulations. This phenomenon can be seen in the experiment measurement too, e.g. as a clear change of colour of the glow discharge. As it has been mentioned in the introductory part, the measurements by the optical emission spectroscopy showed that the concentration of

Fig. 1. The dependence of concentrations of the most abundant charged particles on the initial O_2 to Ar concentration ratio. $c = 0\%$ means pure argon plasma. Discharge parameter $E/N = 60$ Td, initial pressure 133 Pa.

atomic oxygen $O(^3P)$ decreases profoundly with increasing oxygen content in Ar- O_2 mixture, reaching its maximum at $c = 5\%$. It was verified several times [4], [20]. This oxygen excited state plays an important role in initiation of the O^+ ions [21]. This fact can probably explain the 'strange' behaviour of the concentration of the O^+ ions in Fig. 1 where the concentration increases with the Ar content in the mixture, reaching a maximum very close to pure argon. The results can be compared with Kutasi [21] where practically the same behaviour of the charged particle concentrations was observed excluding the O^+ ions mentioned above. However, it could be caused by different plasma conditions used.

The second part of the results is about investigation of both the static and dynamic properties of multicomponent plasma near the surface of immersed substrates for various pressures and discharge parameters. The potential distributions in the sheath and presheath were obtained and the spatial distributions and time evolutions of the concentrations of the most important charged particles were determined. We concentrated on comparing the sheath for different pressures at the present stage of modelling. The comparison is shown for both the static regime, when a constant value of voltage bias on the electrode was kept, and the dynamic regime, when a sinusoidal voltage bias was applied.

Static regime: Fig. 2 shows the spatial distributions of charged species in the vicinity of the cylindrical probe biased +10 V in the electronegative plasma (Ar- O_2 mixture) for two pressures, 150 Pa and 600 Pa. When comparing these results, we can see that the sheath region is smaller for the higher pressure. This difference is due to the higher volume density of particles in the vicinity of the electrode in the case of higher pressure and hence, it follows better shielding of the electrode voltage bias. We can also see that the sheath region is formed mainly by electrons in both cases. This is induced partly by the composition of electronegative plasma for the experimental parameters (see the concentrations of negative charge

Fig. 2. Concentrations of charged species in the vicinity of cylindrical probe with radius 10^{-4} m in electronegative plasma for Ar: O_2 ratio 50:50. Pressure 150 Pa (left) and 600 Pa (right). Voltage bias +10 V. All concentrations are relative to the undisturbed plasma density $n_r = 10^{15} \text{ m}^{-3}$. Dashed lines show a solution of diffusion equation without the bias. Probe is located at $r = 0$ mm.

particles in the undisturbed plasma mentioned above) and mainly by the different mobility of heavy negative oxygen ions compared to electrons. In addition, we can see that the electron concentration exhibits a peak close to the electrode. The peak is caused by the fact that due to the cylindrical geometry, the flows of electrons are concentrated into a smaller volume, which results in an increase of the local electron concentration.

Dynamic regime: Fig. 3 demonstrates the time developments of concentrations of electrons and argon ions for two pressures (150 Pa and 600 Pa) in the steady state of dynamic processes, whereat a sinusoidal course of voltage bias on the electrode was used, that changed at the frequency of 1 MHz. A different behaviour between electrons and argon ions due to their different masses can be seen. We can also see changes in behaviour of the charged particles for the higher pressure due to the higher volume density of particles causing smaller mobility of the particles. In Fig. 4, the time development of current density of charged species to the substrate for pressure 150 Pa is shown. It is interesting that some ions can be found impinging the substrate after the change of voltage bias to opposite sign, which is caused by their inertial mass.

4 Conclusions

In the first part of the contribution, we presented results from the computer model of volume processes in a DC glow discharge in the Ar- O_2 mixture supported by some experimental results [4]. It is very important to keep in mind that the presented results are very sensitive to the input parameters such as rate constants of chemical re-

Fig. 3. Time developments of concentrations of electrons (left) and Ar ions (right) in the vicinity of substrate at the steady state of dynamic processes. Parameters: pressure 150 Pa (top) and 600 Pa (bottom), sinusoidal course of voltage bias on the electrode (shown below), frequency 1 MHz. The other parameters are the same as in Fig. 2.

Fig. 4. Time developments of current density of electrons, positive argon ions, positive and negative oxygen ions, positive and negative molecular oxygen ions (current density of ions is $1000\times$ magnified). Pressure 150 Pa, sinusoidal course of voltage bias on the electrode, frequency 1 MHz. The other parameters are the same as in Fig. 2.

actions. We tried to use various rate constants found in literature in the course of design of our model. However, the values of a given rate constant are so different in some cases that more experimental measurements will be needed for this purpose.

The second part of the contribution deals with a study of the sheath structure during the interaction of a multicomponent plasma consisting of electrons and five species of both positive and negative ions. A difference of the sheath region for different pressures in electronegative plasma was shown. We presented a part of the results from simu-

lations of the interaction between multicomponent plasma and immersed substrate in dynamic regime, whereas a sinusoidal course of voltage bias was used. These simulations based on particle models are very time consuming but we would like to use these parallel programs prepared for the simulation of plasma-solid interaction with higher frequency of bias. Our final goal is to reach the radio frequency used in technological processes.

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