KINETICS OF REACTIONS IN DC GLOW DISCHARGE IN OXYGEN

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1. Introduction

In the contribution physical and chemical processes in low temperature oxygen plasma are studied by computer experiment. The main task for our modelling is the study of plasma oxidation of metals. The complete plasma oxidation process consists of several parts: volume interactions in chemically active plasma, transport of active species through the sheath and presheath to metal substrate, surface processes on the substrate, growth of oxide layer and transport of both oxygen and metal ions through it. The present contribution is the continuation of our paper [1].

2. Volume processes

In the paper [1] the model consisting of 106 reactions between 12 kinds of neutral, charged and excited particles was suggested. This model was further enlarged in order to achieve its consistency. For the present moment the model of oxygen plasma generated by dc glow discharge consists of 196 reactions between following 17 kinds of particles:

- electrons
- neutral species: O, O_2, O_3
- charged species: O^+, O_2^+, O_3^+, O_4^+
  O^-, O_2^-, O_3^-, O_4^-
- excited species: $O(^1S)$, $O(^1D)$, $O_2(a^1\Delta)$, $O_2(b^1\Sigma)$, O_2^* (i. e. $O_2(c^1\Sigma)$, $O_2(c^3\Sigma)$, $O_2(A^3\Sigma)$).

The complete list of reactions will be published later in the final paper.

The model of processes in the bulk of oxygen plasma is based on a macroscopic kinetic approach. The steady-state concentrations of various species in plasma can be found as a solution of the set of ordinary differential equations which origin in the one-dimensional balance equations for individual species. The analysis was simplified by assumption that both drift and diffusion can be neglected. The resulting stiff system of differential equations was integrated by a semi-implicit extrapolation method (Bader-Deufhard method [2]).

As a result the concentrations of individual species were obtained for various experimental conditions. It was found (similarly as in [1]), that the neutral and excited species are much more important than the charged particles (while the relative concentrations of both atomic oxygen and excited dioxygen can be of order of 10^{-1}, the relative concentrations of most important charged particles – O_2^+, O^- and electrons – are of the order of 10^{-6} or less).

3. Interaction of oxygen plasma with substrates

During plasma oxidation process the active particles from the undisturbed plasma cross the sheath near the metal substrates and both their energy distributions and concentrations are changed. As it is supposed that especially O^- ions and electrons are the most important species, which stimulate the growth of oxide films, the transport of negatively charged particles was studied in detail. For the modelling of movement of charged particles which origin in undisturbed plasma to substrates under various biases the particle simulation technique was used – the combination of molecular dynamics and Monte Carlo method. The trajectories of charged particles in local electric fields were calculated according to molecular dynamics algorithm, while their scattering by neutral particles was treated in a probabilistic way.

It was found that the transport of charged particles through the sheath and even presheath would change their energy and angular distributions profoundly. As an example the change of original Maxwell distribution (solid line) of charged particles after their transfer through the region of disturbed plasma near metal substrates is demonstrated in Fig. 1. In the figure the velocity distributions according to the total velocity v, its normal component v_x and the angular distribution $N(\Theta)$ are shown. From this figure it can be deduced that the fluxes of charged particles will be profoundly influenced, too. However, for detailed analysis of processes, which take part during plasma oxidation on metal surfaces and inside the growing oxide film, our model of oxygen plasma is too large and it must be reduced without loss of its consistency.

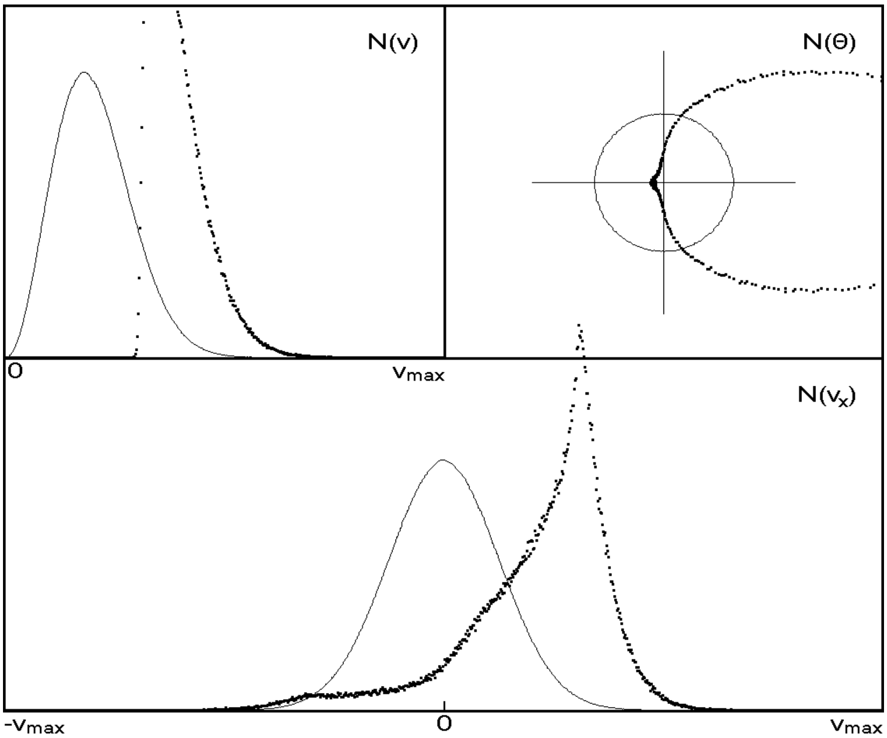

Fig. 1. Distribution of electrons impinging the substrate. Accelerating bias.

4. Simplified model of oxygen plasma

The analysis of the complete set of volume reactions was performed and it was found that reactions could be divided into two groups. Some reactions are highly important and influence the composition of oxygen plasma profoundly, while the other reactions have only a small influence on the final concentrations of active species basic from the point of view of plasma oxidation process.

As an example, reactions important for two main species in the plasma oxidation process – O^- and electrons – together with their relative importance for given species (in per cents) are:

ions O^-

O	+	O^-	->	O_2	+	e	-96.1 %
O_2	+	e	->	O	+	O^-	75.5 %
e	+	$O_2(a^1\Delta)$	->	O	+	O^-	23.3 %
O^-	+	$O_2(a^1\Delta)$	->	O_3	+	e	-2.3 %
O^-	+	$O_2(a^1\Delta)$	->	O	+	O_2^-	-0.75 %
e	+	$O_2(b^1\Sigma)$	->	O	+	O^-	0.72 %

electrons

O	+	O^-		->	O_2	+	e		72.5 %
O_2	+	e		->	O	+	O^-		-57.0 %
O_2	+	e		->	O_2^+	+	e	+ e	24.8 %
e	+	$O_2(a^1\Delta)$		->	O	+	O^-		-17.6 %
O_2^+	+	e		->	O	+	O		-12.7 %
O_2^+	+	e		->	O	+	$O(^1D)$		-11.2 %
O^-	+	$O_2(a^1\Delta)$		->	O_3	+	e		1.7 %
O_2^+	+	e	+ e	->	O_2	+	e		-0.85 %
e	+	$O_2(b^1\Sigma)$		->	O	+	O^-		-0.54 %

It can be seen that there are reactions yield of which is many times smaller than peak values of other reactions. However, the simplification must be done in the whole system of chemical reactions and for all basic species in the same time.

From these important reactions the new simplified model of the bulk of oxygen plasma can be formed. If following species – O_3^+, O_4^-, $O(^1S)$ and O_2^* – are excluded from the model, the list of really import reactions can be reduced to 37 only. This reduced set of reactions is convenient for further development of the complex model of plasma oxidation process, namely the physical processes in growing oxide film as well as processes and reactions in various mixtures (O_2/Ar, etc.) can be studied by computer experiment and included into the whole system.

Acknowledgement

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References

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[2] Press W.H., Flannery B.P., Teukolsky S.A. and Vetterling W.T.: Numerical Recipes in Fortran (2nd Edition). Cambridge University Press, p. 727 (1992).