Modelling and diagnostics of AR/O_2 plasma

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Abstract

The simulation of dc glow discharge in argon/oxygen plasma is used for the study of plasma oxidation of aluminium films. Two steps for complete simulation are shown – a model of chemical reactions in the bulk plasma and a transport of charged species through the sheath to substrates. The experimental data about plasma parameters were obtained by OES and QMS.

Introduction

When a metal or semiconductor surface is exposed to oxygen, an oxide layer will be created. There are two basic techniques of the film growth. High-temperature processes as thermal oxidation or chemical vapour deposition often give rise to defect formation. Therefore, the low-temperature techniques become to be popular. One of the most important of them is the plasma oxidation [1] utilising highly activated oxygen plasma. Substrates immersed into the plasma are held on various biases relative to plasma. Typical procedure uses the positive external bias (so-called plasma anodization) in order to enhance the diffusion of oxygen ions through the growing oxide film, however the oxidation without external bias or even with negative bias is sometimes used, too. The typical plasma oxidation process consists of two reverse mechanisms – growth of the oxide film by flux of oxygen atoms or ions, and film etching due to an ionic bombardment [2] . The intensity of these processes depends on substrate bias, which influences the fluxes of individual species and energies of impinging ions. Therefore, it is important to obtain detailed information about the processes taking part near substrate as they control the whole oxidation process.

Aluminium oxide thin film is a transparent insulator and hard coating material applied in mechanics and as a protective layer, and could also be used as an optical filter. Thanks to their insulating properties, the aluminium oxide layers are applied in semiconductor devices. Plasma oxidation is one of the promising low temperature techniques used to grow oxide films on metal or semiconductor surfaces [1] .

For the discussion of processes taking part during plasma oxidation of aluminium, a computer experiment was prepared. This computer experiment must consist of similar stages as the real plasma oxidation process. The results of simulation are compared with the experimental data taken from the literature as well as from our measurements performed by OES, QMS, and AFM techniques.

Experiments

The experiments were carried out in the system for the plasma-chemical surface modification of thin films [3]. A process plasma monitoring was used both to choose optimum plasma oxidation conditions and to control contamination of the plasma. Plasma parameters during plasma oxidation were estimated with optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS). It is helpful to know the nature and the relative abundance of neutral species presented in the plasma. The QMS analysis of neutral gas composition provides the data for detailed study of plasma chemistry.

2.1 Optical emission spectroscopy measurements

The most important plasma species in plasma oxidation process are atomic oxygen ions. Several wavelengths corresponding to atomic transitions in oxygen were used to analyse the plasma emission spectra. The most significant oxygen lines in our experimental conditions were the 777.4 nm and 844.67 nm lines, see Fig. 1.

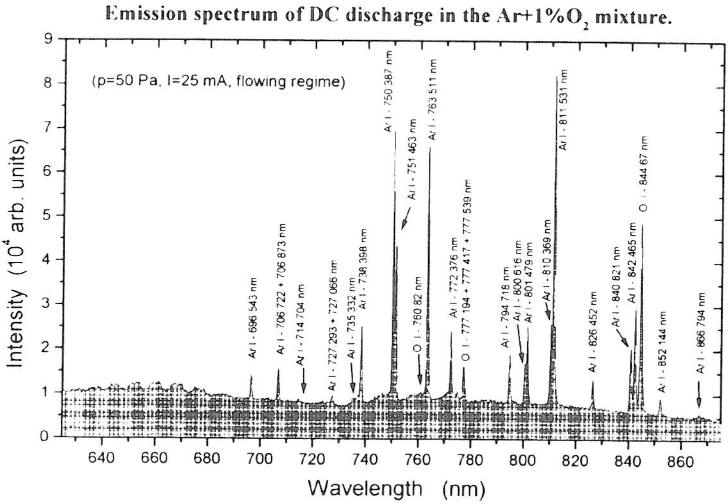

Fig. 1 *Emission spectrum of DC discharge in the Ar/O$_2$ mixture (99: 1) in flowing regime*

These lines correspond to the deexcitation of the oxygen atom in the state $^5P(O^*)$, whose creation is predicted by the following ways [4]

$$e + O_2 \quad e + O^* + O$$

and

$$e + O \quad e + O^*,$$

i.e. dissociative excitation or direct impact excitation of oxygen atom, respectively.

The fraction of O atoms with respect to O_2 molecules is enhanced in oxygen/argon mixture due to the production of O atoms by the quenching reaction Ar^M metastables with O_2, i.e.

$$Ar^M + O_2 \quad Ar + O + O.$$

To increase the atomic oxygen density in the oxygen/argon mixture plasma it is useful to add a specific amount of argon [3]. This enables to optimize plasma oxidation process. The importance of an optimal set-up of oxygen/argon mixture is evident from comparison Fig. 1 (DC discharge in mixture 99 % argon and 1 % oxygen) and Fig. 2 (DC discharge in mixture 50 % argon and 50 % oxygen).

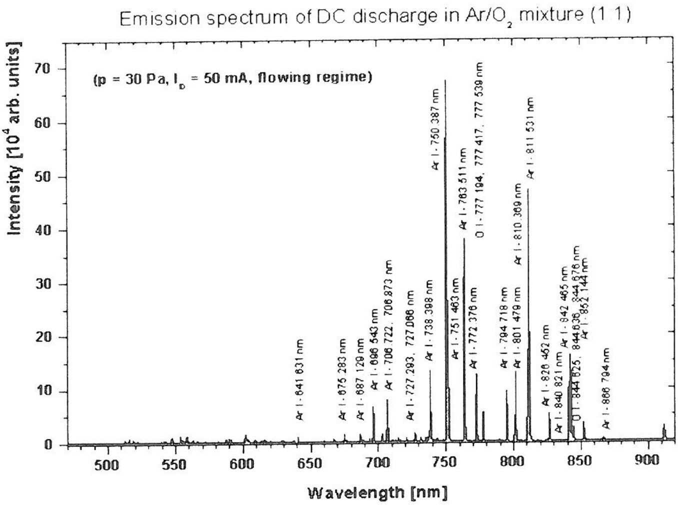

Fig. 2 *Emission spectrum of DC discharge in the Ar/O_2 mixture (1:1) in flowing regime*

2.2 Mass spectrometry of neutral species measurements

All impurities even in small concentrations can play a significant role in plasma oxidation process. Plasma–solid surface interactions in plasma source can generate trace impurities that may affect the growing films.

The on-line QMS gas analysis system can be used to explain the role of small admixtures of impurities in plasma. The QMS measurement of the effluents pumped from the discharge tube during plasma oxidation give us information on the formation and variation of neutral species resulting from interactions between plasma and discharge tube walls and sample surface.

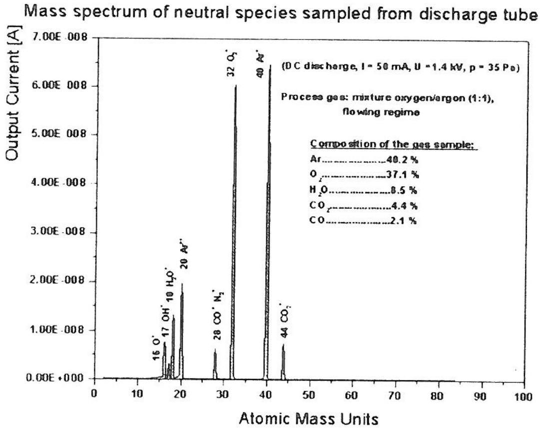

Fig. 3 Mass spectrum of neutral species sampled from argon/oxygen mixture (1:1) discharge during plasma oxidation of thin aluminium films.

These measurements are essential for the plasma process purity monitoring. Our previous results indicate the presence of impurities in the discharge tube when the carbon substrates and Teflon components are present in the discharge. The presence of fluorocarbon radicals' impurities in the discharge plasma was significantly reduced after the discharge tube reconstruction when only glass is touch with the plasma, se Fig. 3.

2. 3 AFM measurements structural properties of alumina thin films

Atomic Force Microscopy (the AFM system Metris-2001A-NC, manufactured by Burleigh Instruments Inc.) was applied in the contact mode for both surface structure and roughness observation and for interpretation of the surface modification. The thickness of Al, Al-Al_2O_3 structures was derived from the AFM images of surfaces with a mechanical scratch.

Computer experiment

The discussion of the experimental results has been done by means of computer experiment. The computer model consisted of several stages similar to the process of plasma oxidation of metals itself – activation of oxygen and argon atoms in the discharge, transport of charged particles through the sheath, surface processes on the substrate and the transport of oxygen and metal ions through the growing dielectric film.

Bulk processes in the oxygen/argon plasma were analysed by our model of dc glow discharge [5] in that plasma. Model of physical and chemical processes in the bulk of oxygen/argon plasma was based on a macroscopic kinetic approach. The model consisted of nearly 190 reactions between many kinds of neutral, charged, and excited particles. The reaction set consisted of three parts - reactions between oxygen particles, reactions in argon and mixed reactions oxygen-argon. The resulting set of stiff equations was integrated with the help of a semi-implicit extrapolation Bader-Deuflhard method [6] . Steady-state concentrations of stable products were derived as a result of this stage of simulation.

As results of our simulations show, the presence of Ar atoms or ions influences the consequent chemical composition of the mixture in plasma insignificantly. The resulting mixture composition in oxygen/argon plasma depends on a percentage abundance of argon only in that way that the fraction of electrons increases with argon positive ions. The mixed reactions oxygen-argon have not a big influence on the mixture composition. Hence, it is well possible to use the steady-state concentrations of products obtained by simulations in pure oxygen, at least for qualitative studies.

The next data show the concentrations of neutral, excited and ionized products found for oxygen plasma discharge for our experimental conditions at E/N = 60 Td (all concentrations are given in relative scale – compared to molecular oxygen):

- neutral and excited species:

  O_2: 1.00 $\quad$ O: $7.53\cdot10^{-1}$ $\quad$ $O_2(^1\Delta_g)$: $1.48\cdot10^{-1}$

  $O_2(^1\Sigma_g^+)$: $4.34\cdot10^{-3}$ $\quad$ O_3: $7.70\cdot10^{-5}$ $\quad$ ...

- charged species:

  positive $\quad$ O_2^+: $1.60\cdot10^{-6}$ $\quad$ O^+: $5.17\cdot10^{-10}$ $\quad$ O_4^+: $3.00\cdot10^{-10}$, ...

  negative $\quad$ electrons: $1.33\cdot10^{-6}$ $\quad$ O^-: $2.62\cdot10^{-7}$ $\quad$ O_2^-: $8.60\cdot10^{-9}$

  O_3^-: $4.64\cdot10^{-10}$ $\quad$ ...

This data are used for the next part of our simulations.

Further, the transport of charged particles through the region of disturbed plasma near substrate was studied. The technique used was a standard PIC-MC simulation (e.g. [7]). The model is one-dimensional in space and two-dimensional in velocities. We assume source of particles in the undisturbed plasma region according to our previous model. All particles have Maxwell velocity distribution and plasma density is 1.10^{15} m^{-3}. Only elastic collisions and charge transfer interactions with mean free paths given by experimental data [8] are taken into account. Gas temperature is 300 K, electron temperature 20,000 K, time step for electrons $1\cdot10^{-11}$ s, and time step for ions $1\cdot10^{-8}$ s. The complete model was written in FORTRAN 95 programming language and solved on a PC (Pentium III/1 GHz). The simulations resulted in fluxes of individual species in the following table:

U [V]	-10	-8	-6	-4	-2	0	+2	+4	+6	+8	+10
O^-	-	-	-	-	-	6.5	16.1	16.4	17.4	18.8	18.5
O_2^-	-	-	-	-	-	0.07	0.35	0.36	0.37	0.38	0.38
O_3^-	-	-	-	-	-	0.002	0.013	0.017	0.023	0.032	0.033
e^-	0	0.06 x 10^5	0	0.25 x 10^5	0.50 x 10^5	1.03 x 10^5	1.12 x 10^5	1.17 x 10^5	1.21 x 10^5	x 10^5	1.28 x 10^5
O^+	0.22	0.21	0.20	0.12	0.09	0.02	-	-	-	-	-
O_2^+	452	417	376	307	200	17.8	-	-	-	-	-

Tab. 1 *Fluxes of various types of charged particles to the substrate at bias voltage U relative to plasma potential. Fluxes are given in relative units.*

The energies of impinging charged particles seem to be nearly voltage independent in the bias range from –10 to +10 volts. This result can be explained by the fact that especially at higher pressures the scattering in the sheath is so intensive that only the electric field very close to the surface determines the velocities of charged particles. This field is nearly bias voltage independent for planar substrates as one can conclude from our simulations. The main influence of applied voltage bias was the increasing fluxes of impinging species. It can be seen from ***Tab. 1***, that the minimal flux of all types of oxygen ions can be found without external bias. Therefore, if we suppose that the oxidation is caused mostly by oxygen ions coming from the undisturbed plasma, the minimal oxidation rate is expected for substrates held on the plasma potential.

Conclusions

Our experimental data were obtained for the case of oxidation of aluminium films in the oxygen/argon mixture DC glow discharge by OES and QMS methods. They help us for a discussion of results of our simulations. Another advantageous experimental technique is the investigation of surface properties of the film by AFM. We used the AFM for a study of the film morphology. Moreover, we used results of our further diagnostic technique – RBS. As we know from them, the oxide film thickness depends on the substrate bias; increases with the bias (the alumina thickness being about 40, 50 and 60 nm for bias 0, +10 and +20 volts).

The results of our model presented here show that the flux of oxygen ions O^- is enhanced by substrate bias voltage. To have enough oxygen ions O^- in the glow discharge it is fruitful to use oxygen/argon mixture plasma. This fact results also from our OES measurements, which were made, in the mixture plasma. As argon metastables contribute to the oxygen atoms and consequently O^- ions rise, they are hence important to be arised oxide films thicker. Plasma anodization in the oxygen/argon mixture plasma seems to be useful technique for a production thicker alumina film as it was found also by experimental investigation. More positive bias voltage produces thicker oxide films.

Acknowledgements

The research was sponsored by the European Community through the INCO-COPERNICUS Grant No. ERB IC15 CT98 0805 and by The Ministry of Education of Czech Republic (Projects OK 401 and COST 527.50). The financial support of research intent No. MSM 134300001 is gratefully acknowledged.

References

[1] J. Siejka, J. Perriere: *Plasma Oxidation*, in *Physics of Thin Films*, Eds. M. H. Francombe, J. L. Vosen, Vol. 14, Academic Press Inc., Boston (1989).
[2] J. W. Metselaar, V. I. Kuznetsov, A. G. Zhidkov, J. Appl. Phys. **75** (1994), 4910-4916,.
[3] V. Hrachova, A. Kanka: Proc. of ICPIG XXIII – Vol. II, Toulouse, July 17-22, 1997, 20-21
[4] V. Hrachová, A. Kanka: Vacuum **48**, (1997), 689-692
[5] R. Hrach, J. Pavlik, Proc. ECAMP VI, Siena, Italy, Europhysics Conf. Abstracts, Vol. 22 D, 5-10, (1998).
[6] W.H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, in Numerical Recipes in Fortran, Cambridge Univ. Press (Second Ed.), 727, (1992).
[7] R. Hrach, Czech. J. Phys. **49** (1999), 155-165.
[8] S. C. Brown, in Basic Data of Plasma Physics: The Fundamental Data on Electrical Discharges in Gases. AIP Press, New York (1994).