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Study of argon/oxygen plasma used for creation of aluminium oxide thin films

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The aim of this work was to investigate a low temperature plasma used for plasma oxidation. The experiments were performed in a system for plasma-chemical surface modification of thin films. In our experiments we used a DC discharge or capacitively coupled RF discharge to generate the plasma in various oxygen/argon mixtures. The main diagnostic techniques applied to determine plasma parameters were the optical and probe diagnostics. The combination of the above mentioned diagnostic techniques enabled to evaluate the influence of plasma parameters during plasma oxidation upon the quality of the aluminium oxide films.

1. introduction

Plasma oxidation, utilising a highly activated oxygen plasma, is one of the low temperature techniques used to grow dielectric films on metal and semiconductor surfaces [1]. In this paper, the newly developed plasma oxidation apparatus is described along with an investigation of argon/oxygen mixture plasma characteristics.
There are following main reasons of this investigation:
- to understand the mechanisms of plasma oxidation of aluminium thin films
- to find basic factors which play the dominant role in the studied process
- to find factors which determine properties of created oxide layers and M-I-M structures of the type of $Al/Al_2O_3/Al$.

2. Experimental apparatus

The experiments were carried out in the system for the plasma-chemical surface modification of thin films. The details of the experimental setup are given in [2]. However, we briefly outline it here.

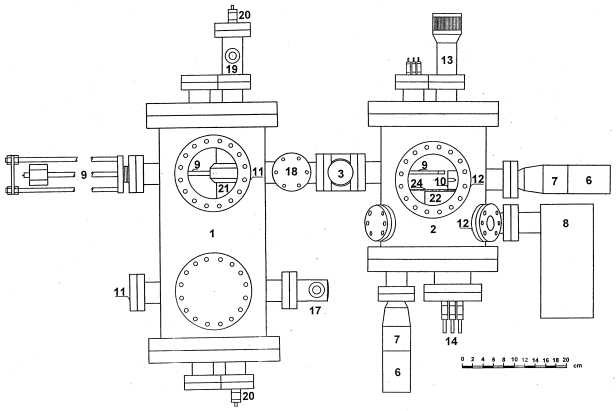

FIG. 1. The front view of the plasma-chemical system

The experimental arrangement is shown in Fig. 1, 2 and 3. The system consists of two stainless-steel chambers (HV process chamber and UHV analytical chamber) which are separated by a gate valve.

Two types of discharges were applied: DC glow discharge and 13.56 MHz RF discharge in pure oxygen or oxygen/argon mixture (purity: argon 99.9999 %, oxygen 99.995 %).

The DC flowing discharge was produced in a Pyrex tube (inner diameter 70 mm and 450 mm length) at typical total gas pressure p = 50 Pa, flow rate $Q = 2.5\times10^{-4}$ l s^{-1} and discharge current I = 25 mA. In the same ranges of the gas pressure and the flow rate, a R.F. discharge is produced in an axial movable tube of inner diameter 18 mm, which is connected to a Pyrex post-discharge tube located in HV chamber. The external ring electrodes were capacitively coupled via a matching unit to an R.F. generator (50 W) of 13.56 MHz.

An absolute capacitance manometer (10^{-3} - 10 mbar) indicates variations in the pressure inside the discharge tube. The system is pumped down by an oil-free pumping system with turbomolecular pump BALZERS TPH 240.

The UHV chamber contains a quadrupole mass spectrometer (Balzers QMG 112) as a residual gas analyser. A PC data acquisition system is coupled to a mass

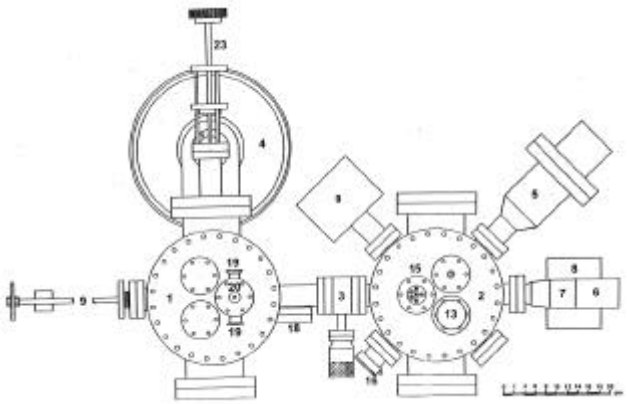

FIG. 2. The top view of the plasma-chemical system

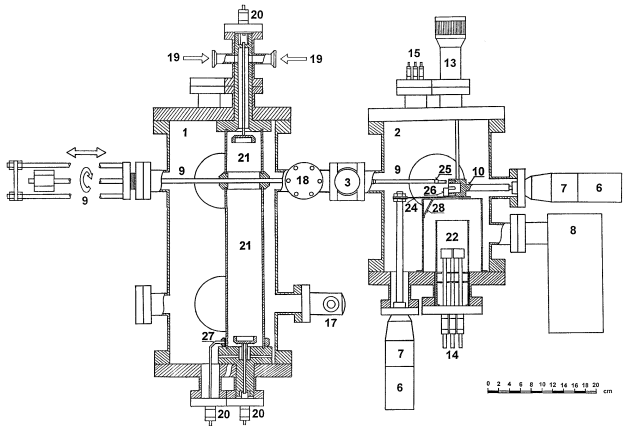

FIG. 3. The inner facility of the plasma - chemical system

Legend for numbers in figures 1, 2 and 3.
1 – HV chamber, 2 – UHV chamber, 3 – gate valve, 4 – turbomolecular pump, 5 – quadrupole mass spectrometer, 6 – stepper motor, 7 – rotary motion feedthrough, 8 – titanium sputter ion pump, 9 – linear and rotary movable transport system, 10 – carrousel, 11 – HV viewport, 12 – UHV viewport, 13 – linear motion feedthrough, 14 – power electrical feedthroughs, 15 – multi pin electrical feedthrough, 16 – ionization vacuum gauge, 17 – Pirani and Penning vacuum gauges, 18 – entrance for loading and unloading of samples, 19 – inlet for working gases, 20 – high voltage electrical feedthrough, 21 - DC glow discharge tube, 22 – evaporation system, 23 – movable system with Langmuir probe, 24 – rotary shutter, 25 - sample holder with sample, 26 – crystal sensor head, 27 – supporting starting electrode, 28 - mirror

spectrometer. The PC data acquisition system is controlled by software designed specifically for this purpose [3].

The UHV chamber comprises an evaporation system. The source providing the evaporation can be as a part of the experimental device easily separated out of the UHV chamber. The evaporation of various materials might be carried out by means of two independent tungsten filaments. The evaporated materials flow (aluminium is of 99.9999 % purity) laid out on a sample is strongly limited by inner housing and rotary shutter with different exchangeable masks.

Glass substrates with the dimension of 10 × 4 × 1 mm^3 were well cleaned and mounted in a sample holder and placed into a vacuum system. First, the aluminium layers were prepared by thermal evaporation. Deposition rates and thicknesses were monitored during deposition using a conventional quartz crystal system (5 MHz) with water-cooled head. Then a layer of aluminium oxide was obtained by the plasma oxidation. In our case the sample was kept on the plasma floating potential. After plasma processing the sample was stored in carrousel in UHV chamber.

3. Plasma parameters determination

The experiments have been performed in a DC or RF discharges in argon/oxygen mixture in a flowing regime.

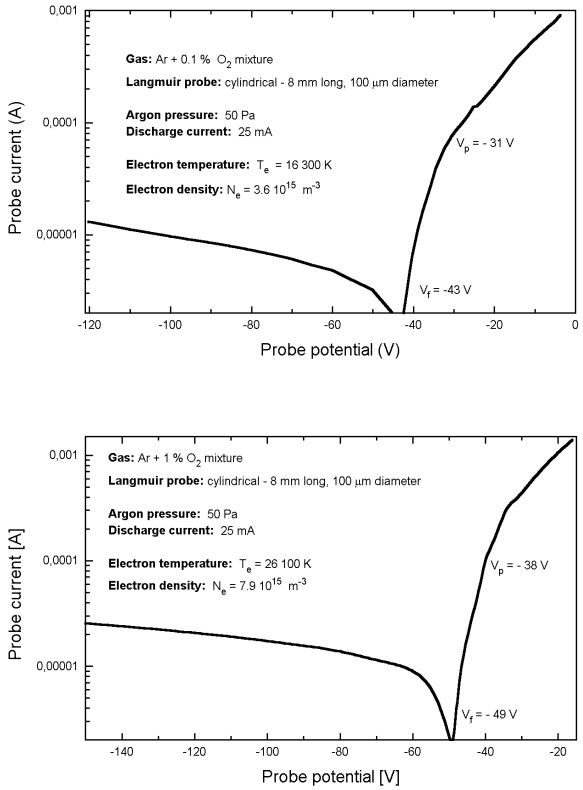

FIG. 4. Langmuir probe characteristics measured in DC discharge in Ar/O_2 mixture.

3.1 The Langmuir probe techniques

To optimise the plasma oxidation process it is unavoidable to specify plasma parameters at different places of the discharge tube over the radius of the tube. One can measure those plasma parameters by means of the radial movable system of the Langmuir probe (Pt wire, 8 mm long and 100 μm diameter). The Fig. 4. shows the probe characteristics measured in the DC discharge in both the Ar+1% O_2 mixture and the Ar+0.1% O_2 mixture.

The probe was placed in the centre of the discharge tube. From the probe characteristics the plasma potential V_p and floating potential V_f, electron density N_e and the electron temperature T_e were determined. The characteristics were evaluated by a computer software described in [4].

The relative radial distribution of Langmuir probe ion saturation current is similar to the Bessel radial distribution.

3.2 Optical emission spectroscopy

Optical emission spectroscopy (OES) is often used for diagnostics of reactive plasmas, where the use of other techniques is impractical. The main advantage of the method is non-invasive character of measurements.

OES measurements are very sensitive to changes in the high-energy fraction of the EDF, which is responsible for a

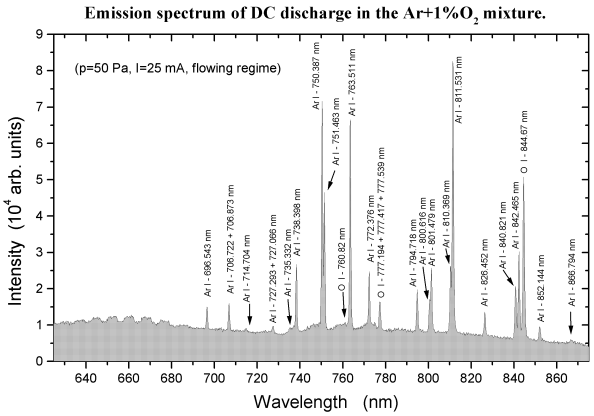

FIG. 5. Emission spectrum of DC discharge in the Ar/O_2 mixture in flowing regime.

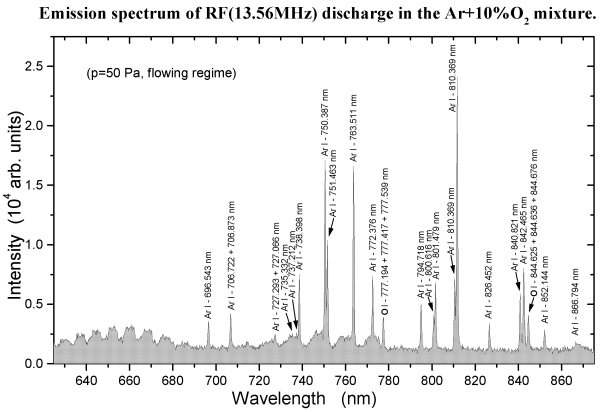

FIG. 6. Emission spectrum of RF discharge in the Ar/O_2 mixture in flowing regime.

production of radicals and ions in reactive plasmas. By a monitoring of line emission, information about the rates of important processes can be obtained.

The optical emission spectroscopy system consists of a quartz fiber (600 μm diameter), the imaging spectrograph Jobin-Yvon CP-200 (0.6 nm resolution) and the CCD camera ST-7I, manufactured by Santa Barbara Instrument Group.

The optical emission spectrum in visible and near infrared regions of DC discharge in the Ar/O_2 mixture is shown in Fig. 5. The argon pressure was 50 Pa, the oxygen flow was 1% from the value of argon flow.

The optical emission spectrum in visible and near infrared regions of RF discharge in the Ar/O_2 mixture is shown in Fig. 6. The argon pressure was 50 Pa, the oxygen flow was 10 % from the value of argon flow.

4. Results and discussion

Plasma parameters during plasma oxidation were estimated with a single Langmuir probe and OES. The electron temperature was about 0.5 – 1.5 eV. Plasma density was of the order of 10^{15} m^{-3}.

The emission spectra were measured to obtain the optimum oxidation conditions.

The plasma characteristics are influenced by factors such as the argon gas pressure and the flow of oxygen in the case of Ar/O_2 mixtures. The argon pressure was 50 Pa, the oxygen flow was 0.1 %, 1 %, 5 % or 10 % from the value of the argon flow.

The oxide growth during plasma oxidation is probably caused by existence of O^- negative ions. The ions can be created in the bulk of plasma or on the substrate surface. Several wavelengths corresponding to atomic transitions in argon and 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. These lines correspond to the deexcitation of the oxygen atom in the state ^5P (O^*), whose creation is predicted by the following ways $e + O_2 \rightarrow e + O^* + O$ and $e + O \rightarrow e + O^*$, i.e. dissociative excitation or direct impact excitation of oxygen atom, respective [5]. 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. $Ar^M + O_2 \rightarrow Ar + O + O$. The main mechanism of the Ar I 750.4 nm emission line is caused mostly due the direct

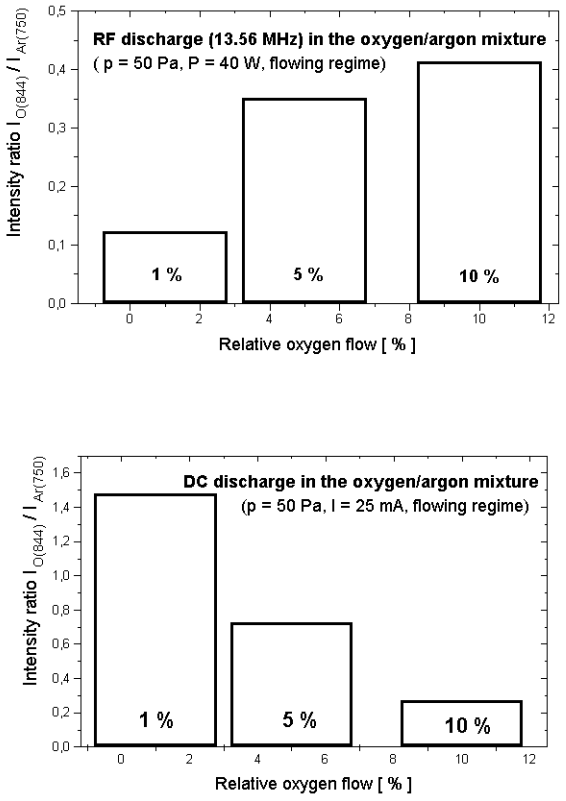

FIG. 7. Dependence of the intensities ratio on oxygen flow.

electron-impact excitation from the ground state. To estimate the atomic oxygen density in the oxygen/argon mixture plasma, it is useful to plot the dependence of intensity ratio of lines OI 844.67 nm to ArI 750.4 nm (which is affected with changes of discharge conditions) on the oxygen flow.

Fig.7 shows the dependence of the relative emission intensities of $I_{O(844.67)}/I_{Ar(750.4)}$ on oxygen flow. The intensities ratio reaches its maximum at 1 % oxygen flow in the case of DC discharge and near 10 % oxygen flow in the case of the RF discharge.

The morphology of the film surface before and after plasma oxidation was studied by optical microscope. Obtained first results indicate that the evaporated aluminium thin films are porous. The surface morphology was modified during the plasma oxidation. It was found that the films have a relatively flat surface after plasma oxidation.

5. Conclusion

The plasma-chemical system for plasma oxidation of aluminium thin films has been presented. The Langmuir probe technique and optical emission spectroscopy have been described as the main techniques. These techniques enable the achievement of the main goal – the optimise the plasma oxidation process. Experiments on plasma oxidation of aluminium thin films in argon/oxygen mixture plasma were described.

It was found that optimum ratio of Ar/O_2 mixture was at 1 % oxygen flow in the case of DC discharge and near 10 % oxygen flow in the case of the RF discharge.

Acknowledgements

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