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Study of processes in a pulsed magnetron Ar/O_2 plasma by mass spectrometry

P. Pokorný, M. Novotný, J. Bulíř, J. Lančok, M. Mišina, J. Musil

Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic

Introduction

The pulsed magnetron sputtering (PMS) is well introduced technique for deposition of insulating films such as alumina using a metallic target and a reactive gas mixture [1][2][3]. The primary goal of the pulsed power is to significantly reduce the formation of arcs and consequently improve on quality of deposited films. The operation conditions, i.e. metallic, transition and oxide modes critically dependent on the properties of the pulsed plasma in the vicinity of the magnetron. The conditions are typically optimized empirically, however to reach and maintain condition for the highest deposition rate is still challenging task. It is necessary to study the plasma parameters and processes in detail to understand better these effects [3]. However, little has been published on the plasma diagnostics of the pulsed magnetron discharge by means of the energy-resolved mass spectrometry. Mass spectrometer (MS) were used to characterize the deposition process of alumina thin films by a pulsed magnetron sputtering. Mass spectra of argon, oxygen, aluminum and AlO as a function of Ar/O_2 ratio and p_p (partial pressure expressed in flow) of oxygen, magnetron DC voltage U_d and power P_d were investigated in details. The energy of ions impinging on the growing film is one of the most important parameters influencing the quality of deposited films and the mass and energy spectra of positive and negative ions may contain important information on the status of the cathode and the plasma [5]. The main attention was devoted to processes in the transition mode. Obtained results can be used to optimize deposition conditions in sputtering of alumina thin films.

Experimental details

DC pulsed magnetron discharge was generated in two cylindrical deposition chambers with a diameter of 250 mm pumped down by i) turbo pump 1500 l/s and ii)oil diffusion pump 2000 l/s with water cooling to base pressures $p_{tot} = 5x10^{-5}$ Pa and $p_{tot} = 2x10^{-3}$ Pa, respectively. The round shape magnetron with Al (purity 99,99) target of a diameter 100 mm was used for sputtering. DC magnetron voltage was changed in the interval from 100 to 600 V. A DC power supply Huettinger 3000 combined with pulse generator MELEC operated at the discharge voltage $U_d = 500$ V, power $P_d = 400$ W, the repetition frequency f = 10 kHz, pulse length $\tau = 50$ μs and duty cycle $\tau/T = 0.5$, were T is the period of pulses, were used for main part of experiments. The magnetron discharge was maintained at pressures ranging from 0.1 to 1 Pa, a main part of experiments was done at constant pressure of 0.5 Pa. Argon (purity 99.99) was used as a working gas, Ar flow Q_{Ar} was kept constant at 16 sccm, and for oxidation processes oxygen gas of purity 99.999 was used, O_2 flow was varied from 0 to 8 sccm. Al target was sputtered in Ar/O_2 mixture at total pressure ranging from 0.2 to 1 Pa. Plasma properties in metallic, transition and oxide mode of sputtering were investigated.

The plasma of DC pulsed magnetron discharge was investigated by means of mass spectrometry. The mass spectrometer (MS) EQP 500 HIDEN Analytical Ltd. with three orifices of diameters 0.8, 1.5 and 2 mm in the first, second and third stage of MS [6] was used in the device pumped by the turbo pump and MS equipped only one orifice of diameter 0.2 mm was used in the apparatus pumped by the oil diffusion pump. The individual stages of MS were pumped down using turbo pumps with pumping speed of 60 l/s. The distance d between target and the orifice of MS was 100 mm, i.e. it was the same as that one used for film deposition. The position of "race track" was r = 35 mm. Prior to every measurements of mass

spectrum a composition of base rest atmosphere was measured to ensure the same initial conditions (Fig.1).

Experimental results and discussion

Very detailed measurement of the transition region of the so-called transition mode (Fig.2,3) was carried out. This measurement allows adjusting precisely the experimental conditions in the transition mode. Fig.3 allows to set up various conditions (voltage or oxygen flow) and thereby change of the deposition rate and ev. composition of alumina film. Therefore, all subsequent measurements were carried out in the transition mode region and at oxygen flow rate Q_{O2} varying from 0 to 8 sccm. Mass spectra of neutrals in the plasma were measured on the axis as well as at the race track level.

To ascertain the processes taking place in the plasma during deposition under transition mode conditions, mass spectra of neutrals were measured at a distance of 100 mm on the target axis, where the substrate is located during deposition. We obtained spectra of neutrals containing gases used in the plasma chamber, i.e. O, O_2, Ar and atomic Al, as well as smaller amounts of AlO and AlO_2 radicals. Residual traces of hydrogen H and H_2, water and nitrogen were also detected on the background. Identical measurements were carried out for +/- ions as a function of O_2 flow rate from 0 to 8 sccm (Fig. 4). This figure shows the spectra of +ions in the transition mode at the target axis as functions of Q_{O2} flow rate in the range mentioned above. The measurements have shown the creation of some radicals in the discharge, such as O^+, Al^+, O_2^+ and Ar^+, but also some new ones, such as AlO^+ and Al_2O^+, and even some unexpected radicals probably of short half-life, e.g. $AlAr^+$. Later, in the oxid mode, even a weak increase of Al_2O^+ concentration is observed. Simultaneously, the temperature at the entrance orifice MS was measured and was found to reach the values T = 300 – 450 °C in agreement with [7].

In accordance with [6], one can see the creation and gradual growth of O^+ and decrease of O_2^+ in the transition mode: partial decomposition of O_2 takes place here and a part of oxygen atoms is consumed in the formation of Al_2O_3, which follows from the decrease of the Al^+ and Al^{2+} intensities. At the same time, slight increase in the concentration of AlO^+ radical (m/q = 43) is detected.

It is evident from the presented results that variations in the oxygen flow lead to profound changes in the plasma: some radicals and neutrals disappear. The distribution of energies of particles forming the plasma is one of the fundamental data on the plasma behaviour and properties. Fig.5 shows the energy distribution of O_2^+ ions (m/q = 32). Energy distribution was measured as a function of the discharge voltage (position on the hysteresis loop in the transition mode - see Fig.3). As seen from the figure, the number of O_2^+ ions is very small at a voltage U = 400 V (metallic mode) and the energy maximum occurs approximately at U = -8 V related to a ground potential of the MS orifice. A shift along the hysteresis curve in the transition mode towards lower voltages (towards oxide mode) thus results in an increase of the number of free O_2^+ ions (see Fig.4), hence the dissociation of O_2 molecules takes place at the measured energy maximum (about -8 V). In the range of U = 350 – 330 V, the energy distribution curve shifts to a value of U = -4.7 V, which is in agreement with [8]. These conditions result in the highest intensity of ions. On further shift to even lower voltages, we reach the onset of the oxide mode. Here the number of O_2^+ ions starts to drop and their energy distribution shows two maxima, at values U = -8 V and U = -2.5 V. Thus it seems most advantageous for the proper growth to set up conditions corresponding to the voltage U = 340 - 330 V. The layers deposited at these values are indeed characterised by much higher deposition rates, in agreement with the expectation. Those results like as a deposition rate with properties of thin films of Al_2O_3 will be presented at the Eleventh International Conference on Plasma Surface Engineering, PSE 2008.

Conclusions

Main results in this investigation can be summarized as follows:

1. Magnetron discharge generated in a mixture of $Ar+O_2$ exhibits the hysteresis effect which enhances with increasing magnetron power P_d.
2. Sputtering of Al in $Ar+O_2$ mixture gradually changes from metallic mode through transition mode to oxide mode with increasing flow of oxygen Q_{O2}. This change is due to poisoning of the surface of Al target. This phenomenon results in the generation of different kinds and different concentration of plasma species in individual modes of sputtering.
3. Ar^+, Al^+, Ar^{2+}, Al^{2+} dominate in the metallic mode while O^+ and O_2^+ are substantially lower (Fig.4). However, the amount of O^+ and O_2^+ oxygen ions increases with increasing Q_{O2}, achieves a maximum approximately at the end of the transition mode and further slowly decreases with increasing Q_{O2} in the oxide mode. O^+ and O_2^+ dominate in the oxid mode.
4. The width of energy spectrum of positive oxygen ions O_2^+ strongly depends on magnetron voltage U_d. It is very broad peak in metallic mode at $U_d = 400$ V, but relativem narrow ($\Delta E_{FWHM} \sim 5$ eV) in the transition mode. On the other hand in oxide mode two broader maxima at ~ 2 and ~ 8 eV were found.
5. Differences in presence, absence or dominance of plasma species in the magnetron discharge maintening under different deposition conditions their relative intensities can help to explain different properties of Al-O film produced in the transition and oxide mode sputtering.
6. The main goal of the experiments is that using MS it can be adjust best conditions for Al_2O_3 deposition rate.

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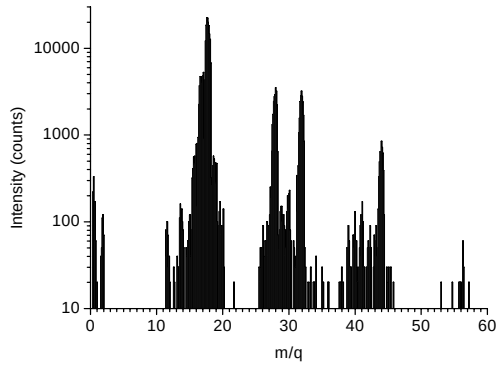

Fig.1: Spectrum of residual gas RGA at $p_{tot} = 1 \times 10^{-4}$ Pa in a chamber

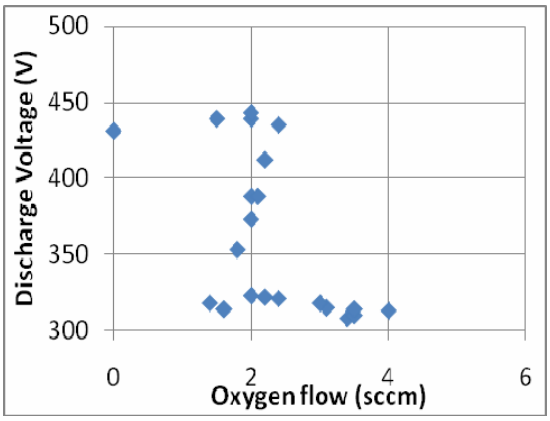

Fig.3: Discharge voltage U_d as a function of Q_{O2} (detailed process)

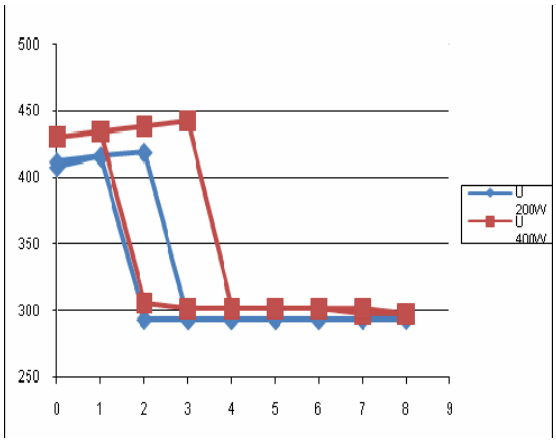

Fig.2: Discharge voltage U_d as a function of Q_O at aconstant value of magnetron power(P_1 =200W, P_2=400W)

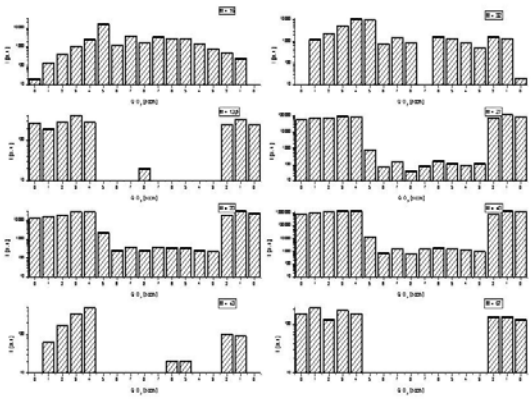

Fig.4: Positive ion intensity on Q_{O2} gas flow

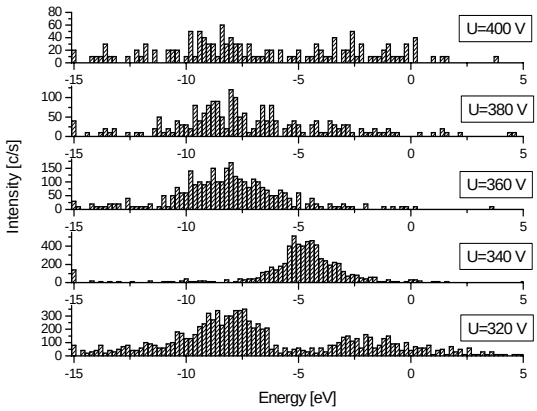

Fig.5: Energy shift of O_2^+ in transition mode(U = 340 V, and U = 320 V)