

Optical emission and mass spectroscopy of plasma processes in reactive DC pulsed magnetron sputtering of aluminium oxide

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Optical emission spectroscopy (OES) and mass spectrometry were used for plasma investigation of DC pulsed reactive magnetron sputtering of aluminium oxide. Aluminium target was sputtered in a reactive oxygen/argon atmosphere. Special attention was paid to the transition from the dielectric to metallic mode. Mass spectra were recorded at the substrate. OES spectra were taken at the target and at the substrate. Both mass and emission spectra obtained in the transition mode revealed distinct changes in plasma composition (O, O₂, Al and AlO plasma species and corresponding positive ions). The transition from the dielectric to metallic mode is followed by a decrease of atomic oxygen intensity, while the intensity of aluminium species increases. AlO molecule appeared in the mass spectra only.

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1. Introduction

Reactive magnetron sputtering (RMS) is widely used technique to fabricate thin films of metal oxides, e.g. Al₂O₃. However, direct current (DC) RMS suffers 'target poisoning' - coverage of the target with the reaction product - which results in violent arcing during the process 0. The problems with the reactive sputtering of oxides can be overcome using radio-frequency (RF) RMS, but the deposition rate is usually very low (typically in the μm/h range) 0-0. Pulsed DC RMS, when the magnetron discharge is usually pulsing in the mid-frequency 10-200 kHz range has been shown as the most promising RMS technique where arc events can be prevented, sufficiently high deposition rate can be reached, high-quality oxide coatings can be deposited and the reactive sputtering process can be stabilised 0-0.

Pulsed RMS operates in metallic, transition and dielectric modes depending on the deposition conditions that depend critically on the characteristics of the pulsed plasma in the vicinity of the magnetron. In order to understand plasma processes taking place in particular deposition modes and effectively control the deposition process, it is necessary to use plasma diagnostics. Plasma diagnostic methods commonly applied in pulsed magnetron systems comprise the Langmuir probe 00, mass spectroscopy 00 and optical emission spectroscopy (OES) 000-0. Since each of these particular methods has some shortcomings, one should combine several of them to obtain more comprehensive information. A combination of mass and OES in case of alumina RMS was performed only at DC RMS 0, but the detailed spectra of plasma composition were not provided and the transition mode was not analysed at all.

In this paper we report plasma characterisation by mass spectroscopy and spatially resolved optical emission spectroscopy in a pulsed DC reactive magnetron sputtering system used for aluminium oxide film fabrication.

2. Experimental details

DC pulsed magnetron discharge was generated in a stainless steel chamber pumped by a diffusion pump down to a pressure of $2 \cdot 10^{-3}$ Pa. The round shape magnetron aluminium target (Al purity of 99,99 %) of 100 mm in diameter was used for sputtering. DC magnetron voltage varied in the interval from 100 to 600 V. A DC power supply Huettinger 3000 combined with a pulse generator MELEC operated at power $P_d = 400$ W, repetition frequency $f = 10$ kHz and a duty cycle of 0.5. The magnetron discharge was maintained in Ar/O₂ reactive atmosphere at a constant pressure of 0.5 Pa being controlled by a throttle valve at the high-vacuum pump gate. Ar flow (Q_{Ar}) was varied from 1 to 16 sccm and O₂ gas flow (Q_{O_2}) was varied from 0 to 8 sccm.

Plasma mass spectroscopy was performed using a mass spectrometer EQP 500 HIDEN Analytical Ltd. Plasma entered the spectrometer through the orifice of 200 μm diameter placed at the racetrack at a distance of 100 mm from the magnetron target. Mass spectra were taken in the range $m/q = 1$ to 100 amu with a resolution of 0.5 amu.

The system for plasma characterisation by optical emission spectroscopy was based on a monochromator Triax iHR550 equipped with a 1200 g/mm or 2400 g/mm grating and with a liquid-nitrogen cooled Symphony CCD camera (2048 x 512 pixels). The OES signal was collected

perpendicularly to the magnetron-substrate axis by a focusing lens and optical fibre. The spectra were taken at the magnetron target and at a distance of 100 mm from it. Spectra were analysed in the wavelength region from 350 to 900 nm with a resolution of 0.05 nm.

3. Results and discussion

Characteristic transition curves for aluminium oxide DC pulsed reactive magnetron sputtering are shown in Fig. 1. In the open loop condition one can clearly see target poisoning and a deep hysteresis preventing us from operation in the desired transition space. A distinct difference in the electrical impedance of the sputtering system operated at dielectric and metallic mode can be observed. This effect was successfully exploited for stabilization of the sputtering process in the transition mode. The sputtering process in the transition mode was stabilized by limitation of the target voltage to a constant level. The transition mode curve displayed in Fig. 1 clearly illustrates that the sputtering conditions can be well stabilized at any point of the transition from the dielectric to the metallic sputtering mode (the target voltage changes from 290 V to 390 V). A stable operation would be even possible regardless of whether the process is started from the metallic or dielectric (poisoned) mode.

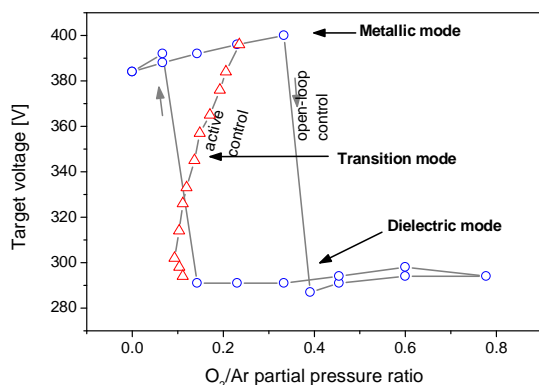


Fig. 1. Voltage transition curves for aluminium oxide reactive magnetron sputtering – dependence of the target voltage on the O_2/Ar partial pressure ratio – displaying the three different sputtering processes (metallic, transition and dielectric).

Adhering to the obtained dependence shown in Fig. 1, we further carried out a detailed measurement of plasma process parameters by combined mass spectroscopy and emission spectroscopy in all metallic, transition and dielectric modes.

3.1 Mass Spectroscopy

The mass spectra reveal the presence of sputtered Al ions and singly ionised species of reactive atmosphere O^+ ($m/q = 16$), O_2^+ ($m/q = 32$), Ar^+ ($m/q = 40$). Doubly

ionised argon atoms Ar^{2+} ($m/q = 20$) also appear in the spectra. Residual traces of hydrogen H and H_2 and water are also detected on the background. The appearance of plasma species and their intensities is commented for each sputtering mode.

In the metallic mode (data not shown here) we observe Al^{2+} ($m/q = 54$), Ar_2^+ ($m/q = 80$), $AlAr^+$ ($m/q = 67$) and AlO ($m/q = 43$) and Al_2O^+ ($m/q = 70$) radicals. The intensity of AlO and Al_2O^+ increases with increasing oxygen/argon flow ratio up to the moment of transition to the dielectric mode (open loop control curve as depicted in Fig. 1), where these spectral lines disappear. We observe O^+ and O_2^+ , but their intensities were low. The intensity of those lines continually increases with increasing oxygen/argon flow ratio.

In the dielectric mode (data not shown here) Al line is barely observed and Al^{2+} line disappears. Oxygen species become dominant in the spectra.

Mass spectra taken *in the transition mode* are displayed in Fig. 2. Detailed spectra of the transition mode were taken at mass spectrometer parameters optimised at mass $M=32$ amu and the plasma energy of -5 eV since at this energy we observed a maximum in the ion energy distribution. We can observe in the mass spectra shown in Fig. 2 and Fig. 4 (displaying in detail the dependence of Al^+ and O^+ ions intensity on the target voltage) that the transition from the dielectric to metallic mode is accompanied by a decreasing number of atomic oxygen ions and an increasing number of aluminium ions. The increase of Al intensity evokes increasing sputtering rate of aluminium target.

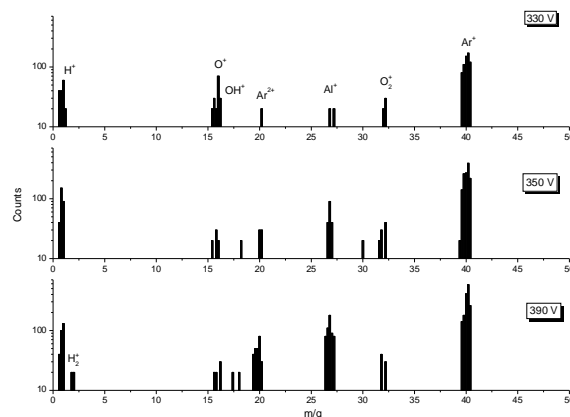


Fig. 2. Mass spectra of plasma of aluminium oxide reactive magnetron sputtering in the transition mode, for three different target voltages: 330 V, 350 V and 390 V.

3.2 Optical Emission Spectroscopy

Characteristic OES spectra of plasma in the transition mode taken in the wavelength regions of 350 – 850 nm are displayed on Fig. 3. The emission lines appearing in the spectra are assigned according 0. Neutral Ar emission lines dominate the OES spectra; however a few weak Ar^+ lines can be also recognized in the spectra. We also detect distinct Al atom emission lines at 394.4 nm, 396.15 nm

and O atom emission triplets at 777.19 nm, 777.42 nm, 777.54 nm and 844.63 nm, 844.64 nm, 844.68 nm. Neither AlO nor O₂ pronounced emission bands were observed in the spectra.

The OES spectra taken *in the transition mode* through the transition from dielectric to metallic mode reveal decreasing intensity of atomic oxygen and increasing intensity of aluminium atoms. This dependence, determined from the spectra taken at the substrate, is shown in Fig. 4 in more detail. A similar tendency of Al⁺ and O⁺ intensity that was derived from mass spectra is noticeable here. Hence, we can suppose that OES intensities in this case reflect concentration of the corresponding plasma species. The OES intensities shown in Fig. 4 were also normalised relative to the Ar line at 750.39 nm because this line seems to be quite convenient for several reasons, as explained further.

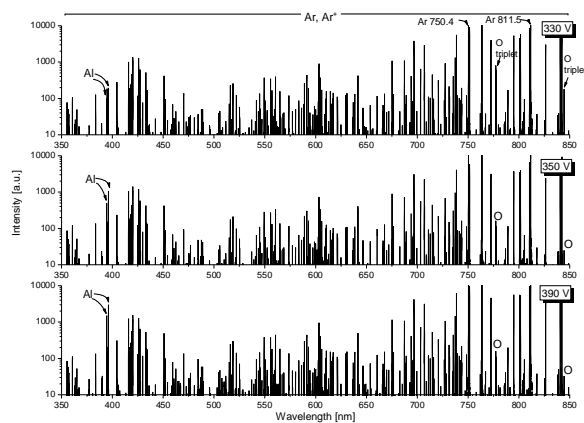


Fig. 3. Optical emission spectra of plasma of aluminium oxide reactive magnetron sputtering in the transition mode, taken at the substrate, for three different target voltages: 330 V, 350 V and 390 V.

The upper levels of Ar (all well above 10 eV) can be populated in different ways, i.e. predominantly by direct electron impact from the ground state (e.g. line at 750.39 nm), from metastable states and from cascades from higher states (e.g. 811.5 nm). The Ar line at 811.5 nm shows the strongest intensity of all lines in the spectra, which is supported by the fact that this line intensity corresponds to the only allowed transition from its upper level. The line at 750.39 nm belongs to transitions terminating in a lower state, which is short-lived (radiative), whereas others can terminate in long-lived (metastable) lower states. Hence the intensity of the 750.39 nm Ar line is assumed to be directly dependent on the number of electrons in the high-energy part of the electron energy distribution function. Since the minimum excitation energy of oxygen atoms lies around 11 eV, we can assume that the same group of electrons (as that in argon case) would excite these states. Therefore we can use the Ar line at 750.39 nm for comparative evaluation of changes in intensities of other species as it is

shown in Fig. 4. However, in the case of aluminium, the minimum excitation energy is much lower (around 3.15 eV). Accordingly, the Al atoms can also be excited by low-energy electrons with energies below 10 eV. Thus, for Al emission intensities, the previous assumption might not be conserved.

The spectra taken at the magnetron target exhibit a similar trend in the dependence of line intensities on the target voltage as that derived from the spectra taken at the substrate. However, intensities of whole spectra are much higher. Ar⁺ lines are well pronounced and O⁺ emission lines (e.g. 441.49 nm and 441.698 nm) appear in the spectra. The presence of excited O⁺ in the vicinity of the target affects the sputtering process since it was reported that the sputter yield of Al is higher for O⁺ than for Ar⁺. The OES spectra suggest higher electron density and temperature that contribute in particular to higher population of excited plasma species in the vicinity of the magnetron. The electron density is also enhanced within the transition mode because of the formation of oxide film at the target, which possesses higher secondary-electron emission coefficient ($\lambda \sim 2-9$) compared to metallic aluminium ($\lambda \sim 1$).

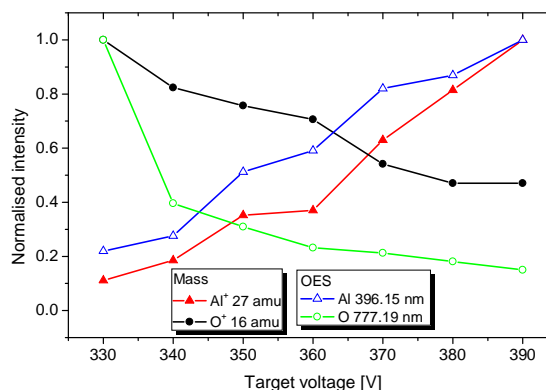


Fig. 4. Intensities of aluminium and oxygen plasma species as function of the target voltage in the transition mode. OES line intensities are also normalized in respect of the intensity of the 750.39 nm Ar line.

4. Conclusions

Plasma in dielectric, transition and metallic deposition modes of pulsed DC reactive magnetron sputtering of aluminium oxide film was characterised by mass and optical emission spectroscopy. Attention was focused on the appearance of O, O₂, Al and AlO species and their corresponding positive ions. Voltage transition curves characterising the deposition modes in the region from 290 V to 400 V were determined. Both mass and emission spectra taken in the transition mode revealed distinct changes in plasma composition in the vicinity of the magnetron target and the substrate. The transition from the dielectric to metallic mode is followed by a decrease of atomic oxygen intensity and an increase of aluminium

intensity. The presence of AIO molecules in the plasma was detected by mass spectroscopy only.

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