Optical emission spectroscopy study on He addition in an Ar/CH_4 reactive DC magnetron discharge aiming for ZrC films deposition

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Argon is the most used process gas in magnetron sputtering deposition processes due to its large atomic mass, inert chemistry, and relatively low cost. However, the choice of sputtering gas may significantly affect the plasma composition, and subsequently the growth and properties of deposited material. In this paper we report on a preliminary OES study of reactive plasma consisting in Ar and CH_4, when He was added into the discharge. It was showed that He addition has a positive effect on methane decomposition in the magnetron discharge. It was obtained an interval of variation of the gas flow rates, for an optimal discharge functioning.

1. Introduction

Plasma discharges in methane or methane–argon gas mixtures are widely used in PVD processes, aiming to coat surfaces with metal carbides [1-3].

In the present study we investigated by optical emission spectroscopy (OES) the excited and ionized species present in a magnetron discharge used for the reactive deposition of ZrC films in a mixture of argon and methane. The aim of this investigation was to study the modification of the plasma due to He addition in the reactive atmosphere.

The direct decomposition of methane using a helium plasma was reported earlier for an RF discharge at high pressures, of about hundreds of Pa [4], although earlier reports indicated that the addition of Ar or He have the same effect on methane decomposition in DBD discharges at atmospheric pressure [5].

The present investigation is based on the assumption that He might determine an increase of the dissociation degree of the methane molecule, and the increase of the ions energy in the plasma, due to Penning ionisation and charge exchange processes in the low pressure magnetron plasma [6, 7].

Therefore, OES was used to study the effects of He addition in a DC magnetron discharge.

2. Experimental details

The UHV deposition system (AJA-ATC-ORION, AJA Inc. USA) is equipped with five 2” confocal magnetrons. A cross-view section of experimental setup is presented schematically in Fig. 1, in order to locate the main items in the discharge chamber and to indicate the plasma emission volume investigated by OES (situated at 150 mm above the cathode's surface). Only one cathode, equipped with a Zr target, was used in this experiment.

The OES analysis was carried out with an HR2000 spectrometer (Ocean Optics, USA). The spectrometer was connected with the vacuum chamber by an optical fibre. The light emitted from the plasma volume located in front of the substrate surface was collected with a collimating device, mounted between the fibre end and the optical quartz window. All the plasma emission spectra were recorded in the interval 200–900 nm using the same spectrometer set-up conditions, in order to exclude any variation related to the optical arrangement.

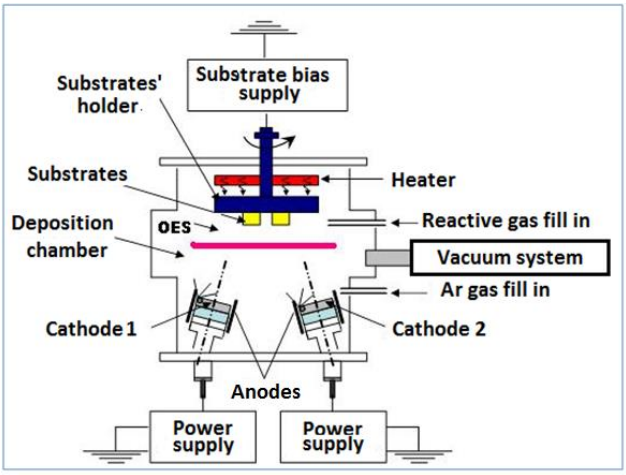

Fig. 1 Schematic representation of the deposition system AJA-ATC-ORION, indicating in magenta the plane where from the OES information was obtained

The base pressure in the system was 2.10^{-5} Pa, and the working pressure was kept constant at 0.67 Pa. The total gas mass flow rate (Q=10 sccm), and the power fed on the magnetron target (DC discharge, P=120 W) were also kept constant. The discharge was running in Ar (aiming for the identification of Ar and Zr lines), Ar+CH_4 and Ar+CH_4+He, respectively.

The intensity evolution of several lines was monitored: Ar, Zr, and those related to the dissociation process of CH_4: H_α (656,1nm 3→2),H_β (486 nm, Balmer 4→2), Hδ (434 nm, Balmer 5→2), Hγ (410 nm, Balmer 6→2), and CH* line (λ = 431.4 nm corresponding to the transition A2Δ→X2Π) for different mass flow rates of Ar, CH_4 and He fed into the discharge.

3. Results and discussions

The typical emission spectra, recorded at different gas mass flow rate ratios and presented in Fig. 2, are suitable for lines identification and for the selection of representative lines to be further used in the investigation.

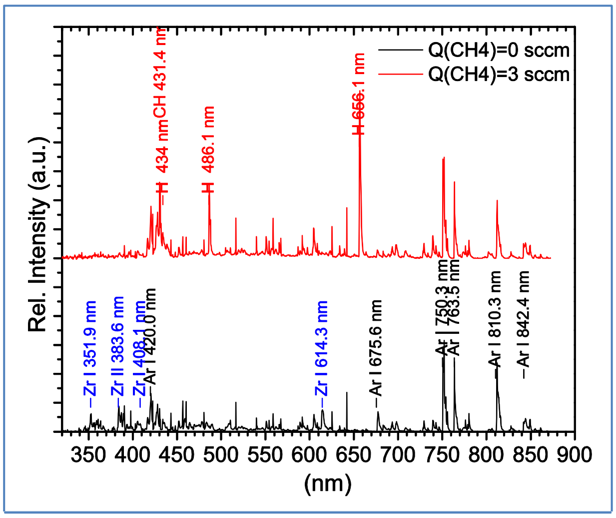

Fig. 2 Emission spectra for two different gas compositions CH_4/(Ar+CH_4): 0/10 and 3/10.

The emission spectrum obtained in a pure Ar discharge is presented in the lower part of Fig. 2, allowing the identification of Ar and Zr lines. The spectrum obtained in a Ar/CH_4 mixture (30% CH_4) is presented in the upper part of the same figure, revealing the presence of H and CH lines, resulting from methane decomposition in plasma. Let us note that only some of the identified lines are marked in Fig. 2, these being the lines used in the investigations carried out in the present study.

The evolution of Ar, Zr, H and CH line intensities are presented in Fig. 3, as a function of CH_4 mass flow rate, Q(CH_4). It can be observed that each type of atom/ion presents a particular evolution, determined by the specific elementary processes which determine the creation and excitation on the investigated radiative levels.

Three different intervals for the discharge functioning were evidenced, marked in Fig. 3:

I. Q(CH_4): 0 – 1.5 sccm. The interval corresponds to the transition from the metallic to the compound regime, in which zirconium carbide starts to cover the target as well as the other surfaces inside the deposition chamber. The metal lines intensities are decreasing, whereas the cathode voltage is increasing, indicating the decrease of the secondary electron emission coefficient of the target surface [8].

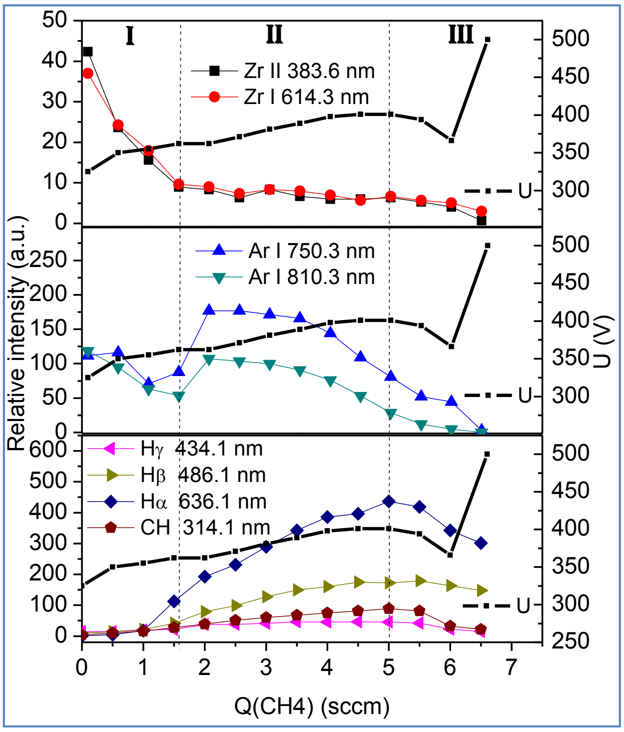

Fig. 3 The evolution of the intensity of some Ar, Zr, H and CH lines vs. Q(CH_4). The evolution of the discharge voltage U is also represented.

II. Q(CH_4): 1.5 – 5 sccm. This interval is corresponding to a fully compound mode, the target being practically totally covered with the reaction product (ZrC). It was observed a further reduction in the intensity of the metal lines, and an increase of the H and CH lines. These lines exhibit their maximum intensity for Q(CH_4) = 5 sccm.

III. Q(CH_4): 5 – 6.5 sccm. The interval corresponds to an intensity decrease for all lines. At the highest mass flow rate value the discharge became unstable, producing frequent arching events that made the deposition process impossible.

These measurements provided preliminary information about different functioning regimes of the magnetron discharge in the presence of the reactive gas. In the following we investigated the effect of He addition in the discharge, aiming for a more efficient CH_4 dissociation. The increase of Q(He) was concomitant with the decrease of Q(Ar), their sum being kept constant at 7 sccm, while Q(CH_4) was fixed at 3 sccm.

The current and voltage variations on Zr target are presented in Fig. 4, for Q(He) variation in the range 0 – 3.5 sccm. It can be observed that the replacement of Ar by He determines only small variations (~3%) of the current and voltage values. It was then concluded that the electrical parameters were not significantly affected by He addition, so that in the following we have investigated the possible volume processes in the plasma discharge.

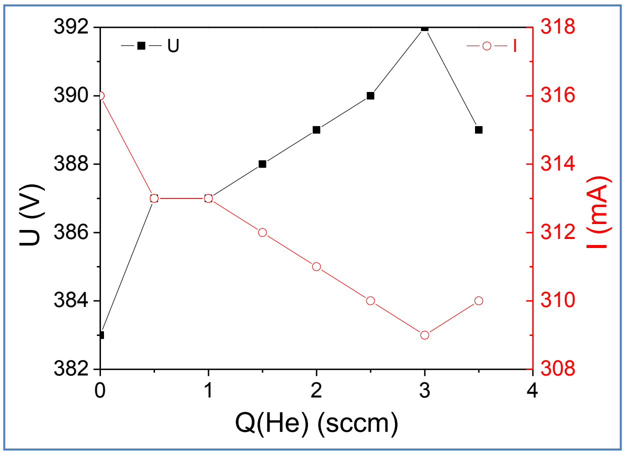

Fig. 4 The evolution of the current and voltage on Zr target vs. Q(He), for Q(CH_4) = 3 sccm.

Fig. 5 shows the evolutions of the selected Ar, Zr, H and CH lines as a function of Q(He), for Q(CH_4) = 3 sccm. As expected, the replacement of Ar by He determined the decrease of the density of Ar and consequent decrease of Ar emission lines. It was also observed the decrease of Zr-I lines, due to the lower sputtering efficiency of He as compared to Ar, and subsequent diminishment of the metallic atoms abundance.

It is also to note an increase of the abundance of Zr ions for Q(He) = 2 sccm, as evidenced by the increase of Zr-II line, indicating the production of more energetic ions and/or electrons in the discharge in the presence of He, as reported for Ne addition in an Ar magnetron discharge [9].

The observed increase of the intensities of H_α (~16%), H_β (~14%), and CH (~12%) lines, indicated a more efficient dissociation of the methane in the presence of He. These facts may be ascribed to the presence of the metastable He atoms and He ions, which can induce an increased production of CH^+_n radicals by Penning ionization and charge exchange reaction, respectively [10]. This effect was up to now reported only for high pressure discharges [4, 11]. At low pressures, it was previously reported the increase of the dissociation of N_2 molecule in a mixture of Ar, N_2 and He [11, 12].

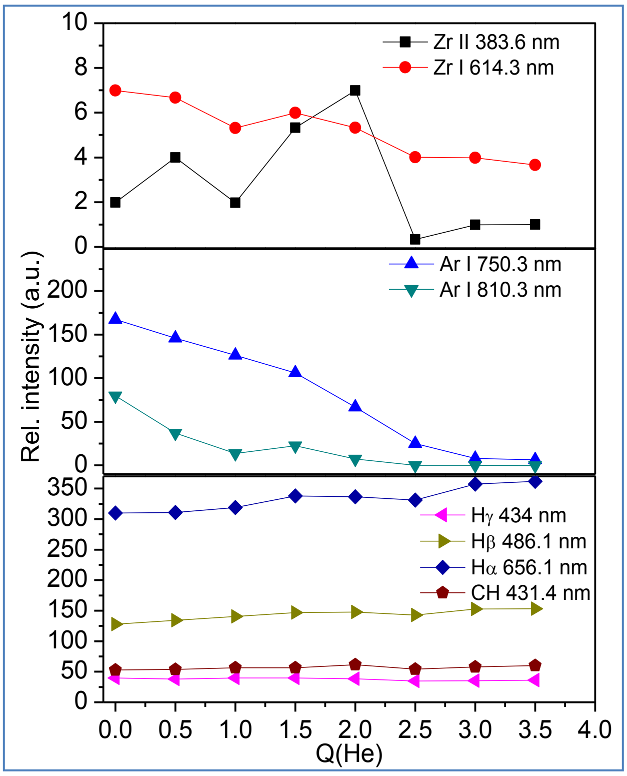

Fig. 5 The evolution of the intensity of the selected Ar, Zr, H and CH lines vs. Q(He), for Q(CH_4) = 3 sccm.

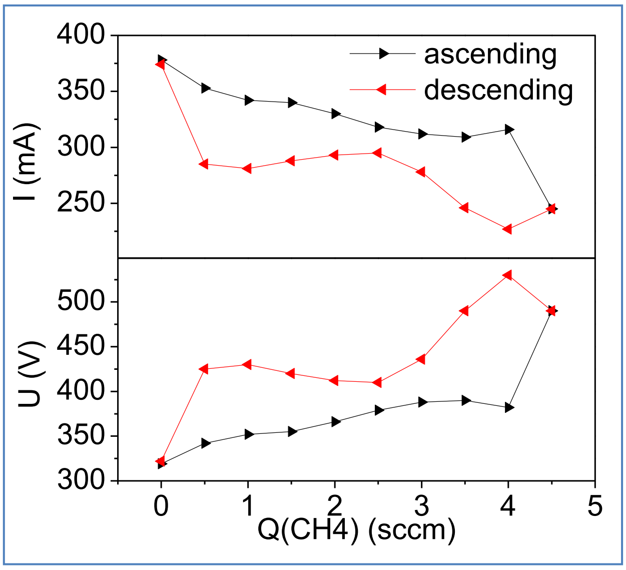

Fig. 6 The evolution of the current intensity and voltage on Zr cathode vs. Q(CH_4), for Q(He) = 3 sccm, showing the presence of the "hysteresis" effect

For the discharge conditions in Fig. 5 the intensity of the metal lines is relatively low, as the discharge is working in the compound mode. Therefore, we studied in the following the "hysteresis" effect, specific for the reactive magnetron discharges in which different process parameters depend on the process "history". For a constant He concentration (Q(He) = 3 sccm), $Q(CH_4)$ was varied in the range 0 – 4.5 sccm, corresponding to a region in which the target is partially covered by the reaction product ZrC.

The current and voltage hysteresis curves are presented in Fig.6, and the hysteresis curves for Ar I, Zr I, H_α and CH lines in Fig. 7. The variation of the electrical parameters of the discharge (Fig. 6) indicates that in the constant power regime, the increase of $Q(CH_4)$ determined the increase of the voltage, in order to compensate the current decrease, due to Zr target contamination.

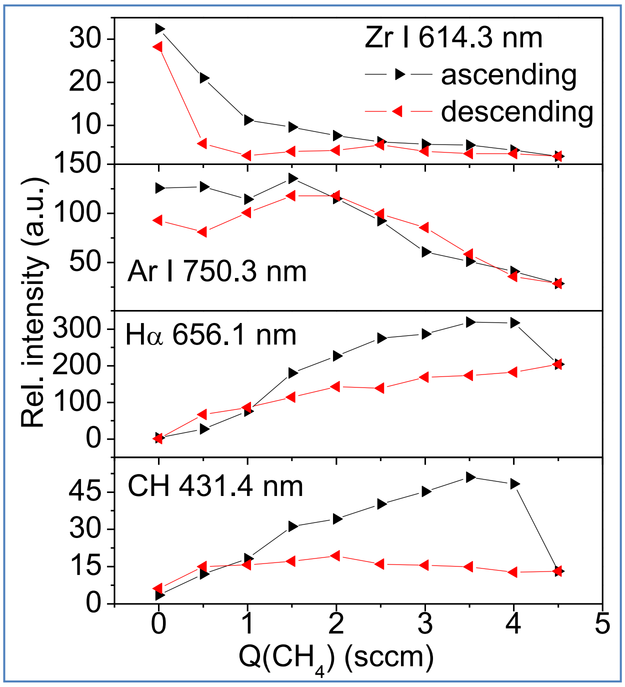

Fig. 7 The evolution of the intensity of Ar I, Zr I, H_α and CH lines vs. $Q(CH_4)$, for a constant Q(He)= 3 sccm.

The Ar line intensity presents a plateau in the range $Q(CH_4)$: 0 – 2 sccm, and a rapid decrease in the next interval $Q(CH_4)$: 2 – 5 sccm. This evolution indicates the presence of some additional processes for the excitation of Ar atoms for low CH_4 concentrations (0 – 2 sccm), processes due to the presence of He which partially compensate the diminished Ar concentration in the gas mixture. Also, the hysteresis effect is almost negligible for this line. The lines ZrI, CH, H_α, and H_β, H_δ (not shown here) presented a marked hysteresis effect.

A peculiarity of the evolution of H and CH lines is that the ascending and the descending curves are intersecting each other for $Q(CH_4) \leq 1$. The position of this intersection points to the closing of the hysteresis loop, indicating a steady-state functioning point which is not sensible either to the increase or the decrease of the methane flow.

4. Conclusions

Summarizing, the analyse of the optical emission spectroscopy data permitted to find an optimum interval of deposition, in terms of the flux of the discharge gases, as follows:

i. the methane mass flow should not be higher that the mass flow of (Ar+He);

ii. the addition of He has a positive impact on the methane decomposition;

iii. an optimum value for the He dilution in Ar was determined, for which an increase of Zr ions abundance was obtained.

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5. References

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