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Optical Diagnostics of RF Argon and Xenon Magnetron Discharges

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Abstract. — A comparison of magnetron discharges in Ar and Xe gases with Al and BN targets has shown that a similar electron kinetic is producing about the same quantity of Ar and Xe metastable atoms: $(1-3) \times 10^{10}$ cm⁻³ at gas pressures of 25 and 100 mTorr and RF powers, W, from 5 to 50 watts. The electron density is varying as $W^{\frac{1}{2}}$ in the two gases. The sputtering yields of Al and BN targets are lower in Xe than in Ar, by factors of 1.1–1.2 for Al and of 3 for BN.

Résumé. — La comparaison de décharges magnétrons dans des gaz d'argon et de xénon, avec des cibles en Al et BN indique que des quantités équivalentes d'argon et de xénon métastables sont produites, à savoir $(1-3) \times 10^{10}$ cm⁻³ à des pressions de 25 et 100 mTorr et des puissances RF, W, de 5 à 50 watts. La densité électronique varie comme $W^{\frac{1}{2}}$ dans les deux cas. Les taux de pulvérisation de cibles d'Al et de BN sont plus faibles dans le Xe que dans l'Ar, d'un facteur 1, 1-1, 2 pour Al et 3 pour BN.

1. Introduction

Magnetron sputtering is widely used for thin film deposition, in various technological fields [1]. Despite the large number of applications, only a few studies are devoted to the diagnostic of such magnetised plasmas. Results from emission and absorption spectroscopy of argon magnetron discharges with an aluminium target have been recently reported [2,3]. Variations of Ar, Ar⁺ and Al line intensities, of Ar (${}^{3}P_{2}$, ${}^{3}P_{0}$) metastable and of Ar (${}^{3}P_{1}$, ${}^{1}P_{1}$) resonant atom densities and of Al ground state densities have been obtained by changing numerous parameters such as the target thickness, gas discharge pressure, electric power and distance from the target.

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Fig. 1. — Experimental set-up of magnetron discharge with optical arrangement for emission and resonant absorption spectroscopy. 1. gas inlet; 2. optical fiber; 3. spectrometer; 4. photomultiplier;
5. PC control; 6. matching network; 7. turbomolecular pump; 8. optical source; 9. vernier; 10 cooling;
11 copper conductor; 12. RF generator - 13.56 MHz.

Magnetron discharges in Xe are presently of great interest to study the sputtering of BN ceramics in Xe ion sources for Stationary Plasma Thrusters (SPT) [4].

In the present work, the Xe radiative states and the Xe metastable atoms in magnetron Xe discharges are studied by emission and absorption spectroscopy in a similar way as for argon. The results are analysed for Al and BN target cathodes.

2. Experimental Setup

The experimental setup has been detailed elsewhere [2,3]. It is reproduced in Figure 1. The magnetron cathode can be made in aluminium (thickness 5 mm) or in a BN ceramic (thickness 3 mm) of diameters 33 mm. The cathode is located inside a stainless steel chamber at the ground potential which acts as the anode of magnetron discharge. Also the cathode is surrounded by a guard ring at ground potential.

On the cathode surface, the magnetic induction is such that the electrons are confined in the plasma at about 1 cm in front of the surface. After a base pressure lower than 10^{-6} Torr is achieved, the Ar or Xe gas is introduced to maintain a pressure ranging from 3 to 150 mTorr. The 13.56 MHz RF power can vary from 1 to 50 watts.

As shown in Figure 1, the plasma is analysed by emission spectroscopy *via* a quartz optical fiber bundle (diameter 1 mm). The optical absorption is performed with an optical source which can be a Philips Ar or Xe lamp or a Perkin-Elmer lamp.

Two optical lenses (L_1 and L_2 in Fig.1) focused the source light beam and collected the plasma light on the optical fiber with a spatial resolution which is estimated to be 2 mm for emission and absorption measurements. The spectral line intensities in emission and absorption



Fig. 2. — Xe energy levels.

are recorded by means of a Jobin-Yvon HR 1000 spectrometer with an Hamamatsu 166 UH photomultiplier for the Ar and Al lines and by means of a chromex 2501 S monochromator with a CCD camera for the Xe lines.

3. Density of Xe (³P₂) Metastable Atoms

The Xe energy levels are reproduced in Figure 2. The first excited level configuration $(5p^56s)$ at about 6 eV contains two metastable $({}^{3}P_{2}, {}^{3}P_{0})$ and two resonant $({}^{3}P_{1}, {}^{1}P_{1})$ levels.

The density of Xe $({}^{3}P_{2})$ can be determined by the resonant absorption method of Mitchel-Zemansky as it is detailed in references [2] and [3]. The absorption coefficient A_{L} of a spectral line along the absorption length is given by:

$$A_L = 1 - I_t / I_0 \tag{1}$$

where I_t and I_0 are the transmitted and incident intensity of the chosen Xe (6p-6s) line.

In the present absorption measurements, I_0 is recorded without plasma, I_t is deduced by subtracting the total intensity (I_{t+p}) of both transmitted from the lamp (I_t) and emitted from the plasma (I_p) and the I_p plasma intensity alone as the lamp is masked.

Table I. —	Oscillator	strengths	for	the	most	$\mathit{intense}$	spectral	lines	of	the	Xe	$(5p^5$	6s –	5p ⁵	'6p)
transitions.							•								

Transitions	${}^{1}S_{5} - {}^{2}P_{6}$	$^{1}\mathrm{S}_{4}\mathrm{-}^{2}\mathrm{P}_{5}$	${}^{1}S_{2} - {}^{2}P_{3}$	${}^{1}S_{5} - {}^{2}P_{7}$	$^{1}S_{5}-^{2}P_{8}$	${}^{1}\mathrm{S}_{5} {-}^{2}\mathrm{P}_{10}$	${}^{1}\mathrm{S}_{4} {-}^{2}\mathrm{P}_{9}$
λ (nm)	823.2	828	834.7	840.1	881.9	980	992.3
Oscillator strengths	0.227	0.103	0.337	0.0146	0.485	0.207	0.428
(5,6)							

 A_L is related to the optical thickness $k_{\sigma_0}L$, which is given by the following equation:

$$k_{\sigma_0}L = 8.25 \times 10^{-13} \frac{f}{\delta \sigma_{1/2}^{\rm P}} L \ n_{Xe}({}^3{\rm P}_2) \tag{2}$$

(*f*-oscillator strength of the absorbing levels, whose the Doppler broadening in the plasma is $\delta \sigma_{1/2}^{\rm P}$, *L*-absorption length and $n_{\rm Xe}({}^{\rm 3}{\rm P}_2)$, density of metastable atoms), via the following factor:

$$\alpha = \frac{\delta \sigma_{1/2}^{\rm S}}{\delta \sigma_{1/2}^{\rm P}} \tag{3}$$

 $(\delta \sigma_{1/2}^{S} \text{ source line broadening})$. k_{σ_0} and $\delta \sigma_{1/2}$ are in cm⁻¹, L is in cm and n in cm⁻³. f is dimensionless.

The oscillator strengths for several spectral lines originating from the Xe $({}^{3}P_{2}, {}^{3}P_{1}, {}^{1}P_{1})$ levels are reproduced in Table I following references [5] and [6].

We have checked the broadenings of these spectral lines emitted from the Philips lamp by assuming, first a Doppler broadening at T = 300 K and second, a self broadening for a density of Xe (³P₂) metastables atoms between 10¹¹ and 10¹² cm⁻³ in the lamp with a radius R = 1 cm.

For a Doppler broadening $(\delta \sigma_{1/2}^D)$ of a spectral line (gaussian shape), the self-broadening $\delta \sigma_{1/2}^S$ can be calculated by using the following equation:

$$\frac{\delta \sigma_{1/2}^{\rm S}}{\delta \sigma_{1/2}^{\rm D}} = \left[\frac{1}{\ln 2} \ln \left(\frac{k_{\sigma_0} R}{\ln \left(\frac{2}{1 + \exp{-k_{\sigma_0} R}} \right)} \right) \right]^{1/2} \tag{4}$$

where k_{σ_0} is calculated with equation (2).

The Xe I 823.16 nm (6p-6s) line is chosen to determine the Xe (³P₂) metastable density. The absorption measurements are performed outside the magnetized plasma where we assume the gas to be at room temperature. Consequently, the α factor is given by equation (4) where $\delta \sigma_{1/2}^{\rm D} = \delta \sigma_{1/2}^{\rm P}$. It has been found $\alpha_{823} = 1.2-2.1$.

The L absorption length has been estimated by measuring A_L versus the z-axial distance above the magnetron cathode [2]. It has been found that A_L decreases versus z. For p = 25 mTorr, A_L is half its maximum value, A_L^M , for $z(A_L^M/2) = 3 \pm 1 \text{ cm}$, for an RF power of 50 W. By assuming a spherical plasma, it is determined $L = d_c + 2z(A_L^M/2)$ where $d_c = 3.3 \text{ cm}$ is the cathode diameter. It is obtained L = 10 cm at 25 mTorr, 50 W and L = 8 cm at 100 mTorr, 50 W. With Xe, the absorption length is smaller than with Ar where L = 16 cm and 12 cm was found at 25 and 100 mTorr, 50 W respectively.

With an Al cathode of thickness 5 mm, it has been determined the Xe $({}^{3}P_{2})$ values as reported in Table II, for two gas pressure (25 and 100 mTorr), and at a distance of 1.5 cm

Xe $({}^{3}\mathrm{P}_{2})/p$ (mTorr)	25	100
Al cathode A_L	0.54	0.5
$n(10^{10} { m cm}^{-3})$	1.2 - 2.6	1.3 - 2.6
BN cathode A_L	0.506	0.41
$n(10^{10}~{ m cm^{-3}})$	1.1-2.2	1-1.8

Table II. — Xe $({}^{3}P_{2})$ densities for two gas pressure and the Al and BN cathodes, d = 1.5 cm.

above the cathode. It is also reported in Table II, the Xe $({}^{3}P_{2})$ density values obtained with a BN ceramic cathode, in the same conditions as with the Al cathode.

It has been found constant values of Xe $({}^{3}P_{2})$ densities in the RF power range from 5 to 50 W. It is concluded that the Xe $({}^{3}P_{2})$ atoms have reached saturated values as well as the Ar $({}^{3}P_{2})$ atoms [2] do, thus indicating that these metastables are mainly produced and destroyed by electron collisions. As previously discussed [2], the electron density disappears in the kinetic equation of metastable atom density, explaining its nearly constant value when W increases.

Thus it can be concluded from Table II that the Xe $({}^{3}P_{2})$ metastable densities are not really affected as the cathode material is Al or BN.

With argon discharges, in similar experimental conditions (25-100 mTorr, 5-50 watts), distances 1–3 cm from the Al cathode), it has been found [2] [Ar $({}^{3}P_{2})$] = $(3-6) \times 10^{10}$ cm⁻³ at 25 mTorr, and [Ar $({}^{3}P_{2})$] = $(2-3) \times 10^{10}$ cm⁻³ at 100 mTorr.

About same values of metastable densities are then obtained in Ar and Xe discharge with Al cathodes.

4. Intensity of Radiative Species (Xenon and Sputtered Atoms)

Intensity of Xenon and sputtered atom lines have been recorded at 1 mm above the cathode, at the maximum of the negative glow. The spectral line intensity $I(\lambda_{if})$ is related to the radiative state density n_i by

$$I(\lambda_{\rm if}) = c(\lambda_{\rm if})n_{\rm i}A_{\rm if} \tag{5}$$

where i and f are the initial and final states, $c(\lambda_{if})$ is the spectral response of the spectrometer and A_{if} the radiative frequency. The radiative state density depends on the electron density n_e as it follows:

$$n_i = \frac{n_0 n_e C^i}{\sum_{\rm f} A_{\rm if} + n_e C_{\rm i}}$$

where C^{i} and C_{i} are the production and destruction rates by electron collisions respectively and n_{0} the neutral gas density.

The radiative frequencies are about 10^7 s^{-1} and C_1 is of the order $10^{-6} - 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. In the case of magnetron discharges $n_e < 10^{12} \text{ cm}^{-3}$, thus the spectral line intensity is given by:

$$I(\lambda_{\rm if}) = K_{\rm if} n_0 n_{\rm e} C^{\rm i} \tag{6}$$

with

$$K_{
m if} = C(\lambda_{
m if}) rac{A_{
m if}}{\displaystyle{\sum_{
m f}}} A_{
m if}$$



Fig. 3. — Variations of ln I versus ln W of Xe I 840.9 nm and Al I 396.1 nm lines at 25 and 100 mTorr.

Variations of $\ln I_{\lambda}$ versus $\ln W$ are reproduced in Figure 3 for the Al396.1 nm and Xe 840.9 nm lines at the maximum of negative glow (1 mm). It is deduced $I_{\lambda} = W^{\beta}$ variations with $\beta = 0.5 (\pm 0.03)$ for the Xe line and $\beta = 1.9 (\pm 0.5)$ for the Al line. In the case of argon, it was also found [2] a mean β value of 0.5 for the argon lines when the excitation of radiative states is by direct electron collisions on the Ar ground state.

Then at a given Xe pressure, it can be deduced from equation (7) that $I_{\lambda}(\text{Xe}) \sim n_{\text{e}}$, with $n_{\text{e}} \sim W^{0.5}$ in a similar way as for Ar magnetron discharges. Such a result confirms that the Xe and Ar discharges have a similar electron kinetics.

The β value for the Al intensity ($\beta = 1.9$) is somewhat higher in Xe than in Ar where $\beta = 1.3 - 1.6$. As discussed for argon discharges [2–7], the Al intensity is proportional to the sputtering ion density and to the electron density and to the γ_{Al} sputtering coefficient. As n_{Ar^+} or $n_{Xe^+} \approx n_e$, it can be written:

$$I_{\lambda}(\mathrm{Al}) \sim \gamma_{\mathrm{Al}} n_{\mathrm{e}}^2$$
 (7)

(8) With $n_{\rm e} \sim W^{1/2}$, it is deduced $\gamma_{\rm Al}({\rm Xe}) \sim W^{0.9}$ (to compare with $\gamma_{\rm Al}({\rm Ar}) \sim W^{0.3-0.6}$). The variation of $\gamma_{\rm Al}$ with W arises from the fact that, when W increases, the cathode potential increases. The ion energy and hence the sputtering coefficient increase with increasing W.

The ln *I versus lnW* variations of B, $\lambda = 249.7$ nm and Ar, $\lambda = 750.4$ nm, 451 nm spectral lines at the maximum of negative glow (1 mm) are reproduced in Figure 4 for the 100 and 25 mTorr Ar gas pressures. The β_{Ar} values are in the same way as previously determined with an Al target: $\beta_{Ar} = 0.5 (\pm 0.2)$ [2]. The β_{B} value of 2.1 can be related (see Eq. (8) for the B line) to γ_{B} (Ar) $\sim W^{1.1}$ which is about twice $\gamma_{Al}(Ar) \sim W^{0.3-0.6}$.



Fig. 4. — Variations of $\ln I$ versus $\ln W$ of Ar I 451 nm, 750.4 nm and B I 249.7 nm lines at 25 and 100 mTorr.

Table III. — Variations of the intensity ratio $r = I_{Al(Xe)}/I_{Al(Ar)}$ of Al I 396.1 nm versus the RF power in Xe and Ar discharges.

$W_{\rm RF}$ (Watts)	5	10	20	50
$r 25 \mathrm{mTorr}$	0.6	0.8	0.86	0.91
$r 100 \mathrm{mTorr}$	0.93	0.74	0.81	

Now, if the Al I 396.1 nm intensity is compared in the two Ar and Xe discharge, it is found the results as reproduced in Table III for the two gas pressures: 25 and 100 mTorr and a RF power between 5 and 50 W. It is deduced from Table III that the Al line intensity is 10 to 20% lower in Xe than in Ar discharges.

With the BN ceramic cathode, the B, $\lambda = 249.7$ nm line has been detected at 1 mm above the cathode. It has been found a weak intensity of the B line in Xe discharge, largely smaller than in Ar discharge although the bias voltage is higher in Xe ($V_{\rm b} = -590$ V in Xe compared to $V_{\rm b} = -550$ V in argon). At 25 mTorr - 50 W, the ratio $r = I_{\rm B(Xe)}/I_{\rm B(Ar)}$ is equal to 0.27.

Altogether, it is concluded that the Xe^+ ions have a sputtering rate lower than the Ar^+ ions, by a factor 0.8-0.9 for the Al target and as low than 0.3 for BN target.

5. Conclusions

Magnetron discharges in Ar and Xe are working with similar electron kinetics. In the same conditions of pressure, power and with two cathode targets: Al and BN, it has been found about the same Ar and Xe metastable atom densities: $(1-3) \times 10^{10}$ cm⁻³ and the same electron density variations with the discharge power: $n_e \sim W^{0.5}$. As it concerns the sputtering yields of Al and BN targets lower values have been determined for Xe as for Ar, a factor of 1.1 to 1.2 with Al, dropping to about 3 with BN. It can be concluded that, for BN targets, sputtering with Xe is less effective than with Ar

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