Collisional Radiative Model of a HIPIMS discharge and comparison with time dependent Optical Emission Spectroscopic diagnostic

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The analysis of the HIPIMS discharge working with a Copper cathode in Argon was developed through Optical Emission Spectroscopy (OES) and conducted in parallel by the advancement of the time dependant Collisional Radiative Model (CRM). The goal was to interpret the temporal evolution of the HIPIMS discharge on the basis of the OBELIX code adapted for the actual experiment. This model includes the most important physical processes which permit to follow the discharge kinetics. Experimental data obtained through Optical Emission Spectroscopy are used in parallel to the CRM occurring in the discharge to evidence the key physical – chemical processes which control the time evolution of the discharge.

1. Introduction

High Power Impulse Magnetron Sputtering (HIPIMS) plasmas are now extensively studied in order to improve the quality of deposited thin films in terms of density, adhesion and wear resistance. In parallel to the analysis of deposited thin films it is essential to optimize the process for instance in terms of deposition rate, composition of the film and limitation of self-sputtering.

One route towards better understanding and optimisation of the sputtering process is the plasma modelling. The most important part to be considered in the model corresponds to the magnetized region in front of the cathode. There, due to the presence of a magnetic field nearly parallel to the cathode surface biased to a negative voltage at a few hundred volts, electrons are efficiently confined along by the magnetic field in the so-called negative glow. In this region, collisions of electrons with the buffer gas and sputtered metallic species produce efficient ionization. Ions which are formed impact the cathode surface inducing sputtering of metallic species and, at the same time, the emission of secondary electrons.

A realistic model must include, as far as possible, the main physical/chemical processes involving production and loss of species at the cathode and in negative glow region. To do this, it is necessary to predict simultaneously mean temporal electron densities and their energy distribution but also incoming and out coming fluxes of species of the negative glow region (electrons, Ar and sputtered ions, neutral metallic species …).

Electrons emitted at the cathode through secondary emission are accelerated approximately to eV_d in the cathode sheath, producing excitation and ionization of atoms, radicals or molecules, mainly in the magnetized region. The energy degradation of energetic electrons lead to the formation of a continuous electron energy distribution function (eedf) extending till eV_d and which is by far, non-Maxwellian. The eedf evolves quite fast depending upon the pressure and needs to be determined all along time, particularly in the case of HIPIMS plasma due to the quite fast voltage evolution.

Collisions of energetic electrons with heavy particles (atoms and molecules) produce excitation, leading generally to the emission of radiation. The amount of radiation gives information about the evolution of radiative species formed within the plasma and, in particular, for the respective densities of metallic and buffer gas neutral and ionic species, but it is also intrinsically related to the eedf and the density of plasma electrons. By comparing the spectral emission intensities, which can be registered by optical emission spectroscopy (OES), with relative densities of excites states resulted from the model one can validate the results of a model adapted for a specific discharge configuration. Therefore, a specific 0D Collisional-Radiative Model (CRM), called OBELIX (Orsay Boltzamnn equation for ELectrons coupled with Ionization and EXcited states kinetics) devoted to the HIPIMS magnetron discharge working in Argon with a copper cathode, was developed, in order to compare and interpret experimental results obtained through Optical Emission Spectroscopy (OES).

2. The Collisional Radiative Model

Briefly, OBELIX needs to define the most important processes which are taken into account.

Due to the low pressure conditions, electrons emitted at the cathode, through secondary emission, gain an important energy of some hundreds of eV in the cathode sheath; then they are trapped by the magnetic field region and deposit a great part of their energy through mainly ionization and excitation of atoms or molecules. So we have to deal with a cascade of electronic collisions with heavy particles. The model is based on the Boltzmann equation [1] which can be written as follows

$$\frac{\delta n(\varepsilon,t)}{\delta t} = \frac{\delta J_{e-n}(\varepsilon)}{\delta t} + \frac{\delta J_{e-e}(\varepsilon)}{\delta t} + K_{ion} + K_{exc} + L_D(\varepsilon) + S(\varepsilon)$$

in which $n(\varepsilon,t)$ is the time dependant of electron energy distribution function. In this equation ε is the electron energy. In the RHS of this equation takes account of the transfer of electrons in the energy space due respectively to elastic collisions with neutral atoms or molecules, e-e Coulomb collisions, ionisation processes, excitation and de-excitation (super-elastic collisions) of atoms with electrons, loss of electrons through diffusion and, finally a source of electrons injected in the discharge. This last term in the RHS of Eq 1 correspond to the injection of new born electrons emitted at the cathode through secondary emission. This source term *S(ε)* corresponds to the flux of electrons entering per second and per unit volume $\boldsymbol{V_p}$ which corresponds to the negative glow of the discharge.

$$S(\varepsilon) = \frac{J_{es}}{e}\frac{G(\varepsilon)}{V_p}$$

G(ε) is a Gaussian function centered at the energy eV_d assuming that electrons acquire this energy of the order eV_d when crossing the cathode sheath towards the negative glow where they are confined by the magnetic field.

OBELIX includes the main states of Argon and Copper levels which play a major role in the kinetics of the plasma. The main neutral excited states and corresponding radiative transitions for Ar are taken from REF [1] and those for Cu from REF [2].

However, one must take care of the influence of self absorption of radiation; this self absorption can be calculated which permits to give access to more reliable relative species density by making correction of the real emission and therefore to relative species densities of the low emitting excited species.

Concerning losses from the negative glow HiPIMS requires also consider inter-diffusion processes between excited neutrals and ions formed in the negative glow with the buffer gas, known also as 'gas rarefaction'. Due to relatively low gas pressure in the discharge chamber, the exchange of species through diffusion processes between the magnetized negative glow and the non-ionized region of the discharge is important.

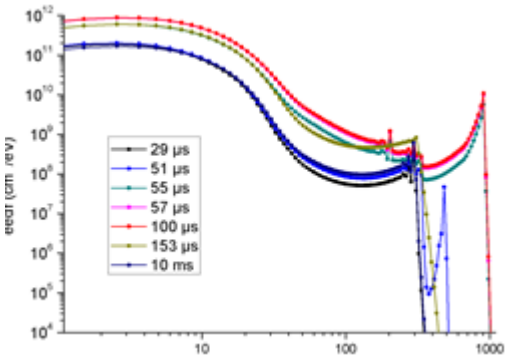

Figure 1. Calculated characteristic eedf at different times of the discharge.

In addition, OBELIX treats the transfer of excitation and ionization between states of the buffer gas (Argon) to sputtered atoms, which are also non-maxwellian.

The typical result of eedf shapes at different moments during the pulse are shown in Fig. 1, as solution of Boltzmann equation written above.

3. Experiment

In this work a home-made pulsed power supply has been used, comprising the following modules: resonant capacitor charger, high power pulser, driving generator, pre-ionizer bias supply and arc handling module. The frequency and pulse width are linearly adjustable in the ranges 1–100 Hz and 50–150 µs respectively. The pre-ionizer bias module is a 5 mA–100 mA constant current power supply and 1000 V in open circuit. The magnetron discharge, with a 2 inch diameter Copper target, was operated with DC pre-ionization, in order to ensure a steady state plasma regime before the high power delivered during the pulse.

Hence, the original version of CRM, detailed in REF [1], can be used for the pre-ionization phase and the new version OBELIX deals with the time-dependency at higher powers.

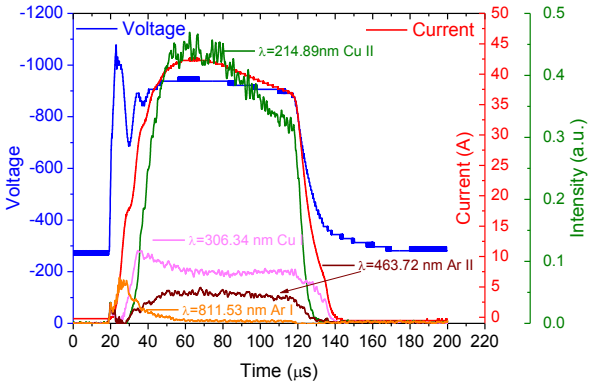

Figure 2. Typical time evolution of selected emission lines during the 100 μs high power pulse, on a Cu target in Ar gas

From the emission spectrum a number of emission lines belonging to both metal and gas lines (neutrals and ions) were chosen. Their time evolution was monitored, to show their behavior during the high power pulse.

In figure 2 the evolution of selected emission lines is represented during the pulse, along with the current and voltage waveforms. Some specific features for each type of atom/ion can be observed, as follows: the metal lines are roughly following the current shape and they are shifted in time with respect to the start of the pulse; the Ar atom line increases simultaneously with current, but has an abrupt decrease after only 10-20 microseconds later.

4. Model-Experiment comparison

The direct comparison between the model and experimental results is possible only if some experimental parameters are used as input into the model. The plasma driving parameter, triggering the pulse behaviour, is the applied voltage onto the cathode. A numerical approximation was employed, to give a voltage shape close to the one measured experimentally. In the upper part of figure 3 both experimental voltage and the one introduced into the model are represented. One can see that most of the features of the experimental curve were reproduced in the model.

The value of the voltage however was reduced to 80% in the model as compared with the experiment. This takes into account the fact the electrons gain energy mainly form the cathode fall, which is typically 80% from the applied voltage.

Let us note that the main difference with respect to Ionization Region Model (IRM) [3], is that OBELIX self-consistently calculate the discharge current to the cathode as an output of the code, while IRM need the total power as input, namely the voltage and the current waveforms during the pulse.

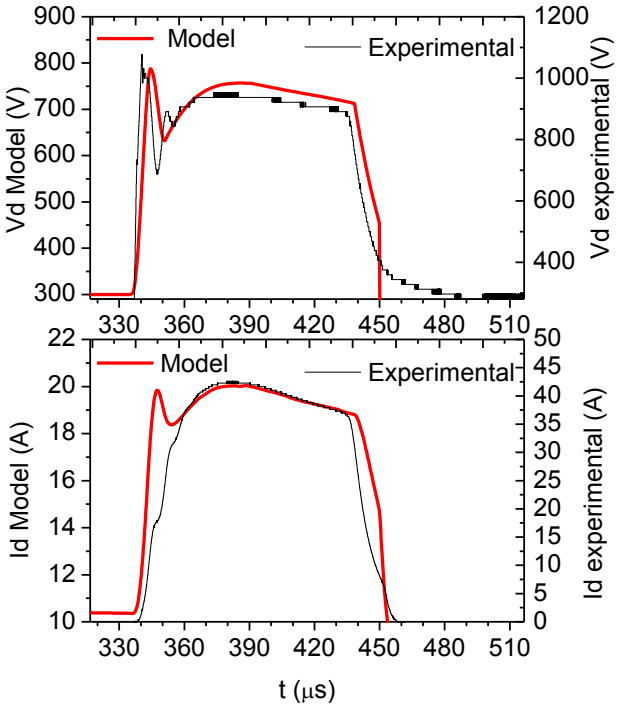

Figure.3 Voltage and current evolution during the pulse, measured in experimental conditions (black curves) and used in the CRM (red curves).

Hence, the calculated current waveform can be compared to the experimental one, as represented in figure 3 (bottom). The very good agreement between these two macroscopic parameters are taken as a strong indication of the strength of our model. Beyond the temporal behaviour of electrical parameters (voltage and current), OBELIX calculations permit a direct comparison of model and experimental OES results.

The link between the OBELIX and OES can be made by comparing, respectively, the relative density of the excited level with the emission intensity of one specific line, emitted by the same level. Such a comparison is made in figure 4 for Ar emission line at 811 nm, in relation with the Ar2p9 excited level, calculated by OBELIX. One can see a good correlation between the two, with an initial increase at the beginning of the pulse followed by an exponential-like decay towards the end of the pulse. This proves that the main production and loss mechanisms, concerning the Ar gas excitation, are well taken into account in the present model. Moreover, OBELIX follows quite precisely the temporal evolution of the excited Ar level, at a time scale of tens of microseconds or less.

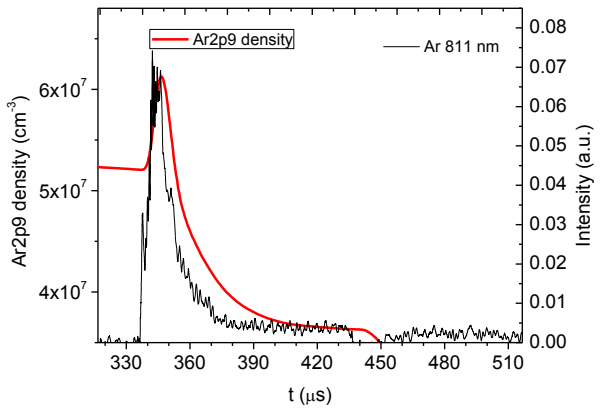

Figure 4. Direct comparison of Ar2p9 level density in the model and Ar 811 nm emission line in the experiment.

As for the metal excited states the comparison is made for Cu4p'D_J excited level (OBELIX), responsible of the 306 nm emission line. The model and experimental results are presented in figure 5. For the sputtered species, a slight shift is visible at the beginning of the pulse, corresponding to a delayed emission in the experiment. This is related to the fact that the synchronization, the beginning of the pulse, is considered to be the increase of the voltage, and not of the current. The line intensity specific to metal atoms is directly related with the current intensity, which is slightly shifted in the experiment (see also figure 3). This apparent discrepancy is therefore only related to this current intensity shift. On the other hand the overall shape of the waveform (Fig. 5) looks similar. First, there is a rapid increase, synchronous with the current increase, followed by a moderate decrease and a plateau towards the end of the pulse. Generally, both shapes obtained from modelling and experiment follows roughly the current intensity.

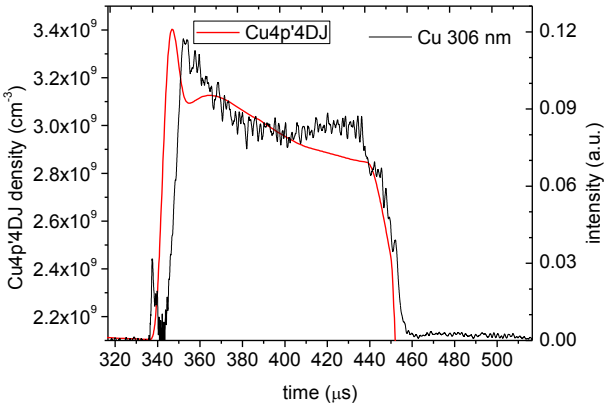

Figure 5. Direct comparison of Cu4p'D_J level density in the model and Cu 306 nm emission line in the experiment.

5. Conclusions

The development of a CRM model – OBELIX – adapted for temporal description of the HiPIMS process was performed. OBELIX takes into account the kinetics of Cu sputtering vapour in an argon plasma, and uses an important number of excited states for both species, along with the most relevant production and loss mechanisms. The direct comparison with OES of a similar experimental system is considered the first validation and improvement of the current version of the model, in terms of temporal behaviour. Moreover, it is proved that the relevant input parameter is the discharge voltage, the current being self-consistently obtained from the model. Further development will be performed to include: geometrical constrains, different pulse shapes, exact shape of external electrical parameters (current, voltage), other relevant processes, etc.

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