First-principles simulation of optical emission spectra for low-pressure argon plasmas and its experimental validation

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Abstract: First-principles simulation of optical emission spectroscopy (OES) for low-pressure radio-frequency-driven capacitively-coupled argon plasmas is performed using a one-dimensional particle-in-cell/Monte Carlo collision (PIC/MCC) code coupled with a global collisional radiative model (CRM) model. Comparison of calculated intensities with experimentally-observed OES data show good agreement up to 20 Pa. Above 20 Pa, the processes involving metastable atoms are found to play a significant role.

Keywords: OES, simulations, argon, PIC/MCC, CRM

1. Introduction

Optical Emission Spectroscopy (OES) is a widely-used diagnostic tool to characterize real-time plasma conditions due to its simplicity and non-invasiveness. Due to the wealth of information contained in the spectra, it is often used to characterize the chemical composition of the plasma and check for impurities. Relating the OES data to plasma parameters such as the electron density (n_e), electron temperature (T_e) and the density of excited states, however, is not an easy task. A collisional radiative model (CRM) is often used to determine the n_e-T_e combination that best fits the experimental OES intensities [1-3]. The alternative, namely the use of first-principles plasma simulations to model the plasma parameters and the corresponding OES line intensities has not yet been comprehensively studied. This approach would enable the use of neural networks and artificial intelligence to aid the diagnostics of plasmas. The first step along this path is the check for self-consistency with the experimental results.

Therefore, in this work, first-principles simulation using a one-dimensional particle-in-cell/Monte Carlo collision (PIC/MCC) code coupled with a global collisional radiative model (CRM) model is performed to simulate the argon (Ar) spectral line intensities from corresponding plasma parameters. A unidirectional coupling (PIC+CRM) between the two simulation methods is implemented by using the electron density and EEDF calculated from the PIC/MCC simulation method as input parameters to the CRM. The resulting computed intensities are then compared to the intensities measured using OES.

2. Experimental Set-up

The experiments were performed in a geometrically symmetric capacitively-coupled plasma (CCP) source such that the experimental conditions are compatible with 1D PIC/MCC simulation. The argon RF plasma was enclosed inside a cylindrical quartz chamber wall. The set-up involves symmetric parallel-plate metal electrodes having a gap distance of 4 cm, with each electrode having a radius of 7.1 cm. The upper electrode was powered by a 13.56 MHz generator which was coupled to the plasma system through a matching network. The lower electrode was grounded. The peak-to-peak value of the RF voltage was set to 300 V.

OES measurements were done using a Carl Zeiss Jena PGS-2 spectrometer equipped with an APHALAS CCD-S3600-D-UV detector. The intensities of specific argon lines in the 696 - 826 nm wavelength range were measured.

3. Simulation Method

A one-dimensional Particle-in-cell/Monte Carlo Collision (PIC/MCC) simulation was performed using the PICit! code [4]. A 13.56 MHz CCP Ar plasma having a voltage of 300 V with pressure ranging from 2 Pa – 100 Pa was simulated. To align with the experimental set-up, the electrode gap was set to 4 cm and the gas temperature was taken from Tunable Diode Laser Spectroscopy (TDLAS) measurements. The PIC/MCC code traces the electrons and the Ar^+ ions present in a homogeneous background Ar gas. An electron reflection coefficient of 0.5 and a secondary electron emission coefficient of 0.07 were implemented at the electrode surfaces.

The collisional radiative model used in this work takes into account the population model of the first 14 excited states of Ar (1s and 2p states in Paschen's notation) [1]. The processes included are the electron impact excitation and de-excitation, electron impact ionization, pooling ionization, collisional quenching of 2p states by Ar atoms, metastable diffusion, and spontaneous emission with radiation trapping.

4. Results and Discussion

The intensities measured using OES and calculated using PIC+CRM are compared and the resulting comparison for pressures of 2 Pa, 20 Pa, and 50 Pa is given in Fig. 1. Here, the intensities are normalized such that $\tilde{I} = I_k / \sum I_k$ (where the index k represents the individual spectral lines considered in the comparison). Here, we can see that the agreement is better at lower pressures, especially at 20 Pa. To quantify the deviation between the intensities, the root-

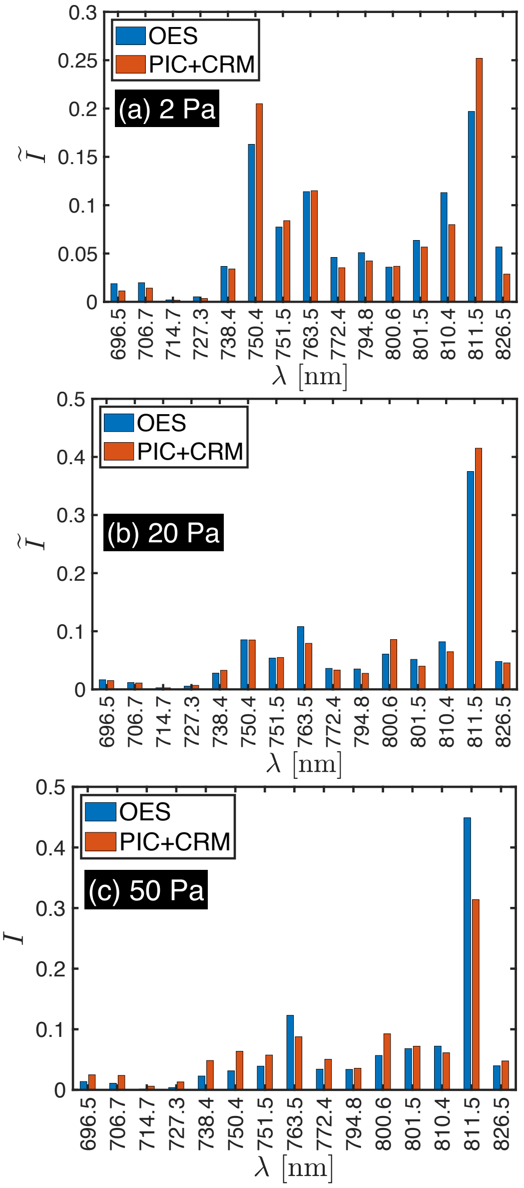

Fig. 1. Measured and calculated normalized intensities at (a) 2 Pa, (b) 20 Pa, and (c) 50 Pa

mean-square error (RMSE) is calculated by

$$RMSE = \sqrt{\frac{1}{N}\sum_{k=1}^{N}\left(\frac{I_{OES}(\lambda_k)}{I_{CRM}(\lambda_k)} - 1\right)^2} \tag{1}$$

where $N = 15$ is the number of spectral lines compared, and $I_{OES}(\lambda_k)$ and $I_{CRM}(\lambda_k)$ are the measured and calculated intensities at the spectral line λ_k respectively. The resulting RMSE values are given in Fig. 2 as a function of pressure. Here, it can be seen that the agreement between the measured and simulated intensities is fairly good at the low-pressure region up to 20 Pa. One possible reason for the increasing discrepancy of the intensities at pressures higher than 20 Pa is that at these pressures, the processes (e.g., ionization) involving the metastable states become more significant. This is due to the fact that the density of

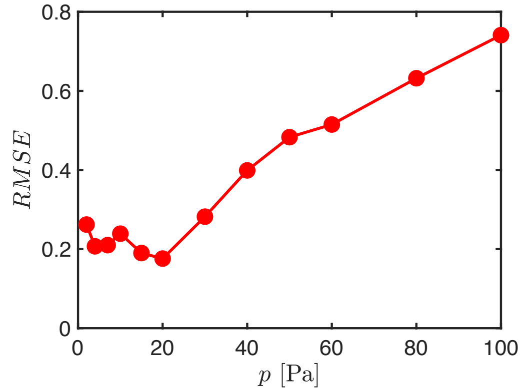

Fig. 2. Root Mean Square Error (RMSE) of the relative deviation of the spectral intensities (refer to Eq. (1))

these states generally increases with the pressure. Figure 3 shows the ionization rate from the ground state and from the $1s_5$ metastable state as calculated using PIC+CRM. It can be seen from this figure that above 20 Pa, the ionization from the $1s_5$ metastable state becomes more important than that from the ground state. This is due to the significant difference in the ionization energy threshold (E_{iz}) between the ground state (E_{iz} = 15.76eV) and the $1s_5$ metastable state (E_{iz} = 4.2 eV), as well as the higher $1s_5$ density at these pressures. The neglect of ionization from the metastable states in the PIC/MCC simulation could therefore cause a difference in the plasma parameters at this higher-pressure range. This aspect will be investigated as a next step.

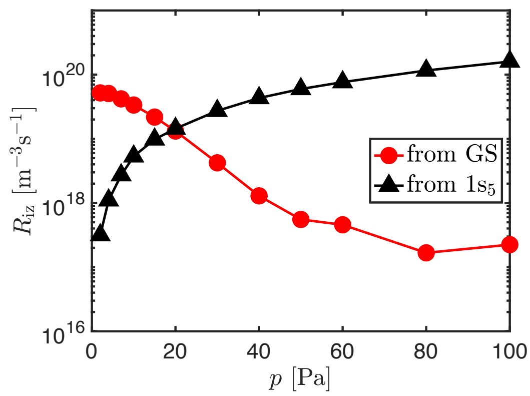

Fig. 3. Rates of ionization from the ground state and the $1s_5$ metastable state as calculated by PIC+CRM.

5. Conclusion

In this work, a one-dimensional PIC/MCC simulation was done for a symmetric capacitively-coupled radiofrequency argon plasma discharge. The pressure was varied from 2 Pa to 100 Pa and the peak-to-peak voltage was set to 300 V. The electron density and electron energy distribution function calculated from PIC/MCC were used as input parameters to the global CRM in order to model spectral intensities. These calculated intensities were then compared to measured OES intensities. Results showed good agreement up to 20 Pa. The deviation present at higher pressures was mainly attributed to the neglect of the processes involving the metastable states in the PIC/MCC simulation.

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