Experimental investigation of vacuum ultraviolet emissions in microwave argon plasmas: dependence on microwave power and discharge pressure.

Susana Espinho, E. Felizardo, J. Henriques, E. Tatarova, F.M. Dias, and C.M. Ferreira

Institute of Plasmas and Nuclear Fusion, Instituto Superior Técnico, Technical University of Lisbon, 1049-001 Lisbon, Portugal

Vacuum ultraviolet emission from argon wave driven microwave (2.45GHz) plasmas operating at low pressures (0.2 – 1 mbar) has been investigated. The emitted spectra show the presence of argon atomic and ionic lines in the range 80 – 110 nm. The relative emission intensities of excited Ar atoms (at 104.8 nm and 106.6 nm) and ions (at 92.0 nm and 93.2 nm) were investigated as a function of the microwave power and pressure of the discharge. Both atomic and ionic emission lines increased linearly in intensity as the power was raised. Concerning the dependence on pressure, experimental results show that atomic and ionic lines decreased linearly in intensity as the pressure was increased. The plasma electron density was estimated to be in the order of $10^{12}$ cm$^{-3}$.

1. Introduction

Vacuum ultraviolet (VUV) radiation is emitted in the spectral region below 200 nm, corresponding to very energetic transitions. The properties of this kind of radiation are extremely attractive for several fields of plasma research and applications, such as ultraviolet light sources for sterilization [1], decontamination [2], surface cleaning and modification [3], etc. There are several kinds of UV sources such as short wave ultraviolet lamps (normally containing mercury), gas-discharge lamps (such excimer lamps for materials processing [4]), ultraviolet lasers (such as soft x-ray laser with argon at 46.9 nm [5]). Microwave discharges, belonging to the group of gas-discharge lamps, have the potential to become competitive VUV sources. One of the main advantages over other sources, is their versatile operation over a wide range of conditions and geometries [6, 7]. This makes them economical and easy to operate. They can operate continously for long periods of time and they are electrodeless. As such they do not require maintenance of electrodes, as in the case of radio-frequency (RF) discharges. Another of the main advantages is that microwave discharges have a high energy coupling efficiency, meaning that the microwave power used to create the discharge is effectively transmitted to the plasma. This means that microwave discharges can easily reach high densities of active species. This is a great advantage for some of the applications mentioned above since these active species can then provide high levels of ultraviolet radiation. However, before using microwave discharges as VUV sources, we need some fundamental research to understand the mechanisms behind the emission of this kind of radiation, and its behavior with discharge operational conditions and plasma parameters.

There are several papers concerning the investigation of radiation emitted by pure argon discharges in the visible [8-10] and also recent works concerning VUV radiation emitted above 110 nm in argon mixture plasmas [11,12]. However, experimental results below this wavelength in microwave discharges are quite scarce because most of the experimental setups are not able to measure radiation in this spectral range. First of all, spectrometers capable of detecting VUV radiation are often quite expensive. Second of all, VUV radiation is highly absorbed by molecular oxygen in air and so we need vacuum systems in order to detect it below 150 nm. Measurements of VUV emissions in an argon inductively coupled plasma [13] and in an electron cyclotron resonance etcher in argon [14] suggest that the main species emitting in this spectral region is the argon atom at 104.8 nm and 106.7 nm. Furthermore, measurements in microwave discharges in mixtures of argon-hydrogen also suggest the emission of argon ions Ar$^+$ at 91.98 nm [15-17]. It is possible that these ions can also be detected in pure argon discharges. More measurements need to be carried out in order to establish a clear idea of which species emit in argon discharges below 110 nm. There is also the need to complement these investigations and provide more information on the behavior of the spectral lines intensity with the variation of discharge conditions, for the specific case of microwave discharges. Most of the applications require specific wavelengths (energies) and so we must understand how to take the most
advantage out of the operational conditions so as to obtain the desired properties for each specific case.

Here we will take on a preliminary research concerning the VUV radiation emitted by surface wave driven argon plasmas operating at microwave (2.45 GHz) frequencies and low pressure conditions (0.2 – 1 mbar). The first goal is to detect spectral emissions from argon species in the VUV region. Then we will focus on the variation of these emissions with the discharge operational conditions and the plasma electron density. Emission spectroscopy measurements in the range 80 – 125 nm were performed to detect radiation from excited argon atoms and ions. The relative intensity of the argon resonance lines, emitting at 104.8 nm and 106.7 nm, and of the ion Ar+, emitting at 91.97 nm and 93.20 nm, are investigated with the variation of microwave power and discharge pressure. Spectroscopy in the visible range is used to estimate the plasma electron density $n_e$ by measuring the H, line (emitting at 486.1 nm). This is achieved by inserting a small fraction of hydrogen in the argon discharge. Stark broadening is one of the most common approaches to determine the electron density in low temperature plasmas. The broadening of this line due to the linear Stark effect is very sensitive to $n_e$ variations in low pressure conditions.

2. Plasma Source and Experimental Set-up

Emission spectroscopy in the VUV and visible range were performed to study the emission spectra of microwave surface wave sustained plasmas. A surface wave sustained discharge at 2.45 GHz with a waveguide-surfatron based setup, has been used as the plasma source. The waveguide-surfatron is the field applicator that couples the microwave power to the surface waves giving origin to the discharge. The experimental setup shown in figure 1 comprises the plasma source as well as the VUV and visible (not shown in the figure) spectrometers. The discharge takes place in a quartz tube with internal/external radii of 1.5/2.5 mm where the background gas (argon) is injected. The gas flow and the pressure have been regulated with mass flow controllers and three pressure sensors. The microwave power delivered to the launcher has been varied from low powers (50 W) to high powers (260 W). Due to the size of the experimental apparatus, it was not possible to increase the microwave power above 260 W. In spite of that, we expect the population of Ar and Ar+ to increase as the power delivered to the discharge is raised.

![Figure 1](image)

**Figure 1** - (a) VUV experimental setup and (b) microwave discharge under investigation. [18]

The microwave discharge is sustained by a propagating surface wave; the bigger part of the plasma column is created on the left side of the field applicator. However, it is the high density plasma on the right side of the launcher that is under investigation here. In fact, the detected VUV radiation is emitted from a small plasma section at the end of the post-discharge zone (shown inside the dashed
rectangular box) because the rest of the plasma is optically thick for this radiation. This means VUV radiation is not transmitted through the plasma, being quickly absorbed by particles from the plasma. The VUV radiation emitted by this slice is collected by a Horiba Jobin-Yvon Plane Grating Monochromator (PGM), which is directly coupled to the discharge tube, thus granting unobstructed line-of-sight over the axis. The fraction of light that enters the PGM passes through a 1mm radius pinhole and a set of horizontally adjustable slits and is then reflected with a 156° deviation angle by a toroidal mirror into one of two plane gratings (1800 or 550gr/mm). The grating rests atop a rotating platform controlled remotely, allowing for the selection of the incidence angle. The diffracted light is then horizontally selected by another pair of slits, located near the end of the spectrometer, before reaching a scintillator (C$_7$H$_5$NaO$_3$), where it is converted by fluorescence into visible radiation. This radiation is detected by a R928 Hamamatsu photomultiplier. The whole VUV light path is kept at relative low pressure ($10^{-5}$ - $10^{-4}$ mbar) by a turbo-pump which is coupled to the spectrometer. The optimization of the whole setup has been performed by measuring the well-known 30.4 nm He$^+$ line emitted from a pure He microwave plasma. The VUV spectra have been detected in the range 30 - 125 nm and they are all background corrected.

The visible radiation (from the same region as the VUV radiation) was collected by an optical fiber, positioned perpendicularly to the discharge tube, which transmits the radiation to the entrance slit of Jobin- Yvon Spex 1250M visible spectrometer. The spectral resolution of the measurements in the visible range (2400 gr/mm grating) is 0.06 Å. To perform these measurements we introduce only a small fraction of hydrogen in the argon discharge. The resolution is then limited by the size of the slits which was chosen in order to obtain the maximum signal for the measured hydrogen line H$_\beta$ (486.1 nm).

3. Results

Emissions from Ar and Ar$^+$ were detected in the 85 – 110 nm spectral range. A spectrum measured in this region is shown in figure 2, where one immediately distinguishes the dominant emission of atomic resonance lines at the wavelengths 104.8 nm and 106.7 nm. Radiative decay of argon resonant states from the 2s$^2$3p$^4$4s configuration to the ground state gives rise to these lines, the corresponding photon energies being 11.83 eV and 11.62 eV respectively. Emission from excited Ar$^+$ ions has also been detected at wavelengths 91.98 nm and 93.20 nm, the corresponding photon energies being 13.48 eV and 13.30 eV. For more detail, the energy levels originating all the observed transitions are summarized in figure 3. The weakest emission lines observed in this spectral region have wavelengths between 86 – 90 nm. These lines originate from resonant transitions of the argon atom with energies between 13.86 and 14.30 eV. Besides being the weakest emissions observed, these lines emit at very close wavelengths. As such, they appear convoluted in the spectrum hence being difficult to investigate separately. As such, only the dominant resonance lines and the ion lines were investigated in this work in more detail. Additionally, the hydrogen Lyman-β line at 102.6 nm can easily be identified in the spectrum shown in figure 2. The presence of this line is due to the hydrogen impurity that is inevitably present in the discharge.
Figure 2 - Experimental argon spectrum measured at low pressure in the 85 – 110 nm range. Emission lines from atomic transitions are detected (Ar I) as well as ionic transitions (Ar II).

Figure 3 - Energy levels showing the observed Ar and Ar\(^+\) transitions [19 - 22].

The relative VUV emission intensities of excited Ar atoms (at 104.8 nm and 106.6 nm) and ions (at 92.0 nm and 93.2 nm) were investigated as a function of the microwave power and pressure of the discharge. As it is well known, spectral lines suffer a number of different broadening mechanisms – they appear as peaks spreading over a small range of wavelengths. The intensity of the spectral lines is then investigated by calculating the integral intensity, which corresponds to the area under each peak after performing a background-noise correction. Results concerning the intensity dependence on power and pressure are presented in figures 4, 5 for the atomic resonance lines, and in figures 6, 7 for the ion emission lines.
Figure 4 - (a) Spectrum of the argon resonance line at 104.8 nm for constant pressure 0.2 mbar and two different delivered powers; (b) integral intensities of the measured resonance lines at 0.4 mbar and different powers, normalized to the maximum intensity of the 104.8 nm line.

Figure 5 - (a) Spectrum of the argon resonance line at 104.8 nm for constant power 260W and two different discharge pressures; (b) integral intensities of the measured resonance lines at 260 W and different discharge pressures, normalized to the maximum intensity of the 104.8 nm line.

Figure 6 - (a) Ar$^+$ emission lines at 91.97 nm and 93.20 nm at discharge pressure 0.2 mbar. Integration time is 30 s and slit width is 1 mm; (b) integral intensities of the measured ion lines at constant 0.2 mbar and different applied powers, normalized to the maximum intensity of the 91.97 nm line.
Figure 7 - (a) Ar$^+$ emission lines at 91.97 nm and 93.20 nm at discharge power 200 W and different pressures. Integration time is 30s and slit width is 1mm; (b) integral intensities of the measured ion lines at 200 W and different pressures, normalized to the maximum intensity of the 91.97 nm line.

In addition, the plasma electron density has also been measured for different powers applied to the discharge. Optical emission spectroscopy was used to measure the hydrogen H$_\beta$ line at 486.1 nm (this is achieved by inserting a small quantity of hydrogen in the discharge tube). This hydrogen line has a well defined Voigt profile which can be fitted using the spectrometer’s software SpectraMax. Fitting this line profile as shown in figure 8, we retrieve the Stark broadening width, which in low temperature plasmas is commonly expressed in terms of the electron density for the case of hydrogen species [20]. The results are also shown in figure 8.

Figure 8 - (a) Experimental profile of the hydrogen H$_\beta$ line and respective Voigt fitting; (b) plasma electron density as a function of power.

4. Discussion

The most intense lines of the measured spectrum are the argon atom resonance lines at wavelengths 104.8 nm and 106.7 nm. The integral intensities of these lines show a linear dependence with power: they increase by a factor of two as the delivered microwave power increases from 100 to 220 W at constant pressure 0.4 mbar (figure 4). The relative intensities presented in this figure are normalized to one and the same value. Measurements of the H$_\beta$ line Stark broadening demonstrate that the electron density $n_e$ increases from $1.5 \times 10^{12}$ cm$^{-3}$ to $4 \times 10^{12}$ cm$^{-3}$ in this case (figure 8). The Lorentz component of the full-width-half-maximum (fwhm) of the H$_\beta$ line relates to the electron density through the Stark broadening width as follows: $\Delta \lambda \sim n_e^{2/3}$. The increased intensity of the argon
resonance lines with power is related to this increase of the electron density. In the low pressure conditions here considered, the main population mechanism of the emitting states is direct electron impact excitation and the main loss channel is radiative decay. Thus, an increase of \( n_e \) results in more populated resonant levels which rapidly decay to the ground state emitting the observed lines. Remember the intensity of a spectral line is proportional to the population of the emitting level — the increase in electron density leads to more intense spectral lines. Concerning the dependence on pressure it was found that the intensities of these lines decrease by a factor of two as pressure increases from 0.2 mbar to 1.2 mbar (figure 5). This is likely due to the depletion of the high energy tail of the electron energy distribution function and, consequently, decreasing of the electron excitation rates when the pressure increases. Self-absorption of these lines can also be an important mechanism leading to these pressure dependence results. Prior investigations suggest that self-absorption of these resonant argon lines is not important at low-pressure conditions [13]. However as the pressure is raised, this may no longer be valid and self-absorption may result in the decrease of observed spectral intensity. In order to understand if this valid or not, more measurements need to be carried out and current modeling of these results is being performed.

The intensity of the ion lines strongly increases with power. The intensity of the 91.97 nm line increases also linearly as the delivered microwave power increases from 50 to 200 W (figure 6). In fact, the power dependence is much stronger for these lines than for the atomic ones. This is mainly due to the strong impact of the electron density on the ionization process: higher power means higher electron density which results in more ionized atoms. Concerning the dependence on pressure, it was found that the intensity of these lines strongly decreases as the pressure varies from 0.2 mbar to 0.9 mbar (figure 7). Once again, these are preliminary results and the discussion concerning the pressure dependence is being complemented with calculations from a collisional-radiative model.

5. Conclusions

VUV radiation emitted by an argon surface wave driven discharge plasma operating at 2.45 GHz and low pressure conditions (0.2 – 1 mbar) has been investigated. The argon resonance lines at 104.8 nm and 106.7 nm, two ionic lines at 91.97 nm and 93.20 nm as well as five atomic argon lines in the range 86 – 90 nm have been detected. The relative emission intensities of excited argon atoms (at 104.8 nm and 106.6 nm) and ions (at 92.0 nm and 93.2 nm) were investigated as a function of the microwave power and pressure of the discharge. The spectral intensity of these lines shows a linear dependence with power and pressure — the intensity of both atomic and ionic spectral lines increases as the power is raised, and decreases as the pressure is raised. However we should note that the \( \text{Ar}^+ \) emissions show a stronger dependence on power. This is mainly due to greater impact of the electron density on the ionization process. The plasma electron density also shows a linear dependence with microwave power. It increases in the range \( 10^{12} \text{ cm}^{-3} \) for constant pressure 0.4 mbar and delivered powers ranging from 90 to 260 W.

In order to have more insight into the mechanisms governing VUV emission by atomic and ionic species, the next step is to compare experimental results and model predictions. The experimental results are currently being analyzed using a 2D self-consistent theoretical model based on a set of coupled equations including the electron Boltzmann equation, the rate balance equations for the most important electronic excited species and for charged particles, the gas thermal balance equation, and the wave electrodynamics [23]. The dominant collisional and radiative processes for neutral and ionized argon levels are accounted for. We expect good agreement between calculations and experiments concerning the power measurements, since the electron density has the expected behavior when increasing the microwave power. For the pressure results, the calculations may vary a little when taking into account self-absorption of the lines at higher pressures.

To complement the theoretical calculations, more measurements need to be carried out for these atomic and ionic argon lines. Also, the weaker emissions in the VUV region should also be investigated. Five other atomic lines were detected in this work and can also be investigated as a function of power and pressure. Plus, argon has other atomic and ionic emissions below 80 nm that can be investigated. Indeed, the lower wavelength region corresponds to energetic transitions that may play an important role in several applications. For now, this work provides novel measurements concerning the most intense emissions below 110 nm: the intense resonant lines as well as two ion...
lines were investigated with the variation of operational conditions. Their clear dependence on microwave power shows that the control of experimental conditions can strongly affect the emission of VUV radiation in microwave discharges at low pressures.

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References

[20] NIST atomic database;