CHAPTER 4

Probing magnetron discharge plasma with ion acoustic wave

This chapter contains the results of an experimental observation of ion acoustic wave propagation in the bulk region of oxygen added argon magnetron discharge plasma. The variation of the relative negative ion density as a function of reactive gas addition is studied using the ion acoustic wave diagnostics.

4.1 Introduction

As already mentioned in the introduction of this thesis, the conventional plasma diagnostics like the Langmuir probe, the optical emission spectroscopy have their limitations while using in DC planar magnetron discharge. The probe tip of the Langmuir probe is used to get coated by the material sputtered from the magnetron target during prolonged deposition. It will increase the charge collection area of the Langmuir probe and it may lead to erroneous results. Thus while using the Langmuir probe; precautions must be taken in order not to coat the tip during data acquisition. In order to overcome such limitation, the ion acoustic wave can be used as a suitable alternative diagnostic tool. Ion acoustic waves have been used as a diagnostic tool for determination of electron temperature and electron density for long. For the relative measurement of ion density, ion acoustic wave is certainly a more precise diagnostic tool than that of the Langmuir probe [1]. In this chapter, a detail study of probing the magnetron discharge plasma in the presence of negative ions is reported. Presence of negative ions is very advantageous for measurement of the relative ion density as it significantly affects the propagation of the ion acoustic wave [2]. Negative ion containing argon magnetron discharge is obtained by adding little amount of oxygen (O₂) in the argon (Ar) magnetron discharge. As oxygen is electronegative gas, it can create
volume produced negative oxygen ions by dissociative attachments with low temperature electron [3].

Multi-component oxygen additive argon plasma finds wide applications in the magnetron discharge plasma for various industrial processes. This reactive sputtering technique is widely used for the deposition of thin films of metal oxides such as SiO₂, TiO₂, Al₂O₃ etc [4-6]. The negative ions coming from the driven phase of the discharge transfer energy flux to the substrate which can be more significant than from the positive ions [7]. Also, the negative ions created in the bulk region of the discharge can alter the properties of entire discharge affecting the process and deposition characteristics. Thus, for the optimization of sputtering process a precise determination of the relative negative ion density is very essential.

In this chapter, we present an experimental study of the effect of oxygen addition on the relative negative oxygen ion concentration using ion acoustic wave diagnostics in the magnetron discharge plasma. The experiments in this study are performed in a magnetron discharge by adding oxygen gas gradually in argon plasma at an argon partial pressure of 8×10⁻⁴ mbar. The phase velocity of the ion acoustic waves in the discharge is measured, leading to a determination of the value of the relative negative ion concentration. The measured values of relative ion density at each discharge condition using ion acoustic wave diagnostic is benchmarked with that of a Langmuir probe measurements.

The chapter is organized in following sections. In next section (4.2) the details of the experimental arrangements for the ion acoustic wave measurement are given. The theoretical model for propagation of ion acoustic wave is presented in the section 4.3.
Detail discussion of ionic processes in oxygen containing argon plasma surface has been discussed in the section 4.4. In the following section (4.5) the estimation of the relative concentration using ion acoustic wave and benchmarking the obtained value with the Langmuir probe diagnostic is achieved. The findings of the chapter are summarized in the section 4.6.

4.2 Experimental set up and diagnostic procedure

The experiment is carried out in a DC planar magnetron system and its schematic diagram is given in the Fig. 2.10 of Chapter 2. The method of ion acoustic wave excitation technique with the block diagram of the wave launcher is explained in the section 2.3.2 of Chapter 2. The water-cooled Titanium target of diameter 70mm is used as the cathode of the magnetron sputtering system. The chamber is evacuated by a diffusion pump backed by a rotary pump up to a base pressure of $10^{-4}$ Pa. Initially; argon plasma is produced at a working pressure of $8 \times 10^{-2}$ Pa with applied power of 100W DC. Multi component plasma with negative oxygen ions is then formed by gradually adding oxygen in the argon plasma keeping the applied power constant. The partial pressure of oxygen is varied from $4 \times 10^{-3}$ Pa to $8 \times 10^{-3}$ Pa keeping the argon partial pressure constant at $8 \times 10^{-2}$ Pa. Ar and O$_2$ are fed into the deposition chamber by digital mass flow controllers (Aalborg Make). For processes operated at a constant power, the observation of a decrease in the target voltage must be accompanied by a corresponding increase in the ion current and in the secondary electron coefficient ($\gamma_{se}$). Similarly, the observation of an increase in target voltage must be accompanied by a corresponding decrease in the ion current and in the secondary electron coefficient ($\gamma_{se}$). Because the change in the secondary electron coefficient ($\gamma_{se}$) is not
significant as a function of working pressure [8], the change in voltage is compensated by a corresponding change in the ion current, which is related to the discharge current by [9]

\[ I_d = (1 + \gamma_\infty)I_i \tag{4.1} \]

For most metals \( \gamma_\infty \approx 0.05 - 0.2 \), so the dominating fraction of the discharge current at the target is the ion current [8]. The observed values of the discharge current and the target voltage at a constant power of 100 W are given in Table 4.1. It is clear that with an increasing partial pressure of oxygen there is a gradual decrease of ion current and a corresponding increase in discharge voltage.

Table 4.1: Current and voltage values in the discharge at various discharge conditions

<table>
<thead>
<tr>
<th>Oxygen partial pressure (Pa)</th>
<th>Voltage (V)</th>
<th>Current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>550</td>
<td>183.63</td>
</tr>
<tr>
<td>(4 \times 10^{-3})</td>
<td>587</td>
<td>170.15</td>
</tr>
<tr>
<td>(6 \times 10^{-3})</td>
<td>598</td>
<td>167.20</td>
</tr>
<tr>
<td>(8 \times 10^{-3})</td>
<td>605</td>
<td>165.28</td>
</tr>
</tbody>
</table>

The plasma parameters of electron temperature \( T_e \), electron density \( n_e \) and ion density \( n_i \) are measured with the Langmuir probe in a region that is practically free of any magnetic field \(|B| = 0\) [10]. Ion-acoustic perturbations are excited by using an arbitrary function generator to apply a positive sinusoidal voltage pulse of suitable amplitude (3.0–6.5 V) and a frequency of 50-100 kHz [11-12] to a circular fine mesh stainless steel
grid (8 cm diameter) inserted in the downstream region of the discharge. The position of the excitation grid is 10 mm above the substrate. The stainless steel grid has 20 meshes per centimeter and has a transparency of 70%. The detail procedure of excitation and detection of the ion acoustic wave is given in the Chapter 2 (Section 2.3.2). The density perturbations ($\partial n_e/\partial n_e$) are detected using an axially adjustable planar Langmuir probe (of 6 mm diameter) biased positively with respect to the plasma potential and placed in front of the center of the mesh. The distance of the planar probe from the center of the excitation grid is varied along the axial line for the time-of-flight measurement. In this study, the phase velocity is measured from the temporal evaluation of the observed wave pattern. The range of exciting voltage is chosen such that $\partial n_e/\partial n_e << 1$ and the signals are recorded in a digital storage oscilloscope. The position of the probe used to detect the density perturbation is kept the same as that of the cylindrical Langmuir probe.

The Optical emission spectroscopy measurement is performed using a 0.5 m Digikrom Spectrometer (CVI Laser Corp, USA. Digikrom Model DK 480). A Crystal Thickness Monitor (DTM-101) manufactured by HIND-HIVAC, Banglore, India monitored the deposition rate at various discharge conditions. The monitor head is placed at the same horizontal plane as the substrate holder.

4.3 Theory of ion acoustic wave in multi-component plasma

The propagation of the ion acoustic wave in the presence of negative ion is different than from the propagation in normal single component plasma. For the study of ion acoustic wave propagation, we assume that argon-oxygen magnetron plasma is effectively composed of $\text{Ar}^+$, $\text{O}^-$ and electrons. The assumption is based on the fact that the density of $\text{Ar}^+$ and $\text{O}^-$ ions is greater than the other positive and negative ions present in such plasma.
[14]. In order to obtain the dispersion relation for ion acoustic wave in such plasma we can couple the continuity and momentum equation into Poisson equation. For such cold plasma the Poissons equation can be expressed as,

$$\frac{\partial^2 \phi}{\partial x^2} = 4\pi e (n_e - n_1 + n_2).$$

(4.2)

Here, $n_e, n_1$ and $n_2$ are electron, positive ion and negative ion density respectively.

After we perturb and linearize the continuity equation and momentum equation, and couple it to the Poisson's equation assuming the electrons to be Maxwellian, the Eq. (4.2) can be written as

$$-k^2 \phi = \frac{4\pi^2 e^2 n_{e0}}{k_B T_e} \phi \left[1 - \frac{n_{10}}{n_{e0}} \frac{k^2 k_B T_e}{m_e \omega^2 - 3k_B T_e k^2} - \frac{n_{20}}{n_{e0}} \frac{k^2 k_B T_e}{m_i \omega^2 - 3k_B T_e k^2}\right],$$

(4.3)

where $n_{e0}, n_{10}$ and $n_{20}$ are equilibrium density of the electron, positive ion and negative ion, respectively. If we assume such a multi-component plasma for $n_0$ positive ions with mass $m_+$, for $\varepsilon n_0$ negative ions with mass $m_-$ and that includes $(1 - \varepsilon)n_0$ electrons in equilibrium, the Eq. (4.3) can be expressed as

$$1 = -\frac{1}{k^2 \lambda_o^2} \left[1 - \frac{k^2 k_B T_e n_e}{m_e \omega^2 - 3k_B T_e k^2} - \frac{k^2 k_B T_e n_i}{m_i \omega^2 - 3k_B T_e k^2}\right],$$

(4.4)

with $\lambda_o = \frac{\lambda_{Do}}{(1 - \varepsilon)^{1/2}}$

where $\lambda_{Do} = \frac{k_B T_e}{4\pi e^2 n_{e0}}$

and $\frac{n_{10}}{n_{e0}} = \frac{\varepsilon}{1 - \varepsilon} = n_-, \quad \frac{n_{20}}{n_{e0}} = \frac{1}{1 - \varepsilon} = n^+, \quad \varepsilon = \frac{n_-}{n^+}$. 

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Eq. (4.4) can be written as

\[ 1 = \frac{1}{k^2 \lambda_0^2} \left[ 1 - \frac{k_B n^-}{m_\gamma} \left( \frac{\omega^2}{m_\gamma k^2 T_e} - \frac{3k_B T_e}{m_\gamma T_e} \right) \right] - \frac{k_B n^+}{m_\gamma} \left( \frac{\omega^2}{m_\gamma k^2 T_e} - \frac{3k_B T_e}{m_\gamma T_e} \right). \]  

(4.5)

Again, Eq. (4.5) can be written as,

\[ 1 = \frac{1}{k^2 \lambda_0^2} \left[ 1 - \frac{n^-}{m_\gamma \left( \frac{\omega^2}{m_\gamma k^2 T_e} - \frac{3T_e}{k^2 T_e} \right)} - \frac{n^+}{m_\gamma \left( \frac{\omega^2}{m_\gamma k^2 T_e} - \frac{3T_e}{k^2 T_e} \right)} \right]. \]  

(4.6)

Here, \( \frac{k_B T_e}{m_+} \) is the ion sound velocity for the positive ions. Thus, the Eq. (4.6) becomes

\[ 1 = \frac{1}{k^2 \lambda_0^2} \left[ 1 - \frac{n^-}{m_\gamma \left( \frac{v_p^2}{c_s^2} - \gamma \tau \right)} - \frac{n^+}{m_\gamma \left( \frac{v_p^2}{c_s^2} - \gamma \tau \right)} \right]. \]  

(4.7)

with

\[ -k^2 \lambda_0^2 = \left[ 1 - \frac{n^-}{m v^2 - \gamma \tau} - \frac{n^+}{v^2 - \gamma \tau} \right]. \]  

(4.8)

where the symbols are defined as,

\[ v = \frac{v_p}{c_s} = \frac{w}{k c_s} \] with \( c_s = \sqrt{k_B T_e / m_\gamma} \) and \( m = \frac{m_\gamma}{m_+} \)

Cooney et al. [15] obtained a similar kind of dispersion relation for the ion acoustic waves in such plasma, and obtained two branches of phase velocity. The speed of one branch (fast mode) increases and the speed of the other branch (slow mode) decreases with increasing \( \varepsilon \).
In the slow mode, positive ions, negative ions and electrons oscillate in phase, while in the fast mode they oscillate out of phase. However, in the cold plasma the slow mode does not exist, and the fast mode phase velocity for the long wavelength reduces to [15]

$$v_f = c_s \sqrt{\frac{1 + \epsilon / m}{1 - \epsilon}}.$$  \hspace{1cm} (4.9)

### 4.4 Description of ionic processes in oxygen containing argon plasma

To study the propagation of ion acoustic wave in oxygen added argon plasma, a study of various ionic processes in the oxygen added argon plasma is essential. When oxygen is added to argon, in addition to ground state Ar atoms, $O_2$ molecules, $Ar^+$, $O_2^+$ and $O^+$ ions, there exists the possibility of the various meta-stable atoms of $Ar$ ($3d^44s^1p_2$) at 11.55 eV above the ground state (denoted as $Ar_m^+$), oxygen molecules in two meta-stable states ($O_2^m$) at 0.977 and 1.672 eV and oxygen atoms at the lowest meta-stable states ($O^m$) at 1.97 eV [14]. The essential reactions in the scope of this study are mentioned in Table 4.2. The species of the Ar/O$_2$ plasma mentioned above undergo different chemical reactions with different rate constants and different relative cross sections. Before experimental analysis of the relative negative ion concentration, it is very important to discuss the relevant reaction routes for the formation and destruction of $O^-$ present in such a plasma. Electron impact dissociative attachment of $O_2$ is the main production scheme of $O^-$, though to a lesser extent electron impact dissociation of $O_2$ is also responsible for the production of $O^-$ ions [14].

$$e^- + O_2 \rightarrow O^- + O$$ \hspace{1cm} (4.10)

$$e^- + O_2 \rightarrow O^- + O^+ + e^-$$ \hspace{1cm} (4.11)
As shown by Panda et al. [16], the creation of O' also takes place through dissociative attachment of a meta-stable oxygen molecule (O2m), which will likely be a very strong production channel in low electron temperatures. However, in the observed electron temperature range in this study (5.78-6.20 eV), the decay of a meta-stable oxygen molecule into pairs of neutral oxygen atoms is far more dominant than the creation of meta-stable molecules.

\[ e^- + O_2^m \rightarrow O^- + O \]  
(4.12)

The O' ions are chiefly lost via neutralization of Ar+ ions throughout the volume of the discharge [3].

\[ O^- + Ar^+ \rightarrow O + Ar \]  
(4.13)

However, in the downstream region of the magnetron discharge, the negative ions are lost by ion-ion recombination via the following routes [3]:

\[ O^- + O_2^+ \rightarrow O + O_2 \]  
(4.14)

\[ O^- + O_2^+ \rightarrow 3O \]  
(4.15)

\[ O^- + O^+ \rightarrow 2O \]  
(4.16)

The electron impact dissociative ionization of O2 is the main production mechanism for O+, while charge transfer of Ar+ with O2 is responsible for the production of O2+ ions [14]. Therefore, it is reasonable that both ion densities increase as a function of increasing O2 partial pressure in the discharge.

\[ e^- + O_2 \rightarrow 2e^- + O^+ + O \]  
(4.17)

\[ Ar^+ + O_2 \rightarrow Ar + O_2^+ \]  
(4.18)
Table 4.2: Reactions and rate coefficients

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate Constant (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$e^- + Ar \rightarrow 2e^- + Ar^+$</td>
<td>$4.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>2.</td>
<td>$e^- + O_2 \rightarrow O^- + O$</td>
<td>$8.8 \times 10^{-11} \exp(-4.4/T_e)$</td>
</tr>
<tr>
<td>3.</td>
<td>$e^- + O_2 \rightarrow O^- + O^+ + e^-$</td>
<td>$7.1 \times 10^{-11} \sqrt{T_e} \exp(-17/T_e)$</td>
</tr>
<tr>
<td>4.</td>
<td>$e^- + O_2^m \rightarrow O^- + O$</td>
<td>$-1.69 \times 10^{-12} + 6.72 \times 10^{-10}/T_e$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-1.30 \times 10^{-10}/T_e^2 + 9.60 \times 10^{-12}/T_e^3$</td>
</tr>
<tr>
<td>5.</td>
<td>$O^- + Ar^+ \rightarrow O + Ar$</td>
<td>$2.7 \times 10^{-7} \sqrt{300/T_g}$</td>
</tr>
<tr>
<td>6.</td>
<td>$O^- + O_2^+ \rightarrow O + O_2$</td>
<td>$2.0 \times 10^{-7} \sqrt{300/T_g}$</td>
</tr>
<tr>
<td>7.</td>
<td>$O^- + O_2^+ \rightarrow 3O$</td>
<td>$2.0 \times 10^{-7} \sqrt{300/T_g}$</td>
</tr>
<tr>
<td>8.</td>
<td>$O^- + O^+ \rightarrow 2O$</td>
<td>$2.7 \times 10^{-7} \sqrt{300/T_g}$</td>
</tr>
<tr>
<td>9.</td>
<td>$e^- + O_2 \rightarrow 2e^- + O^+ + O$</td>
<td>$5.3 \times 10^{-10} T_e^{-0.99} \exp(-20/T_e)$</td>
</tr>
<tr>
<td>10.</td>
<td>$Ar^+ + O_2 \rightarrow Ar + O_2^+$</td>
<td>$5 \times 10^{-11}$</td>
</tr>
<tr>
<td>11.</td>
<td>$O_2^+ + Ar \rightarrow O_2 + Ar^+$</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>12.</td>
<td>$O^+ + Ar \rightarrow O + Ar^+$</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>13.</td>
<td>$e^- + O \rightarrow O^m + e^-$</td>
<td>$4.2 \times 10^{-9} \exp(-2.25/T_e)$</td>
</tr>
<tr>
<td>14.</td>
<td>$O^- + O^+ \rightarrow O^m + O$</td>
<td>$2.7 \times 10^{-7} \sqrt{300/T_g}$</td>
</tr>
</tbody>
</table>

Note that $T_g$ is the gas temperature in K (Kelvin)
Concerning the loss of $O^+$ and $O_2^+$ ions, an asymmetric charge transfer with an Ar atom is found to be the most significant process compared to other possible processes [14].

\begin{align}
O_2^+ + Ar &\rightarrow O_2 + Ar^+ \quad (4.19) \\
O^+ + Ar &\rightarrow O + Ar^+ \quad (4.20)
\end{align}

The meta-stable oxygen atoms ($O^{m}$) created in the discharge play an important role in determining the relative concentration of negative ions in the oxygen additive argon magnetron discharge plasma. Viteralu et al. [17] have shown that $O^-$ ions produced at the target region of the magnetron discharge lead to $O^{m}$ formation in the downstream region of the discharge via electron and argon stripping[18], followed by

\begin{equation}
e^- + O \rightarrow O^m + e^- . \quad (4.21)
\end{equation}

Again, lower energetic $O^-$ ions formed due to electron attachment onto atoms [17] can set up another reaction route to $O^{m}$, given by

\begin{equation}
O^- + O^+ \rightarrow O^m + O \quad (4.22)
\end{equation}

with characteristic emission lines at 777 and 845 nm. In the literature, the intensity of the emission line at 777 nm is used as a representative of the relative density of negative oxygen ions in the discharge [19].

The steady state density of $O^-$ ions at pressures lower than $\sim 4$ Pa can be given as

\begin{equation}
n^- = \frac{k_{da} n_e n_{e_2}}{k_{rec} n_e} \quad (4.23)
\end{equation}

where $k_{da} = 8.8 \times 10^{-17} \exp[-4.4/T_e]$ m$^3$s$^{-1}$ and $k_{rec} \approx 2.5 \times 10^{-13} (300/T_g)^{1/2}$ m$^3$s$^{-1}$ are the rate constants for dissociative attachment (Reaction 2 in Table 4.2) and ion–ion recombination (Reactions 5, 6 and 7 in Table 4.2), respectively [20-21]. Here, $T_e$ is the electron
temperature in eV, \(T_g\) is the neutral temperature in Kelvin, and \(n_{o_2}\) is the neutral density of oxygen. In deriving this equation, it is assumed that for the conditions of electron temperature and working pressure existing in our investigation, the dissociative attachment of \(O_2\) is dominant over other production channels for \(O^-\). Here, \(n^-\) is the density of \(O^-\) ions in the discharge, \(n_+\) is the total positive ion density \((n_+ = n_{Ar^+} + n_{O_2^+} + n_{O^+})\) where the symbol represents the corresponding density of ions. Due to similar reaction rate coefficients of negative \(O^-\) ion recombination with \(Ar^+, O^+\) and \(O_2^+\) ions (Reactions 5, 6 and 7 in Table 4.2) we can assume a single rate constant \((k_{rec})\) for such processes. If we take \(\gamma = n^- (n^+ - n^-)^{-1}\), it will represent the electro-negativity of the discharge. Then Eq. (4.23) can be stated as

\[
n^- = \frac{k_{dc}n_{O_2}}{k_{rec}(1+\gamma)}
\]

When \(\gamma \ll 1\), as in this work, \(n^- \propto n_{o_2} \propto P_{O_2}\), where \(P_{O_2}\) is the partial pressure of the oxygen in the discharge. Thus, a gradual increase in the oxygen negative ion density is expected with an increase in the oxygen partial pressure.

4.5 Results and discussions

4.5.1 Measurement of the relative concentration of ion using ion acoustic wave diagnostics

In this investigation the fast mode phase velocities \((v_f)\) of the grid excited ion acoustic waves are used to determine the relative concentration of negative ions. The fast mode phase velocity of ion acoustic wave in such plasma is given by the Eq. (4.9). With the help of the mentioned equation, determination of the relative density of negative ion is possible
provided the ion sound velocity for pristine argon plasma is known. In the pristine argon plasma, at first the compressive linear perturbations are excited for a transient, weak (3.0 V and 10 μs) sinusoidal excitation pulse. Fig. 4.1(a) shows the evolution of a compressive pulse for the applied excitation amplitude detected as the maximum normalized density fluctuation (\(\frac{\partial n}{n_e}(0.05)\)) by the positively biased Langmuir probe at a different distance (2-8 cm) from the grid. Due to the damping in plasma media the amplitude of the perturbation decreases as it travels further from the excitation grid. Using the time-of-flight technique, the ion sound velocity for pristine argon plasma is measured and found to be \((2.26 \pm 0.19) \times 10^5\) cm/s for the pure argon plasma. The measured value of ion sound velocity is within the range limited by the expression \(c_s = \sqrt{\frac{kT_e}{M_i}}\). After studying the linear characteristic of wave propagation, an attempt was made to study the non-linear propagation of wave by increasing the amplitude of the applied pulse [22]. Fig. 4.1(b) shows the detected signals at the location \(X = 6\) cm for different excitation voltages \((V_{ex})\) of the applied positive pulse. It is observed that the velocity of the wave increases and the width of the wave become narrower with increasing wave amplitude. These are the properties of the propagation of the ion acoustic soliton [2]. A soliton is a non-linear ion acoustic wave which results due to the delicate balance between the non-linearity and dispersion present in the plasma medium. The non-linearity in the wave increases with increasing wave amplitude. Also, when the wave propagates away from the exciting grid, the role of dispersion becomes larger. Soliton is formed at the distance where the non-linearity is balanced by the dispersion present in the plasma medium (in this case at a distance of 6 cm from the centre of the exciting grid in
Figure 4.1(a) Observed signals at several distances from the grid for an initial positive sinusoidal pulse ($V_{ex} = 3.0V$) in pure argon plasma. Partial pressure of argon $P_{Ar} = 8 \times 10^{-2}$ Pa. (b) Detected signal at different amplitudes of the positive excited signal $V_{ex}$ in oxygen added argon plasma. The probe is fixed at $X = 6$ cm. Top trace is applied signal (not to scale).

The evaluation of an initial perturbation with increasing negative ion concentration is shown in Fig. 4.2. The planar probe is fixed at $X = 6$ cm for an excitation voltage ($V_{ex}$) of 6.5 V. It is found that the phase velocity of the ion acoustic wave in the presence of negative ions is faster than in pure argon plasma. Another important observation is the increase in phase velocity with an increasing negative ion concentration (Fig. 4.3). With the addition of oxygen into the pure argon plasma, there is a gradual decrease of electron density, which decreases the resistance to positive ion motion. As a result, the phase velocity of the fast mode increases gradually with the oxygen partial pressure though its amplitude is slightly reduced. The phase velocity is calculated from the mentioned time-of-flight technique in the presence of negative ions. The measured values of the phase velocities at the conditions with oxygen partial pressure of $4 \times 10^{-3}$ Pa, $6 \times 10^{-3}$
and $8 \times 10^{-3}$ are inserted in the Eq. (4.9) to calculate the values of $\varepsilon$ and are found to be 0.042, 0.067 and 0.082 respectively.

![Figure 4.2 Observed signals at X = 6 cm from the grid for an initial pulse ($V_{ex} = 6.5$V) at different oxygen partial pressure. Partial pressure of argon $P_{Ar} = 8 \times 10^{-2}$ Pa. Top trace is the applied pulse (not to scale)](image)

4.5.2 Langmuir probe and optical emission spectroscopy measurement

As oxygen is added to pure argon plasma, the Langmuir probe current-voltage (I-V) plot and its plasma parameters begin to change. The procedure to determine the electron density and electron temperature from the I-V characteristics of the Langmuir probe is mentioned in the Chapter 3 and the electron density is found to decrease with an increase of the oxygen partial pressure in the discharge (Fig. 4.4). Because the ionization potential of oxygen is lower than that of argon, a gradual decrease of electron temperature from 6.20 to 5.78 eV is also observed upon oxygen addition. This effect has been nicely explained by

![Figure 4.3 Variation of Mach number of the ion acoustic wave ($v/c_s$) as a function of oxygen partial pressure.](image)
Aijaz et al. [23] when adding a gas with a higher ionization potential compared to Ar. The electron saturation current reduces as a function of oxygen addition and in addition, the plasma potential decreases and the floating potential become more negative. The plasma potential is determined by using the zero second derivative of the I-V plot. It is defined as the voltage at which the second derivative, \( \frac{d^2I}{dV^2} \) goes to zero. The modulation of the plasma potential and the floating potential are shown in the Fig. 4.5. In a pure argon discharge, the plasma potential is found to be positive because the loss of highly mobile electrons leaves the plasma with a net positive charge. However, with the introduction of oxygen, the electron density decreases as electrons are replaced with negative oxygen ions. Although there is no change in the quasi-neutrality condition, a corresponding fall of plasma potential is observed in this case because negative oxygen ions have a smaller thermal velocity than the electron. Therefore, the loss rate of the negative species decreases,
and the bulk plasma adjusts itself to compensate for this loss rate. The modulation of the floating potential is found to be similar to that of the plasma potential.

Figure 4.5 Plasma potential and floating potential variations as a function of oxygen partial pressure in the discharge

As the oxygen added argon plasma consists of various types of positive (Ar$^+$, O$_2^+$ and O$^+$) and O$^-$ ions, rather than calculating the individual density we have obtained the group density. The procedure of dividing the ions into two groups and calculation of ion density using mean ion mass procedure was already explained in the Chapter 2. For oxygen added argon plasma, the heavy ion group consists of Ar$^+$ and O$_2^+$ while, O$^-$ ions are included in the light ion group. From the Langmuir probe I-V characteristics using the procedure followed in the Chapter 3, the total heavy ion density in the discharge can be easily evaluated, and is given in the Fig 4.6. In this investigation, the partial pressure of oxygen is much smaller than the partial pressure of argon (less than 1:10). Therefore, it is reasonable to expect that the Ar$^+$ ion density is greater than the oxygen positive ion density in this discharge. For
such multi-component plasma the density of ions varies as: \( n_{Ar} \gg n_{O_2}^+ > n_{O}^+ \) [14] where the symbol represents the density of the corresponding ions. However, with the addition of oxygen at a fixed argon partial pressure, the density of the oxygen positive ions should increase [24] for obvious reason. Since the majority of the charge carriers in the discharge are \( Ar^+ \) ions, the density modulation of heavy ions is more indicative of \( Ar^+ \) density variation as is found in the Fig. 4.6.

![Figure 4.6 Modulation of total heavy positive ion density as a function of oxygen partial pressure in the discharge.](image)

Optical emission spectroscopy (OES) is an excellent non-intrusive technique used to determine the concentration of plasma species. To a good approximation the emission intensity of a particular line of an element is considered to be proportional to the density of that particular species in a low pressure discharge [25-26]. The experimental arrangement to probe the plasma with optical emission spectroscopy is explained in details in the Chapter 2. The aim of the OES scan is to qualitatively investigate the density variation of
the $\text{Ar}^+$ as well as the $\text{O}^-$ ions in the discharge. In argon-oxygen magnetron discharge the most prominent excited species are: $\text{Ar}\ I$ lines corresponds to atomic argon emission (696.45 nm, 738.39 nm, 751.46 nm, 763.51 nm, 772.37 nm, 794.81 nm, 801.47 nm, 811.53 nm, 826.45 nm, 840.42 nm, and 852.14 nm), $\text{Ar}\ II$ lines correspond to $\text{Ar}^+$ ionic emission (434.80 nm, 454.15 nm, 472.68 nm, 476.48 nm, 488.0 nm), $\text{Ti}\ I$ line (499.5 nm, 510.53 nm), and excited oxygen atoms with characteristic emission lines at 777 nm and 845 nm [19].

Figure 4.7 The emission lines of the spectra collected for the oxygen added argon plasma at different oxygen partial pressure. The argon partial pressure was kept fixed at $8 \times 10^3$ Pa. The emitting species were identified by comparing with NIST database. The variation in the relative intensities $\text{O}\ I$ line could be observed.

The typical OES scan of the oxygen added argon plasma is shown in the Fig. 4.7. To estimate the value of degree of ionization and relative negative ion density, the intensity of
neutral excited species Ar, O and Ar$^+$ excited ions are considered at 751.46, 777 and 488 nm, respectively. By following the reaction given in Eq. (4.22), it is clear that the intensity of the emission line at 777 nm is representative of the relative density of negative oxygen ions in the discharge. The intensity ratios of the lines of the excited species of Ar$^+$ and O to the neutral line of Ar at 751.46 nm are given in the Fig. 4.8. This ratio is taken to remove any effect due to the evolution of the plasma parameters as a function of different discharge conditions, thereby creating a trend of modulation of the negative oxygen and Ar$^+$ ion concentration that is meaningful. It is clear from the Fig. 4.8 that the oxygen negative ion density increases linearly with oxygen partial pressure, while the Ar$^+$ ion density follows the opposite trend. This fact leads to a gradual increase in the relative in the relative concentration of oxygen negative ions as a function of the oxygen partial pressure.

Figure 4.8 Influence of oxygen partial pressure on the intensity (I) ratio of the 777 oxygen atomic line to 751.46 nm argon line and 488 Argon line to 751.46 nm argon line.
To benchmark the values of the relative negative ion concentration measured by the ion acoustic waves, we have substituted the values of positive ion density \( n_+ \) and electron density \( n_e \) as obtained by the Langmuir probe in Eq. (4.23). The ratios of the negative to positive ion density in our plasma are found to increase from 0.0318 to 0.0877 (Fig. 4.9). The similarity observed in the values \( \varepsilon \), measured by the Langmuir probe and the ion acoustic wave analysis justifies the effectiveness of the ion acoustic wave analysis as a probe for magnetron plasma discharge.

![Figure 4.9](image.png)

**Figure 4.9** Comparison of the ratio of oxygen negative ion to positive ions \( (\varepsilon) \) measured by Langmuir probe diagnostic and IAW diagnostic as a function of oxygen partial pressure in the discharge.

**4.6 Conclusion**

Ion acoustic phase velocity, wavelength and frequency have been the basis of various plasma diagnostics for a long time. In this investigation, we used the temporal behavior of ion acoustic waves to provide the relative negative ion concentration in magnetron discharge plasma. With the addition of oxygen into the pure argon discharge, a gradual
decrease of the electron density, plasma potential, floating potential and electron temperature are observed, indicating the presence of negative ions in this plasma. Optical emission spectroscopy further confirms the gradual increase of the negative ion density as a function of the oxygen partial pressure. The relative negative ion concentration is determined by exciting ion acoustic waves in the downstream region of the discharge, and the phase velocity of the ion acoustic wave is found to scale linearly with the increase of the oxygen partial pressure in the discharge. This corresponds to an increase of the relative negative ion concentration ($\varepsilon$) value from 0.042 to 0.082. We also calculated the values of $\varepsilon$ separately at each discharge condition using a cylindrical Langmuir probe. The measured values of relative negative ion density by the ion acoustic wave diagnostics and the Langmuir probe show good agreement.

References