CHAPTER 3

Study on the effect of target on the plasma parameters of hydrogen added argon DC planar magnetron plasma

This chapter contains the observations on the effects of target material and hydrogen addition in the evaluation of the plasma parameters in the substrate vicinity of the magnetron discharge plasma.

3.1 Introduction

In the magnetron sputtering the target is used as the cathode and it is bombarded by ions. The secondary electrons emitted from the magnetron target due to ion bombardment plays an important role in sustaining the discharge as well as determining the plasma parameters [1-3]. Amount of secondary electrons emitted per ion is known as the ion induced secondary electron coefficient (ISEE). Phels et al. [4] have shown that the ISEE coefficient strongly depends on the condition of the target material and independent of the bombarding ion types for ion energy below 500 eV. Most of the works in the literature using magnetron sputtering have commonly reported the properties of deposited films [5-7]. Many experimental and theoretical works have been performed on the physical properties [8] of magnetron discharge and its dependence on the process parameters like gas pressure, substrate biasing, electrical power etc. But very few reports are available about the dependence of the plasma parameters of the magnetron discharge on the target conditions namely; the target material and degree of chemisorptions in case of reactive sputtering [9]. The target conditions mostly depend on its ISEE coefficient values. The shape of the target current voltage (V-I) characteristics of a magnetron sputtering device is also dependent on the ISEE coefficient [9] that in turn influences the plasma parameters of the magnetron
discharge. Ion flux flowing to the substrate is affected by the ISEE coefficient values significantly. Several authors have published empirical relations for the ISEE coefficient as 

\[ \gamma_{ISE} = 0.032(0.78E_i - 2\phi) \]  \hspace{1cm} (3.1) \\
\[ \gamma_{ISE} = 0.16(E_i - 2\phi) \]  \hspace{1cm} (3.2) \\
\[ \gamma_{ISE} = 0.2(0.8E_i - 2\phi) / E_F \]  \hspace{1cm} (3.3)

Here, \( E_i \) is the ionization energy of the ion, \( \phi \) is the work function and \( E_F \) is the Fermi energy of the metal. Based on these empirical relations, an averaged value of 0.091 for Chromium (Cr) and 0.082 for Cupper (Cu) target materials are calculated. In this chapter, the experimental measurement of influence of the target material on the plasma parameters of the magnetron discharge is reported. Along with the target effect, the trend of modulation of the plasma parameters as a function of hydrogen addition is also studied. The addition of hydrogen is based on the fact that the use of hydrogen radicals as the reducing agents to improve the density and crystallinity of the transition metal nitrides thin films by the DC planar magnetron sputtering is getting an increased interest in the last few years [13].

Cu and Cr targets are selected because of their wide range of utility as coating materials and distinct ISEE coefficient values. Cr and Cu are sputtered deposited on Si(100) substrate in the argon-hydrogen (Ar/H₂) plasma at different discharge conditions. The working pressure and the applied input power are the two most important experimental parameters in magnetron sputtering. First, adding more hydrogen at a fixed argon partial pressure varies the working pressure. These types of experiments are interesting to understand the variation
of the plasma parameters of the discharge during sputtering. Second, at a fixed working pressure the V-I characteristics of the planar magnetron are determined by varying the input power. Finally, measured values of ion density, electron density, degree of ionization, and sputtering rate as a function of working pressure for both targets are reported here. In the section 3.2 the experimental set-up and diagnostics tools are discussed in detail. The variations of plasma parameters and other results obtained are presented in the section 3.3. In the conclusion section 3.4, the important findings of this work are summarized.

3.2 Experimental set up and diagnostic procedure

The details of the experimental set up to study the effect of target on the plasma parameters of the hydrogen added argon DC planar magnetron plasma have been described in the section 2.2 of Chapter 2. The water-cooled Cu and Cr target of diameter 70mm are used as the cathode of the planar magnetron sputtering system. The chamber is evacuated by a diffusion pump backed by a rotary pump up to base pressure of $10^{-4}$ Pa. During the deposition argon (Ar) and hydrogen (H$_2$) are fed into the deposition chamber by two digital mass flow controllers (DFC 26, AALBORG USA). Working pressure in the chamber is varied by increasing the hydrogen concentration [H$_2$] in the argon discharge from 0 to 18.9% at a constant argon flow rate (8.5 SCCM). The concentration of H$_2$ in feed gas is calculated comparing the partial pressure of both the gases. For different percentage of hydrogen flow rate, the total working pressure changes from $4 \times 10^{-1}$ Pa to $10 \times 10^{-1}$ Pa. Again at a constant working pressure ($4 \times 10^{-1}$ Pa), keeping the other conditions same, effective load power is varied from 50W to 350 W. The details of the currents and voltages at different discharge conditions for both Cr and Cu targets are given in Tables 3.1 and Table 3.2. Plasma parameters of the discharge are probed by a cylindrical probe with a
length of 3.0mm and a radius of 0.1mm. To estimate the value of degree of ionization and
the degree of dissociation in the hydrogen by measuring the intensity level of specific
emission, a 1/2 m digikrom spectrometer (CVI Laser Corp, USA. Digikrom Model DK
480) is used.

Table 3.1: Discharge Voltage and Current at various working pressures for Chromium and Copper

<table>
<thead>
<tr>
<th>Target</th>
<th>Chromium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working Pressure</td>
<td>Voltage (V)</td>
<td>Current(A)</td>
</tr>
<tr>
<td>(×10⁴Pa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>587</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>598</td>
<td>0.513</td>
</tr>
<tr>
<td>8</td>
<td>605</td>
<td>0.507</td>
</tr>
<tr>
<td>10</td>
<td>615</td>
<td>0.493</td>
</tr>
</tbody>
</table>

3.3 Results and discussions

To discuss the effect of the target material and hydrogen addition in the evaluation of the
plasma parameters in the substrate vicinity, knowledge of secondary electron density and
the various ionic processes in the hydrogen added argon plasma is very essential. Results
and discussion part of this chapter thus begins with discussing this two important aspects.

3.3.1 Variation of the secondary electron density in the ring region of the
magnetron discharge

There are two categories of electrons in the DC planar magnetron discharge: fast secondary
electrons (hot electrons emitted at the cathode) and bulk electrons created in the main
discharge region. Those electrons that have enough energy to ionize neutrals include mostly the fast secondary electrons. In the ring region [14] of the magnetron discharge, the hot secondary electrons are responsible for ionization of neutrals and thus eventually generating electrons in the plasma bulk and therefore determining the plasma parameters. Therefore, the determination of secondary electron density is the prime aspect for such investigation. Estimating the value of plasma density \( n \), within this ring region and using the data for the ionization cross-section for the secondary electrons, it is possible to determine the value of hot secondary electron density \( (n_s) \) [14]. The Bohm flux can be used to estimate \( n_i \) in the ring region of the discharge and can be given as,

\[
0.61en_iu_B = J_i, \quad (3.4)
\]

where the electron temperature \( T_e \) enters only weakly. Here \( J_i \) is the ion current density and \( u_B \) is the Bohm velocity of ions. Now the ion density \( (n_i) \) can be related to fast secondary electron density \( (n_s) \) within this region as,

Table 3.2: Discharge Voltage and Current at various applied powers for Chromium and Copper Target

<table>
<thead>
<tr>
<th>Target</th>
<th>Chromium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Power (Watt)</td>
<td>Voltage (V)</td>
<td>Current (A)</td>
</tr>
<tr>
<td>50</td>
<td>452</td>
<td>0.11</td>
</tr>
<tr>
<td>100</td>
<td>500</td>
<td>0.21</td>
</tr>
<tr>
<td>200</td>
<td>562</td>
<td>0.36</td>
</tr>
<tr>
<td>300</td>
<td>600</td>
<td>0.51</td>
</tr>
</tbody>
</table>

...
\[ n_i = n_a \nu \sigma_i \nu \]  \hspace{1cm} (3.5)

where \( \nu \) is the drift velocity of the electrons, \( n_a \) is the neutral density and \( \sigma_i \) is the ionization cross section for secondary electrons (\( \sim 5 \times 10^{-17} \text{ cm}^2 \)). Using the above-mentioned equation, the value of fast secondary electron density within the ring region is evaluated. It is observed that with increasing working pressure the secondary electron density decreases from \( 7.8 \times 10^{10}/\text{m}^3 \) to \( 2.67 \times 10^{10}/\text{m}^3 \) for Cr target and \( 6.67 \times 10^{10}/\text{m}^3 \) to \( 2.26 \times 10^{10}/\text{m}^3 \) for Cu target. While an opposite trend of rising secondary electron density from \( 3.34 \times 10^{10}/\text{m}^3 \) to \( 7.5 \times 10^{10}/\text{m}^3 \) for Cr target and \( 2.56 \times 10^{10}/\text{m}^3 \) to \( 6.67 \times 10^{10}/\text{m}^3 \) for Cu target as a function of increasing applied power (50 Watt to 350 Watt) is also found. As expected the value of ion density (of the order of \( 10^{17}/\text{m}^3 \)) is found to be much higher than hot secondary electron density (of the order of \( 10^{10}/\text{m}^3 \)) in this region of the discharge. Also, it is interesting to mention that the density of hot secondary electron decreases when hydrogen is added to the pure argon discharge. Using Langmuir probes diagnostics the densities of bulk electrons are measured in the substrate vicinity and results will be presented in the subsequent sections.

### 3.3.2 Description of ionic processes in H\(_2\) containing argon plasma

Study of basic gas phases is essential to understand the effect of H\(_2\) addition to pure argon plasma. When H\(_2\) is added to argon, besides Ar atoms (in ground state and excited to metastable states (Ar\(_m^*\)) at energy 11.2 ev), Ar\(^+\) ions, several hydrogen species including H\(^+\), H\(_2^+\), H\(_3^+\) ions; ArH\(^+\) ions, the ground state H atom, ground state H\(_2\) molecule and various electronically excited states of H\(_2\) molecules are also possible [15]. All those species in plasma undergo different chemical reactions with different rate constants and relative cross-
sections. The reactions that are essential for the domain of this work are mentioned in Table 3.3. With increasing hydrogen addition a drop in electron and Ar$^+$ ion densities are experimentally observed in literature [16-19]. On the other hand, the densities of hydrogen related ions, i.e., H$^+$, H$_2^+$, H$_3^+$ and ArH$^+$ are expected to increase with H$_2$ addition for obvious reasons. The effect is most pronounced for H$^+$, H$_2^+$, H$_3^+$ and is slightly less significant for ArH$^+$ ions.

Addition of Hydrogen in the argon plasma causes Ar$^+$ ion loss predominantly through the charge transfer (Reaction 1 in Table 3.3) or H atom transfer (Reaction 2 and Reaction 3 in Table 3.3) forming different hydrogen species (ArH$^+$, H, H$_2^+$) [15].

\[
\begin{align*}
Ar^+ + H_2 &\rightarrow Ar (fast) + H_2^+ \quad (3.6) \\
Ar^+ + H_2 &\rightarrow ArH^+ + H \quad (3.7) \\
Ar + H_2^+ &\rightarrow ArH^+ + H \quad (3.8)
\end{align*}
\]

The major loss mechanism for electrons in such plasma is the electron recombination with ArH$^+$ (Reaction 4 in Table 3.3), H$_2^+$ (Reaction 5 in Table 3.3) and H$_3^+$ (Reaction 6 in Table 3.3).

\[
\begin{align*}
e^- + ArH^+ &\rightarrow Ar + H \quad (3.9) \\
e^- + H_2^+ &\rightarrow H + H \quad (3.10) \\
e^- + H_3^+ &\rightarrow H + H + H \quad (3.11)
\end{align*}
\]

Reaction 2 and Reaction 3 are responsible for the formation of ArH$^+$ ions. In such plasma, the densities of H$_3^+$ ions are reported to be several orders of magnitude higher [20-21] than H$_2^+$ and H$^+$ densities in literature. H$_3^+$ ions are mostly formed through proton transfer (Reaction 7 and Reaction 8 in Table 3.3).
\[ ArH^+ + H_2 \rightarrow Ar(\text{fast}) + H_3^+ \]  
\[ H_2^+ + H_2 \rightarrow H + H_3^+ \]  

The Ar meta-stable atoms are mainly created by electron impact excitation (Reaction 9), followed by fast Ar\(^0\) impact excitation and fast Ar\(^+\) impact excitation and relative importance of these processes are more or less same. On the other hand, quenching upon collision with H\(_2\) (Reaction 10) is the main loss mechanisms [15] for Ar\(_m^*\) atoms.

\[ Ar + e^- \rightarrow Ar_m^* + e^- \]  
\[ Ar_m^* + H_2 \rightarrow Ar + H + H \]  

### 3.3.3 Plasma parameters as a function of working pressure

#### 3.3.3 (a) Langmuir probe measurement

The probe measurement is carried out in the downstream region at a distance of 80mm from the cathode, i.e., 10mm above the substrate keeping in mind about the fact that the ions present in this region most significantly affect the growth of thin film on the substrate. Plasma parameters such as the electron temperature \(T_e\), electron density \(n_e\), and ion density \(n_i\) are measured with the probe in practically magnetic field free region. The radius of the probe (0.1mm) was chosen such that it is greater than the calculated deBye length. A Teflon holder is used to cover the probe tip in order to avoid it being coated by sputtered target. Only during the duration of the Langmuir probe scan the probe tip is exposed to the magnetron discharge. Thus, the charge collection area of the Langmuir probe does not vary significantly during the deposition and the values of the plasma parameters is authentic.
Table 3.3: Ar⁺, ArH⁺, Ar⁺⁺ and Hydrogen like ion production and loss processes

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate Constant (K)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ar⁺⁺H₂ → Ar(fast) + H₂⁺</td>
<td>8.0 × 10⁻¹¹ cm³s⁻¹</td>
<td>Charge transfer [22]</td>
</tr>
<tr>
<td>2.</td>
<td>Ar⁺⁺H₂ → ArH⁺ + H</td>
<td>6.0 × 10⁻¹⁰ cm³s⁻¹</td>
<td>H atom transfer [22]</td>
</tr>
<tr>
<td>3.</td>
<td>Ar⁺ + H₂⁺ → ArH⁺ + H</td>
<td>1.7 × 10⁻⁹ cm³s⁻¹</td>
<td>Proton Transfer [22]</td>
</tr>
<tr>
<td>4.</td>
<td>e⁺ + ArH⁺ → Ar + H</td>
<td>1.7 × 10⁻⁷ cm³s⁻¹</td>
<td>Recombination [22]</td>
</tr>
<tr>
<td>5.</td>
<td>e⁺ + H₂⁺ → H + H</td>
<td>1.0 × 10⁻⁷ cm³s⁻¹</td>
<td>Recombination [22]</td>
</tr>
<tr>
<td>6.</td>
<td>e⁺ + H₃⁺ → H + H+H</td>
<td>1.0 × 10⁻⁷ cm³s⁻¹</td>
<td>Recombination [15]</td>
</tr>
<tr>
<td>7.</td>
<td>ArH⁺ + H₂ → Ar(fast) + H₃⁺</td>
<td>1.5 × 10⁻⁹ cm³s⁻¹</td>
<td>Proton Transfer [22]</td>
</tr>
<tr>
<td>8.</td>
<td>H₂⁺ + H₂ → H⁺ + H₃⁺</td>
<td>2.2 × 10⁻¹⁰ cm³s⁻¹</td>
<td>Charge Transfer [22]</td>
</tr>
<tr>
<td>9.</td>
<td>Ar⁺ + e⁻ → Ar⁺⁺ + e⁻</td>
<td>1.0 × 10⁻¹¹ cm³s⁻¹</td>
<td>Ionization [15]</td>
</tr>
<tr>
<td>10.</td>
<td>Ar⁺⁺H₂ → Ar⁺ + H + H</td>
<td>7 × 10⁻¹¹ cm³s⁻¹</td>
<td>Quenching dissociation [15]</td>
</tr>
<tr>
<td>11.</td>
<td>ArH⁺ + Ar → Ar(fast) + H⁺ + Ar</td>
<td>1.5 × 10⁻⁹ cm³s⁻¹</td>
<td>Induced Ionization [15]</td>
</tr>
<tr>
<td>12.</td>
<td>H⁺ + Ar → H(fast) + Ar⁺</td>
<td>2.2 × 10⁻¹⁰ cm³s⁻¹</td>
<td>Charge Transfer [15]</td>
</tr>
<tr>
<td>13.</td>
<td>H₂ + H⁺ → H(fast) + H₂⁺</td>
<td>2 × 10⁻⁹ cm³s⁻¹</td>
<td>Charge Transfer [15]</td>
</tr>
</tbody>
</table>

The typical Langmuir probe I-V plots for Ti, Cr and Cu target are shown Fig. 3.1. The electron \( (n_e) \) and ion density \( (n_i) \) are obtained from the electron and ion saturation current collected by the probe using the following equation,

\[
n_{ei} = \frac{I_{ei,i}}{A_p} \sqrt{\frac{2\pi m_{ei}}{e^3 k_B T_e}}
\]  

(3.16)

with \( A_p \) stands for the probe area, \( m_{ei} \) is either the electron \( (e) \) or ion \( (i) \) mass, \( k_B T_e \) is the electron temperature (in electron volts) and \( e \) the electronic charge. \( k_B T_e \) is calculated from...
retardation region of the I-V characteristic as the inverse slope of the logarithmic electron probe current with respect to the probe voltage. In order to explain the modulation of the plasma parameters as a function of working pressure (i.e., addition of hydrogen keeping argon partial pressure constant), it is necessary to compare the results with the pristine argon plasma. Evolution of electron density ($n_e$) and the ion saturation current density ($I_{sat}(V)$) with working pressure for pristine and hydrogen added argon plasma are shown in the Fig. 3.2. It can be seen that there is a gradual increase of electron density for both the targets in the pristine argon plasma. But the hydrogen addition reduces $n_e$ from $1.4 \times 10^{15}$ m$^{-3}$ to $6.46 \times 10^{14}$ m$^{-3}$ for Cr and $9.5 \times 10^{14}$ m$^{-3}$ to $5.8 \times 10^{14}$ m$^{-3}$ for Cu target, respectively. As the electron density decreases as a function of working pressure the

Figure 3.1 Typical Langmuir probe I-V characteristics traced at working pressure $4 \times 10^{-1}$ Pa for hydrogen added argon plasma for titanium, chromium and copper magnetron target. Input power (P) = 300W for each target.
Figure 3.2(a) Variation of electron density ($n_e$) as a function of working pressure for Cr and Cu target for pristine argon plasma. (b) Variation of electron density ($n_e$) and ion saturation current density as a function of working pressure for Cr and Cu target for hydrogen added argon plasma. Ion density should follow the similar behavior if one refers to the quasi neutrality property of plasma. With this consideration, it is found that the ion saturation current ($I_n(V)$) declines with hydrogen enrichment in argon plasma. The decreasing value of electron density reflects major electron loss rate when H$_2$ is added to Argon plasma. In Ar-H$_2$ plasma the dissociative recombination reactions between electrons and molecular ions (H$^+$, H$_2^+$ and H$_3^+$) formed in the plasma tend to more pronounce than am-bipolar diffusion and Ar$^+$-electron recombination [18,23]. Due to presence of these additional loss processes with hydrogen introduction in such plasma, the electron consumption rate becomes more significant than the various electron production processes. As a result $n_e$ drops as a function of working pressure and this fact can be represented mathematically by the following equation:
\[
\frac{dn_e}{dt} = k_{\text{recom}} n_e n_{Ar} - \sum_i k_{\text{recom}} n_i n_{\text{Htrans}} < 0 \tag{3.17}
\]

Here, \(n_{Ar}\) is the density of neutral argon atoms, \(k_{\text{recom}}\) is the rate constant of electron recombination with the hydrogen-like ions [Eq. (3.9) to Eq.(3.11)], \(n_{\text{Htrans}}\) is the density of hydrogen-like ions and \(k_{\text{ion}}\) is the rate constant for the ionization of argon atom by electrons. For such plasma, a prominent change in electron temperature is also observed. With increasing working pressure, the value of electron temperature increases significantly from 3.3 eV to 6.6 eV for Cr and from 5.20 eV to 7.8 eV for Cu. Since in the ohmic heating regime there is an inverse relation between \(n_e\) and \(T_e\), the observed gradual increase of \(T_e\) upon hydrogen addition can be easily understood [Fig. 3.3].

![Figure 3.3 Influence of working pressure on the variation of electron temperature (\(k_B T_e\) in eV) for Cr and Cu target.](image)

The higher value of the bulk electron density in the magnetron discharge with Cr target than Cu target is due to its high ISEE coefficient value (0.091) compared to Cu (0.082). By particle simulation Kondo et al. [9] have shown that the plasma density in the bulk region
of the plasma is larger for higher value of ISEE. As the electron density value is higher for Cr compared to Cu one could expect lower value of electron temperature. As Ar/H₂ plasma contains various ion species (Ar⁺, ArH⁺, H⁺, H₂⁺, H₃⁺ etc.), it is not possible to determine the density of each ion individually using the Langmuir probe. Also, due to the presence of these ionic species the use of argon ion mass in the calculation for ion density is not valid. As such, we have divided the ions present in such discharge into two groups based on their masses. A heavy group of mass 40 a.m.u (Ar-like ions) consisting of Ar⁺ and ArH⁺ ions and a light group of mass 2 a.m.u (Hydrogen-like ions) consisting of H⁺, H₂⁺, H₃⁺. Rather than calculating the density of each ion, the density of each group is calculated following the mean ion mass procedure as developed by Laidani et al [24]. As explained in Chapter 2, using the ion saturation current (Iᵢ(V)), electron temperature (k_BTₑ) and ion density (nᵢ) values, the mean ion mass is calculated [24] and the trend of its variation as a function of working pressure is found to be similar for both types of targets [Fig. 3.4 (a)].

![Figure 3.4 Variation of (a) mean ion mass and (b) Ar like ion density as a function of working pressure for Cr and Cu target.](image)
It is clear from the figure that presence of hydrogen-like ion decreases the mean ion mass from 40 a.m.u to 25.11 a.m.u for Cr target and 40 a.m.u to 26.42 a.m.u for Cu target, respectively. From the above data and using the fact that total ion density ($n_i$) is the sum of Ar-like ($\text{Ar}^+$, $\text{ArH}^+$) and hydrogen-like ions ($\text{H}^+$, $\text{H}_2^+$, $\text{H}_3^+$), Ar like ion density is calculated and given in the Fig. 3.4 (b). Ar like ion density decreases linearly with the hydrogen percentage enrichment in the discharge. Addition of hydrogen in the argon plasma reduces $\text{Ar}^+$ ion predominantly through charge transfer between $\text{Ar}^+$ and $\text{H}_2$ (Reaction 1 in Table 3.3) or H atom transfer between the between the same (Reaction 2 in Table 3.3). This trend is found to be similar for both types of targets. The observed enhanced value of Ar like ion density for Cr target than Cu target in the discharge is due to higher ISEE coefficient of Cr than Cu.

3.3.3 (b) Optical emission spectroscopy study

The Langmuir probe scan of the plasma at the mentioned discharge condition reveals a decrease of Ar-like ion density in the discharge. As the argon partial is kept constant, it is reasonable to expect a decrease of degree of ionization of argon in such discharge. This fact is qualitatively examined by the optical emission spectroscopy study. In the low pressure plasma discharge, the intensity of spectral emission line is closely related to the density of the species and hence is often used to deduce the evaluation of density [25]. Thus, the line intensity ratio between two suitable spectral lines can be used to estimate the value for degree of ionization of Ar and degree of dissociation $\text{H}_2$. The experimental arrangement for collection of emission intensity from the magnetron discharge was shown in the Fig. 2.11 of the Chapter 2. The emissions are collected by a light collecting system (LCS)
through an optical fiber (F). The variations in the intensity of different species with hydrogen composition are observed with the LCSF placed at a vertical distance of 8 cm below the cathode surface. **Fig. 3.5** shows the comparison between argon and argon added hydrogen spectra. In the argon-hydrogen magnetron discharge the most prominent excited species are: 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), Ar II lines correspond to Ar$^+$ ionic emission (434.80 nm, 454.15 nm, 472.68 nm, 476.48 nm, 480.60 nm) H$_a$ line (656.28 nm) and H$_\beta$ line (487.54 nm). Here, the intensity ratio of argon spectral line at 476.4 nm (Ar II) to at 751.46 (Ar I) ($\delta$) is used to estimate the value of degree of ionization. These two lines are selected as the excitation thresholds are very close and the transition probabilities ($6.4 \times 10^7$ s$^{-1}$ at 476.48 nm and

![Figure 3.5](image-url)  

**Figure 3.5** The emission lines of the spectra collected for the pristine (black line) and hydrogen added argon plasma (red line) at the working pressure of ($4.0 \times 10^4$ Pa). The emitting species were identified by comparing with NIST database.
4.0×10^7 s\(^{-1}\) at 751.46 nm) are almost similar [26, 27]. Also, the intensity ratio of H\(_a\) line (656.28 nm) to Ar(I) line (811.53 nm) can be used to determine the value for degree of dissociation (f\(_D\)) of H\(_2\). Fig. 3.6 shows the variation of Ar I line (751.46 nm), Ar II line (476.48 nm), H\(_a\) line (656.28 nm), Ar(I) line (811.53 nm) intensity as a function of working pressure for the Cr and Cu target respectively. It is clear from the Fig. 3.6 that the intensity of Ar I and Ar II lines decreases with hydrogen addition. The intensity of H\(_a\) line increases rapidly in comparison to the intensity of H\(_\beta\) line. The energy required for direct excitation by electron from ground state to H\(_a\) is 12.1 eV, where as for H\(_\beta\) excitation is 12.7 eV [30]. This explains the faster increase in intensity of H\(_a\) line than the intensity of H\(_\beta\) line.

![Figure 3.6 Observed Intensity (I) of atomic argon line at 476.48nm (Ar II), 751.46nm (Ar I), 811.53nm (Ar I) and H\(_a\) line (656.28 nm) as a function of working pressure (a) Cr target (b) Cu target.](image)

**Figure 3.6 Observed Intensity (I) of atomic argon line at 476.48nm (Ar II), 751.46nm (Ar I), 811.53nm (Ar I) and H\(_a\) line (656.28 nm) as a function of working pressure (a) Cr target (b) Cu target.**

Fig. 3.7 shows that with increase of working pressure, \(\delta\) decreases from 7.1×10\(^2\) to 5.8×10\(^2\) for Cr and 4.3×10\(^2\) to 3.6×10\(^2\) for Cu target. The decline of the value of \(\delta\) as a function of working pressure indeed justifies the trend of Ar-like ion density variation in such plasma. It is reasonable to find higher value of \(\delta\) for Cr to Cu irrespective of discharge
condition. As electron impact ionization of Ar atom is major production mechanism for Ar$^+$ ions, higher electron density for Cr will naturally lead to enhanced value for $\delta$ compared to Cu.

![Graph showing variation of intensity ratio $\delta$ as a function of working pressure.](image)

**Figure 3.7** Variation of the intensity ratio ($\delta$) as a function of working pressure.

The variation of $f_D$ as a function of working pressure is given in **Fig. 3.8**. It can be seen that $f_D$ decreases from 7.2% to 2.94% for Cr and 2.8% to 2.35% for Cu target with hydrogen enrichment in the discharge. In Ar/H$_2$ plasma, the dominant production of H atoms is due to the dissociative excitation of H$_2$ molecules by Ar$_m^*$ atoms [15]. With the addition of H$_2$, the density of Ar$_m^*$ atoms decrease continuously. As the quenching dissociation (due to Reaction 10 in **Table 3.3**) is the most important mechanism for formation of H atoms, it indeed explains the gradual drop in $f_D$. Here also, we have observed a relatively higher value of $f_D$ for Cr target compared to Cu.

**3.4 Influence of target material on V-I characteristics of magnetron discharge**

The Langmuir probe study reveals the higher electron and ion density in the lower working pressure condition. Keeping this fact into account, the variation of input power was done at a fixed working pressure of $4 \times 10^{-1}$ Pa. These types of experiments are interesting to under-
stand the dependence of steepness of the V-I characteristics on the magnetron target during sputtering. The V-I characteristics of magnetron discharge have been proposed by Westwood et al. [31] as,

\[ I = \beta (V - V_0)^2 \] (3.18)

with \( V_0 \) is minimum voltage required to maintain the discharge, \( \beta \) is a constant which is a measure of the steepness of V-I characteristics and \( I \) is the discharge current that comprises mainly of ion current. Value of \( \beta \) can be determined by a linear fit to the square root of current \( (I) \) as a function of the discharge voltage. Based on a PIC/ MC simulation, Kondo et al. [32] concluded that the effect of the ISEE coefficient on the magnetron discharge is qualitatively analogous to the DC glow discharge. Their simulations show that at constant discharge voltage, a higher ISEE coefficient results in a higher plasma density. A higher plasma density results in lower plasma impedance [9], and therefore, a higher
value of $\beta$ is expected in this case. Now, at fixed working pressure of $4 \times 10^{-1}$ Pa, the $V$-$I$ characteristics of both the targets are plotted in the Fig. 3.9 and $\beta \, (\times 10^5 \, V/A^2)$ values are found to be 34.1 for Cr and 21.9 for Cu. Higher value of $\beta$ for the Cr target justifies its superior electron and ion density in the magnetron discharge compared to the Cu target.

![Figure 3.9 - $I$-$V$ characteristics at working pressure of $4 \times 10^{-1}$ Pa.](image)

3.5 Hydrogen effect on the film deposition rate

In order to correlate the observed trend of plasma parameters with physical nature of sputtering process, we have measured the deposition rate for various discharge conditions. The result is given in the Fig. 3.10. It is seen that the sputtering rate is maximum with pure argon plasma compared to hydrogen additive Ar plasma. Addition of hydrogen gradually decreases the sputtering rate from 2.6 $A^0 \, s^{-1}$ to 2.1 $A^0 \, s^{-1}$ for Cr and 5.6 $A^0 \, s^{-1}$ to 4.3 $A^0 \, s^{-1}$ for Cu target, respectively. The sputtering yield of Cr/Cu target to Ar$^+$ and Ar (fast) atoms is greater than to hydrogen-like ions. From the OES and Langmuir probe study, it is clear that the addition of hydrogen in pure argon plasma leads to decrease of degree of ionization of Ar and corresponding density of the Ar like ions. Due to this fact, the drop of sputtering rate as a function of the working pressure is seen. It is interesting to find higher deposition
rate for the Cu target compared to the Cr target at particular deposition condition as sputtering yield of Cu to Ar ($S = 2.3$) is higher than Cr($S = 1.3$) to Ar.

![Graph](image)

**Figure 3.10** Influence of working pressure on deposition rate for Cr and Cu target.

### 3.6 Conclusion

The effect of target on the plasma parameters of the magnetron discharge as a function of working pressure is described in this chapter. For better film deposition the plasma parameters like electron temperature, electron density, degree of dissociation and ionization are key factors. From the Langmuir probe study, it is found that with addition of hydrogen in pure argon plasma, the densities of electrons and Ar like ions drop gradually. On the other hand, a corresponding increase in $T_e$ is observed. To cross check the results we have also performed the OES study which also reveals a gradual decline of the degree of ionization of Ar as well as the degree of dissociation of H$_2$ as a function of working pressure. From the present study, it is clear that the addition of H$_2$ in the pure argon plasma reduces the sputtering rate. Also it is seen that the ISEE coefficient plays a crucial role in
determining plasma parameters while its effect on the sputtering rate of the target material is not observed. The increased value of electron density ($n_e$), ion density ($n_i$), degree of ionization of Ar and degree of dissociation of H$_2$ for Cr compared to the Cu target is explained on the basis of its higher ISEE coefficient value.

References


