CHAPTER 2
Experimental set up

The details of the magnetron setup for depositing the elemental and compound coatings and the deposition parameters chosen for various types of coatings are described in this chapter. Section 2.1 describes the basic considerations in a magnetron discharge, section 2.2 describes the DC planar magnetron set-up used with details of the pumping systems, the arrangement of the magnetron and the substrate, section 2.3 describes various diagnostic tools and techniques, section 2.4 describes the initial plasma characterization experiments done to understand the deposition characteristics of the magnetron for future deposition experiments. As thin film deposition of titanium nitride (TiN) is done on plasma nitrided substrate, a schematic diagram of the experimental setup for plasma nitriding with detailed procedure is given in section 2.5.

2.1 Basic consideration for magnetron operation

The discharge voltage \( V \) that is required to drive the discharge current \( I \) through the magnetron system is a function the system pressure \( p \) \( [1] \). The rate of the thin film formation on the substrate will depend on the amount of sputtering of the target which in turn will depend on the ion flux at the target and on the discharge current. The choice of the sputtering pressure \( p \) and the implied choice of the V-I characteristics are thus important and following section discusses the criterion in selecting the basic parameters and deciding on the nature of the sputtering gas.

2.1.1 Choosing the sputtering gas

As long as the actual sputtering process is concerned, it does not really matter whether we use neutral atoms or ions, but as it is easy to accelerate the ions to the energies required for
sputtering by an electric field, normally ions are used. It is much easier to ionize atoms when they are in the gaseous state; it is obvious to use gases for ion sources. The inert gas will give the highest sputtering yield compared to the other gases [1]. Among the inert gases argon is almost always used in sputter deposition because it is easily available, cheaper and the sputtering yield is only a factor or two down on xenon at sputter deposition energies [2].

2.1.2 Choosing the pressure range

As mentioned in the Chapter 1, the use of magnetic field in the magnetron sputtering device increases the ionization efficiency and hence, the deposition rate is enhanced. Both the glow discharge and film deposition by the sputtering impose the operating pressure limitation. The upper limit of the operating pressure in the magnetron device is set up by the requirement that the minimum target-substrate separation should be equal to the mean free paths of the sputtered neutral collisions with the neutral gas atoms \( \lambda_{N-Ar} \). For sputtered target atoms, the neutral-neutral collision cross-section is observed to be \( \sigma_{N-Ar} = 2 \times 10^{-20} \, \text{m}^2 \) [2]. The mean free paths \( \lambda_{N-Ar} \) is expressed as,

\[
\lambda_{N-Ar} = \frac{1}{n\sigma_{N-Ar}}
\]

Now, for reasonable value of 10 cm as the target-substrate separation (therefore equal to mean free path) and inserting the value of \( \sigma_{N-Ar} \) in Eq. (2.1), we get \( n = 5 \times 10^{20} \, \text{m}^{-3} \) where \( n \) is the neutral argon density and it corresponds to an operating pressure of \( 2.07 \times 10^{-2} \, \text{mbar} \). The glow discharge sets a lower pressure limit. The discharge is sustained by the secondary electrons making ionization collisions with the neutral gas. The number of
ionizing collision decreases with decreasing gas density and hence the gas pressure. Thus a minimum value of the gas pressure exists in order to sustain the glow discharge [3].

2.1.3 Choosing the electrical conditions for the glow discharge

In order to choose electrical condition for planar magnetron sputtering we have to take into account the following factors

(a) Sputtering yield ($\Lambda_{\text{sput}}$) within the allowed pressure range for sputtering.

(b) Sputtering yield per unit energy input ($\Lambda_{\text{sput}} / E$).

(c) Safety and economy of the process which means lower operating voltage.

Fig. 2.1 shows the apparent sputtering yield of a magnetron target (Nickel) as a function of the working pressure. It is clear from the figure that within the allowed range of the operating pressure (below 20 mtorr) the sputtering yield is almost independent of the gas pressure.

![Figure 2.1 Variation of the apparent sputtering yield of the nickel Vs argon gas pressure [4].](image-url)
The rate of the sputtering also depends on the flux of ions and energetic neutrals. The target current consists of the ion flux as well as secondary electrons reaching the target. Fig. 2.2 shows the sputtering yield of the target per unit energy input.

![Sputtering Yield Per Unit Energy](image)

**Figure 2.2** Variation of the sputtering yield per unit energy input for argon with ion energy [5].

According to the predictions of the sputtering target kinetics [5] the sputtering yield increases linearly up to 1keV and after that it is fairly constant. If so, then sputtering yield per unit energy should be a constant and this seems to be the case below 100 eV (Fig. 2.2) and after 1keV, the ratio falls with increasing energy. It is clear from the Fig. 2.2 that above 1keV and below 100eV; it is not expected to sputter very rapidly. In practice a lower limit of 500V is used to achieve adequate current density (0.1-2.0 mA cm\(^{-2}\)) and the upper limit above 5kV is rarely been used.

### 2.2 DC planar magnetron set-up

A cylindrical vacuum chamber made of SS 304 mounted with a planar magnetron of target diameter 75 mm is used as the deposition setup. The diameter of the chamber was 350 mm and the length was 400 mm. The photograph of the device with the accessories for the
pumping, pressure measurement, and plasma diagnostics is shown in the Fig. 2.3 and the schematic diagram of the set up is shown in the Fig. 2.4.

![Fig. 2.3: Photograph of the deposition chamber, with the attached display panel of the magnetron bias power supplies. (A) Planar magnetron (B) Diffusion pump (C) Rotary pump (D) DFC (E) Gas cylinder (F) Pressure gauges (G) Planar magnetron power supply (H) Langmuir probe (I) Optical emission spectroscopy port](image)

2.2.1 Vacuum chamber and accessories

The chamber had an approximate volume of 30 liters and is pumped with a combination of diffusion pump (Make: Hind High Vacuum, Bangalore, India; Model: ULK-06 1000 lps) backed by a rotary pump (Make: Hind High Vacuum, Bangalore, India; Model: ULK-06 585 l/min). A Baffle valve is provided to hinder the entry of oil vapors to the chamber during its
operation. A gate valve is provided on the inlet of the diffusion pump to maintain the low pressure inside the chamber while the chamber was kept idle. The maximum base pressure attained is $1 \times 10^{-6}$ mbar. The pressure is measured using Penning and Pirani gauges and a capacitive manometer attached to one of the axial ports. Argon gas of high purity (99.99%) is used as the sputtering gas for the magnetron targets. For the reactive deposition, the reactive gas such as nitrogen and oxygen are introduced from one of the axial ports. It is done in order to minimize the target poisoning effect [6]. All the gases are introduced into the deposition chamber using gas flow controllers at suitable flow rates to maintain the operating pressure. In one set of experiment hydrogen is also used as the sputtering gas along the argon magnetron discharge. A deposition rate cum thickness monitor (DTM 101, 52
Hind High Vacuum) is mounted on one of the axial ports and could be positioned at various locations below the magnetron at the substrate plane to measure the deposition rate directly as a function of the various operating parameters. The deposition rate measurement is useful to determine the optimum operating parameters of the magnetron.

2.2.2 The planar magnetron and substrates

The planar magnetron used for sputtering the target material is mounted on the vertical port. Targets of diameter 75 mm and approximate thickness 5 mm are mounted on the magnetron cathode. The photograph of the planar magnetron is given in Fig. 2.5.

Figure 2.5(a) Photograph of the planar magnetron, with the attached display panel of (A) Water inlet (B) Shutter (C) Sputtering gas inlet (D) Biasing port (b) Normal view of the planar magnetron. One can easily notice the race-track formed on the target surface.

For the deposition experiments conducted in the study, metallic targets of Titanium (99.99% purity), Chromium (99.95% purity) and Copper (99.95% purity) are used as the magnetron targets and operated in the DC mode (see Fig. 2.6). The magnetron is provided with a mechanical shutter positioned in front of the target. When the magnetron is operated
in the 'closed state' the entire sputtered flux is deposited on the surface of the shutter and only by turning the shutter by more than 90° the magnetron could be brought into an 'open state' such that the deposition can be done on the experimental substrate.

Before commencing the deposition, the magnetron is operated for a few minutes with the shutter in the closed state to sputter off any possible oxide layers formed over the target. A stainless steel disk of diameter 80mm is used as a substrate holder mounted from one of the ports of the chamber using suitable vacuum feed-through. The substrate holder could be positioned at various locations below the magnetron target plane during deposition.

Figure 2.6 Photograph of the planar magnetron targets used in the various experiments of this investigation.

The magnetron is to be operated in the DC mode and the bias power supply is designed accordingly. The specifications of the DC supply used are as follows.

Voltage range: 0 to -1000 V

Current range: 0 to 3A
2.2.3 Calculating the pumping speed and flow rate of gas flow controller

For a chamber made up of electro-polished SS 304 of effective surface area \((A)\) \(4 \times 10^4\) cm\(^2\) and out gassing rate \((R)\) of \(4.3 \times 10^{-9}\) mbar ls\(^{-1}\) cm\(^2\) [7], the total gas load \((Q)\) is given by,

\[
Q = R \times A \tag{2.2}
\]

The required pumping speed \((S)\) is defined as [8],

\[
S = \frac{Q}{P} \tag{2.3}
\]

with \(P\) is the base pressure in the chamber. For typical magnetron operation a base pressure of \(1.0 \times 10^{-6}\) mbar is required. Then, using the Eq. (2.3) the pumping speed of the chamber is calculated as 172 ls\(^{-1}\). But the efficiency of a pump decreases with increasing pressure in the chamber and the pumping speed is significantly lower at the working pressure (1-5 \(\times\) \(10^{-3}\) mbar) condition applicable for magnetron operation. Taking into accounts various other factors such as secondary out gassing source etc., the effective pumping speed should be at least 2-3 times of the calculated value. In practice for such chamber dimension, a diffusion pump of 1000 ls\(^{-1}\) capacity is sufficient enough to achieve such working pressure. Such pump cannot be exposed to atmospheric pressure as the exhaust pressure need to be in molecular flow regime and the additional drag on the fan is reduced. Hence such fore pump is backed by a rotary pump connected in series with the pump and the chamber. The condition of constant throughput is given as,

\[
S_1 P_1 = S_2 P_2 \tag{2.4}
\]

Here, \(S_1 = 172\) ls\(^{-1}\) and \(P_1 = 3 \times 10^{-3}\) mbar. Taking into account the value of lower pressure attained by such pump (5 \(\times\) \(10^{-2}\) mbar) as \(P_2\), the required pumping speed for the backing
pump is calculated as, 10.32 ls\(^{-1}\).

The gas flow rate into the chamber through the mass flow controller is balanced by the pumping speed giving stable chamber pressure and in this respect the Eq. (2.4) becomes,

\[ S_{MFC} \times P_{\text{atm}} = S_{\text{pump}} \times P_{\text{chamber}} \quad (2.5) \]

With \( P_{\text{atm}} = 1000 \text{mbar}, S_{\text{pump}} = 172 \text{ls}^{-1} \) and \( P_{\text{chamber}} = 5 \times 10^{-3} \text{mbar} \), the required flow rate,

\[ S_{MFC} = 8.6 \times 10^{-4} \text{ls}^{-1} = 50 \text{SCCM}. \]

In practice the required total gas flow rate to maintain the chamber of the mentioned dimension at \( 5 \times 10^{-3} \text{mbar} \) is 15 SCCM.

2.3 Plasma diagnostic tools and techniques

The diagnostics mainly used in this experimental work are the Langmuir probe (Cylindrical as well as Plane), Optical emission spectrometer (OES) and Ion Acoustic Waves (IAW). The Langmuir probe is used for determination of the plasma parameters like density and temperature. The IAW diagnostic is used to determine the relative density of negative ions present in such discharge using the phase velocity of the ion acoustic waves. Optical emission spectroscopy is performed to determine the degree of ionization and dissociation of various species of the plasma using the relative intensity of emission line present in the OES spectrograph.

2.3.1 Langmuir Probe

A Langmuir probe is a device named after physicist Irving Langmuir and used to determine the physical properties of the plasma such as the electron temperature, electron density, and electric potential. It works by inserting one or more electrodes into plasma. A constant or time-varying electric potential is applied between the various electrodes or between them.
and the surrounding vessel. The measured currents and potentials in this system determine the physical properties of the plasma. Cylindrical, spherical as well as planar Langmuir probe are used for the measurement of plasma parameters. The electrode that is inserted in the plasma is commonly known as the ‘probe tip’. For cylindrical Langmuir probe, a tungsten filament of length of 3.0 mm and a radius of 0.1 mm and for the planar Langmuir probe a stainless steel disc of diameter 6mm are used as the probe tip. The probe dimension took into account the following considerations,

1. It is ensured that the calculated deBye length ($\lambda_d$) for a plasma with electron temperature 1-5eV and density $10^{15}$ m$^{-3}$ is smaller than the probe radius.

2. The mean free path of collision of the electrons and ions is much larger than the Langmuir probe radius.

The electric connection with the probe tip is ensured with a Teflon coated conducting wire placed inside a stainless steel cylindrical pipe of diameter 7mm. Since the magnetron plasma contained in it the metallic species sputtered from the target, the probe tip upon exposure to the plasma had the tendency to get coated with a conducting film and consequently increasing the effective collecting area, an important parameter for calculating the plasma density. To overcome this concern, the probe tip is fixed at the end of a shaft using holders with a Teflon cap. The Teflon cap insure that the charge collecting area of the probe does not change significantly during prolonged deposition. The block diagram of the modified probe holder is shown in Fig. 2.7. This technique ensures that the charge collecting area of the probe is almost invariant during deposition [9]. The Langmuir
probe is suitably biased (-80 V to +80 V) to the \((I-V)\) characteristic with the electron and
the ion saturation region.

![Figure 2.7 Schematic block diagram of the (a) Cylindrical Langmuir probe (b) Planar Langmuir probe](image)

A typical \((I-V)\) characteristic curve of the magnetron plasma obtained from the Langmuir
probe is sketched in the **Fig. 2.8**. Referring to the probe characteristic of the **Fig. 2.8** we see
that in the region where the probe potential \((V_b)\) is above the plasma space potential \((V_p)\),
the collected current has contribution from the electrons only and the ions are repelled,
while in the magnified region just the opposite occurs and the collected ion current reaches
a saturation value \((I_n)\). By evaluating the slope of the \(I-V\) characteristic in the transition
region the electron temperature \(T_e\) is obtained. By measuring the ion or electron saturation
current and the substituting the value of electron temperature the density can be computed.
The expression of the ion saturation current \((I_n)\), electron saturation current \((I_e)\), floating
potential \((V_f)\) and plasma potential \((V_p)\) is mentioned below [10]. Also, the procedure to calculate the ion density in the presence of two or more gases in the plasma is explained.

Figure 2.8 Typical Langmuir probe I-V characteristics is traced and the values of \(V_p\) (plasma potential) \(V_f\) (floating potential) and the ion saturation current can be easily obtained from the figure.

2.3.1(a) The electron saturation current

The electron saturation current region is the region where all the electrons are collected by the probe. The electron saturation \((I_{\alpha})\) is given by the expression,

\[
I_{\alpha} = -n_e e A \left( \frac{k_B T_e}{2 \pi m_e} \right)^{1/2}
\]

(2.6)

2.3.1(b) The ion saturation current

In order to obtain the ion saturation value the probe voltage must be negative enough to repeal all the electrons. For that the probe voltage should have a magnitude near \(k_B T_e / e\), the electron energy. The sheath criterion requires that ions arriving at the periphery of the
probe sheath be accelerated towards the probe tip with Bohm velocity \([11]\). With all these conditions the ion saturation current expression becomes,

\[ I_{\text{s}} = 0.6n_eA \sqrt{\frac{k_B T_e}{m_i}} \]  \hspace{1cm} (2.7)

where \(m_i\) is ion mass. The net probe current is given by,

\[ I(n) = I_{\text{s}} - n_eA \frac{k_B T_e}{2\pi m_e} \exp\left(\frac{eV}{k_B T_e}\right) \]  \hspace{1cm} (2.8)

where \(V = V_b - V_p\). Thus, the electron current increases exponentially until the probe voltage equals to the plasma potential.

2.3.1(c) Floating potential

Floating potential is defined as the value of biasing potential when the electron and ion currents are equal and the net probe current \((I(V))\) is zero. From the Eq. (2.8) the value of the floating potential \((V_f)\) is given by,

\[ V_f = V_p - \sqrt{\frac{k_B T_e}{m_i}} \ln\left(\frac{m_i}{2.3m_e}\right) \]  \hspace{1cm} (2.9)

2.3.1(d) Mean ion mass \((M_i)\) and ion density measurement in multi-component plasma

In the reactive sputtering when reactive gas such as nitrogen is added, in addition to \(\text{Ar}^+\) ions the plasma will consists of various other types of positive ions such as \(\text{N}^+, \text{N}_2^+, \text{N}_3^+, \text{N}_4^+\) etc. Similar condition prevails when nitrogen is substituted by hydrogen in magnetron discharge. Hydrogen added argon plasma consists of various hydrogen containing species like \(\text{H}^+, \text{H}_2^+, \text{H}_3^+, \text{ArH}^+\) etc. Due to the presence of these ionic species it is not possible to
determine the density of each ion individually using the Langmuir probe. Also the use of argon ion mass in the calculation for ion density is no longer possible in this case. The possible way to determine the densities of ions in such plasma is to divide the ions present in the discharge into two groups based on their ionic masses [12-14]. In that case rather than calculating the density of each ion, the density of each group can be calculated. For example the hydrogen added argon plasma can be divided into two ion groups: a heavy group of argon like ions (Ar$^+$ and ArH$^+$ ions) of mass 40 a.m.u and a light ion group of hydrogen like ions (H$^+$, H$_2^+$, H$_3^+$) having mass 2 a.m.u. The group density is represented by the mean value of masses known as the ‘mean ion mass’. To determine the density of ions belonging to each group at different discharge conditions the procedure is as followed:

1) From the Langmuir probe $I-V$ characteristics the value of $n_e$, $T_e$ and $I_0$ are determined for the pristine argon plasma at various deposition conditions.

2) The values of $n_e$, $T_e$ and $I_0$ are determined for hydrogen or nitrogen added argon plasma at the same deposition conditions.

3) Comparing the values of plasma parameters of the later with pristine argon plasma using the Eq. (2.7), the value of ion mass for multi-component plasma at a particular deposition condition is determined. Since we are comparing it with the pristine argon plasma having ion mass 40 a.m.u, the obtained value of mean ion mass is the representative of the heavy ion group. For example, at a particular deposition condition for pristine argon plasma the value of ion mass $m_0 = 40$ a.m.u. Substituting the values of electron density, temperature and ion saturation current from the Langmuir probe $I-V$ characteristics for
hydrogen or nitrogen added argon plasma at the same condition in the Eq. (2.7) and comparing it with the pristine argon plasma we have,

$$M_i = \frac{40 \times T_e}{n_e I_u} (\frac{n_e I_u}{n_e I_u})^2$$

(2.10)

where \(M_i\) is the mean ion mass for hydrogen or nitrogen added argon plasma and \(n_e, T_e, I_u\) are the values of electron density, temperature and ion saturation current of the same. It will be found in the subsequent chapters that the values of mean ion mass decrease with addition of gases like nitrogen or hydrogen in the argon plasma.

(4) Once the mean ion mass is determined comparing it with the values of pristine argon plasma, the contribution of each group of ions in the discharge can be easily evaluated using the following equation,

$$n_{hary} = \frac{n_i(=n_e)}{40} \times M_i$$

(2.11)

where \(n_e\) is the value of electron density of pristine argon plasma at the same deposition condition. It is worthwhile to mention that in the experiments described in the Chapter 3, 4, and 5, the cylindrical Langmuir probe measurements are taken in the downstream region 80 mm from the cathode, which is 10 mm above the substrate. We took the Langmuir probe measurement near the substrate plane, keeping in mind that the electron and ion density in the vicinity of the substrate can significantly affect the physical properties of the deposited film [15].

2.3.2 Ion acoustic wave (IAW) diagnostic

2.3.2(a) Method of wave excitation
In order to study the wave propagation in the laboratory plasma, an infinitely homogeneous collision less plasma must be created. Inserting a local density perturbation, ion acoustic wave is excited in such plasma. There exist various methods to excite the ion acoustic wave in plasma. The grid excitation mechanism was used by Wong et al. [16], and Hatto and Sato et al. [17] to study the linear propagation of the ion acoustic wave by exciting lower density perturbation ($\frac{\partial n_e}{n_e} < 5\%$). Watatanabe [18] and Okustu et al. [19] extended this technique to study non-linear waves. They found that when density perturbation of sufficient magnitude ($\frac{\partial n_e}{n_e} \approx 10\%$) is employed, the ion acoustic wave may evolve into soliton.

In the grid excitation method the ion acoustic waves are excited by producing a density perturbation with a conducting launch grid immersed in the plasma. The stainless steel grid has 20 meshes per centimeter and has a transparency of 70%. The inter-wire spacing of the grid is ensured greater than the deBye length ($\lambda_D$). In the grid excitation method, the grid is initially biased negatively with respect to plasma potential at time $t < 0$. At time zero, a small positive step potential ($\Delta \phi$) is applied on the grid. Then the grid biased changed from $-V$ to $-V + \Delta \phi$. As the charge collection region ($> 10 \lambda_D$) is a significant portion of the inter-wire spacing, a modulation of the grid bias will produce a varying amount of absorption that results small density perturbation in the grid vicinity and then, it propagates down the plasma column [20]. Since the perturbed ion and electron densities in the ion acoustic waves are very nearly equal ($\partial n_e = \partial n_i$) and the electron current ($\partial n_e e v_{ei}$) is much larger than the ion current ($\partial n_i e v_{ia}$), the most sensitive detection of the ion acoustic waves
by a probe is achieved when it is biased positively to collect the electron saturation current. Here, \( v_{es} \) and \( v_{es} \) are the thermal velocities of the electron and ions respectively. Another advantage of biasing the receiving probe at or above the plasma potential is the resulting fast probe response due to the electron-rich sheath surrounding the probe permits good communication between the plasma proper and the probe surface. The density perturbations \( \left( \frac{\partial n_e}{n_e} \right) \) 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 photograph of the stainless steel grid with fine meshes is this in shown in Fig. 2.9.

2.3.2 (b) The Wave-launcher

The typical discharge condition in this study for bulk region of the DC planar magnetron device where the wave is launched is given as, electron density \( (n_e) = 10^8-10^9 \text{ cm}^{-3} \),

![Figure 2.9 Photograph of the ion acoustic wave exciting grid.](image-url)
electron temperature \((T_e) = 4-6\text{eV}\) and average ion temperature \((T_i) \sim 0.1\text{eV}\). The plasma is assumed to be homogeneous in the experimental region. The noise to background density ratio was below 1% as determined by a probe biased at 30V [21]. Density perturbations that evolved into the waves are excited by applying sinusoidal voltages to a fine mess stainless steel grid that is inserted in the device. The amplitude of the applied signal is chosen as \(|\Delta \phi| < 6.5V\) such that \(\frac{\partial n_L}{n_e} < 10\%\) and the repetition frequency is fixed at 50-100 kHz [22].

The applied frequency is chosen such that its value is about one tenth of the ion plasma frequency.

Figure 2.10 Schematic diagram of the wave Launching set up. \(V_a\) — amplitude of applied voltage signal to the stainless steel, \(V_{pr}\) — Langmuir probe biasing voltage, PL — Plane Langmuir probe, DSO — Digital oscilloscope
For detecting the propagating signal, the probe is biased positively with respect to plasma potential in order to detect perturbation in the electron saturation current. The travelling wave train reaches the movable Langmuir probe in a time longer than the duration of the burst to facilitate a positive identification of the propagating signal. The perturbations in current are passed through a resistor to the ground and the resulting voltage perturbations are displayed on a digital oscilloscope that is externally triggered by the signal generator. A data acquisition software is used to send the experimental data to a computer. The time-of-flight technique is used to measure the phase velocities of the excited ion acoustic waves.

The schematic diagram of the experimental set-up is given in the Fig. 2.10.

2.3.3 Optical emission spectroscopy (OES)

Based on the radiation emitted or absorbed it is possible to identify and determine the structure of atoms and molecules. This procedure is known as Optical emission spectroscopy (OES). The lines from the gaseous discharge are found to consist of discrete lines and bands. The lines and bands correspond to the transition between the characteristic energy levels of atoms or molecules. The physical properties of the plasma affect the intensity and wavelength distribution of such transitions in various ways, such as the line broadening, shift of spectral lines etc [23, 24]. The intensity $I(p,q)$ of a spectral line arising from transition between two bound level ‘$p$’ and ‘$q$’ is given by [24],

$$ I(p,q) = \frac{1}{4\pi} \int n(p)A(p,q)h(p,q)ds $$

(2.12)

where, $A(p,q) =$ Atomic transition probability and $h(p,q) =$ Photon energy.

For excited atoms, molecules and ions in low temperature plasma with very low pressure ($<1$ Pa) and low ionization ratio ($<10^{-5}$) the corona model of emission spectroscopy is
applicable. This is because under such conditions collision processes other than the electron impact excitation from ground state species and the spontaneous radiations from the excited species are not important, and the density of meta-stables is low enough to make a significant contribution to the excitation of excited species [25]. Under such conditions, the emission intensity from an excited state (p) is proportional to its density,

\[ I(p,q) \propto A(p,q)n_p \]  

where \( n_p \) refers to the population density in the in the excited state (p). With such a model, by selecting two excited levels with similar excitation threshold energies, the obtained line ratio is an indicative of the plasma parameters such as degree of ionization, degree of dissociation etc [12, 13].

2.3.4 Experimental set-up for optical emission intensity measurement

The optical emission spectroscopic measurement is performed using a ½ m digikrom spectrometer (CVI Laser Corp, USA. Digikrom Model DK 480). The system consists of a photo multiplier tube (PMT: Model AD110, wavelength range: 185-930nm) and a grating with 1200 grooves/mm for detection in the region \( \lambda = (400 - 850) \) nm. The entrance slit and exit slit of mono-chromator are adjusted at 20 Å to obtain an acceptable spectral resolution sufficient to detect the emission lines. The emissions are collected by a light collecting system (LCS) through the optical fiber (F) that is put on the glass window approximately at a vertical distance of 8 cm from the target in the downward region and kept in a manner to avoid the background radiation as well as to detect maximum emission. The light collecting system with the optical fiber (LCSF) is further aided by a plano-convex lens (diameter 2mm, focal length 3 cm) and a silica fiber of 1.0 mm core (numerical
aperture: 0.22). The view subtended by this LCS was parallel to the discharge column grazing the vicinity of the substrate and always collected radiations from the fixed location. The schematic diagram of the experimental set-up used for OES study is given in the Fig. 2.11.

Figure 2.11 Schematic diagram of the experimental set-up for optical emission spectroscopy measurement.

2.3.5 Measurement of deposition rate: Quartz Crystal Thickness Monitor

The quartz thickness monitor operates on a principle called the Piezo electric effect. When an electric potential is applied to a quartz crystal it vibrates at its natural frequency. At a constant temperature this frequency remains stable unless the mass of the crystal change. Depositing a thin film on the crystal surface will change the mass of the crystal. The increase in mass from the deposition causes the resonant frequency of the crystal to
decrease. Such changes are easily detected electronically by the sensors and the sensor performs appropriate mathematical functions to convert the frequency data to thickness data, both the instantaneous rate and calculated thickness. Such sensors not only read and display the rate and thickness data, but also provide outputs for other deposition system elements. It has an analog drive signal in a closed loop technique based on the rate data and thus able to maintain a preset rate during deposition. It also has a source shutter triggered to close when the preset final thickness is achieved. Since the heat also changes the frequency of vibration of the crystal, the monitor must be cooled to provide accurate reading. The photograph of the quartz thickness monitor is given in the Fig. 2.12.

![Photograph of the quartz thickness-monitor (DTM-101)](image)

**Figure 2.12 Photograph of the quartz thickness-monitor (DTM-101)**

### 2.4 Initial plasma characterization experiments

#### 2.4.1. I/V characteristics acquired at various operating conditions

The Langmuir probe I-V characteristics are acquired for (a) different magnetron targets at varying working pressures and input powers for the hydrogen additive argon plasma. Here, the working pressure is varied by adding hydrogen keeping the argon flow rate same. (b)
different working pressures keeping the nitrogen to argon partial pressure ratio same in the nitrogen added argon plasma with titanium as the magnetron target (c) different oxygen partial pressures in the oxygen additive argon plasma with titanium as the magnetron target. The plasma parameters are evaluated as mentioned in section 2.3.1 and discussed in the subsequent chapters (Chapter 3 to Chapter 5). \textbf{Fig. 2.13} shows the pattern of Langmuir probe I-V characteristics for condition (a). For the same discharge condition the plasma density and electron saturation currents are observed to have a higher magnitude for Ti target than the Cu and Cr target. This is due to the difference in secondary electron yield ($\gamma$) for the materials with $\gamma_{\text{Ti}} > \gamma_{\text{Cr}} > \gamma_{\text{Cu}}$ for a given discharge voltage [26].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_13.png}
\caption{Typical Langmuir probe I-V characteristics traced at working pressure $4\times10^{-1}$ Pa for the hydrogen added argon plasma for titanium, chromium and copper magnetron target. The input power ($P$) = 300W for each target.}
\end{figure}
The pattern of the Langmuir probe I-V as a function of hydrogen partial pressure for Cr target is shown in Fig. 2.14. It is again observed that introduction of hydrogen in argon decreases the plasma density and electron saturation currents. On the other hand the gradual addition of oxygen in the argon discharge will create and enhance the negative ion density in the background of otherwise positive ion-electron plasma [27]. With the introduction of negative ions the shapes of Langmuir probe I-V characteristics and as such, the magnitudes of plasma parameters change. Here, electrons are replaced with negative ions having thermal velocities and therefore mobility close to that of positive ions. Thus the electron saturation current decreases. A review and interpretation of probe diagnostic technique in negative ion plasma is elaborately explained by Amemiya [28] et al. A detail evaluation of the plasma parameters for such plasmas will be given in the Chapter 4.

Fig. 2.14 Typical Langmuir probe I-V characteristics traced with input power (P) = 300W for hydrogen added argon plasma for chromium magnetron target. The parameter is working pressure and argon partial pressure \(3.7 \times 10^1\) Pa) was kept constant.
2.4.2. Measurement of optical emission line intensity

The emission from the discharge is monitored for the experimental conditions mentioned in 2.4.1(a)-2.4.1(c). The collected spectra is shown in the Fig. 2.15(a) to Fig. 2.15(c). The procedure to estimate the value of the degree of ionization and degree of dissociation of the selected species based on the above spectrograph is mentioned in Chapter 3 and Chapter 5.

Figure 2.15 (a) The emission lines of the spectra collected for the hydrogen added argon plasma at different working pressure. The parameter is working pressure and the partial pressure for argon (3.7 x 10^4 Pa) was kept constant. The emitting species are identified by comparing with NIST database.

In the Fig. 2.15(a) the intensity variation of the species of Ar I [3s^2 3p^5 (2p_{3/2}) 4s] → [3s^2 3p^5 (2p_{1/2}) 4p] at 696.45 nm, 738.39 nm, 801.47 nm, 811.53 nm; Ar I [3s^2 3p^5 (2p_{1/2}) 4s] → [3s^2 3p^5 (2p_{3/2}) 4p] at 751.46 nm, 763.51 nm, 772.37 nm, 794.81 nm, 826.45 nm, 840.42 nm, 852.14 nm; Ar II [3s^2 3p^4 (^3p) 4s] → [3s^2 3p^4 (^3p) 4p] at 434.80 nm, 454.15 nm,
The emission lines of the spectra collected for the nitrogen added argon plasma at different working pressure. The nitrogen to argon flow ratio is kept fixed. The emitting species were identified by comparing with NIST database. The variation in the relative intensities of Ar II and Ar I could be observed.

472.68 nm, 476.48 nm, 480.60 nm; $H_\alpha$ line (656.28 nm) and $H_\beta$ line (487.54 nm); Cu I at 510.554 nm, 515.324 nm, 521.820 nm, 529.252 nm are shown. It is observed that the intensity profile of Ar and Cu transitions follow the discharge current, i.e. intensity of all these transitions peaked when discharge current is the maximum. The intensity of $H_\alpha$ line increases rapidly in comparison to the intensity of $H_\beta$ line. The energy required for direct excitation by electron from the ground state is 12.1 eV corresponding to $H_\alpha$ line and for $H_\beta$ excitation it is 12.7 eV [29]. This explains the faster increase in the intensity of $H_\alpha$ line than the intensity of $H_\beta$ line.
Similarly in the Fig. 2.15(b) intensity variation of the most prominent species of nitrogen such as $N_2^+$ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) at 391.58 nm and $N_2$ ($C^3\Pi_u \rightarrow B^3\Pi_g$) at 356.85 nm, Ti I line at 499.5 nm, and 510.53 nm in the nitrogen added argon plasma are shown. Also in the Fig. 2.15(c) the gradual increase of intensity of the oxygen atomic lines O I [2s$^2$ 2p$^3$ (4$S^0$) 3s] $\rightarrow$ [2s$^2$ 2p$^3$ (4$S^0$) 3p] at 777 nm and 845 nm with increasing oxygen partial pressure in oxygen added argon magnetron discharge with Ti target can be seen easily. For the low-temperature plasmas with very low pressures (< 1 Pa) and low ionization ratios (< $10^{-5}$) such as the DC planar magnetron discharge, the corona model is valid and is used to determine the plasma parameters [30-31].

![Intensity plot](image)

Figure 2.15 (c) The emission lines of the spectra collected for the oxygen added argon plasma at different oxygen partial pressure. The argon partial pressure is kept fixed at $8 \times 10^2$ Pa. The emitting species are identified by comparing with NIST database. The variation in the relative intensities O I line is observed.
2.5 Plasma nitriding experimental set-up

Plasma nitriding is plasma based surface hardening process that utilizes the nitrogen-hydrogen plasma for supplies of the ions, excited atoms and molecules as well as radicals for nitrogen incorporation into the iron and iron alloys [32]. The differences of the operating conditions between the two processes are mentioned in the Table 2.1. It is generally done in the abnormal glow region. In typical plasma nitriding condition the substrate is kept negatively biased between 400V to 800V having typical current density of 1.5 mA/cm² [33]. The ions from the plasma sheath boundary (i.e. negative glow) accelerated towards the cathode. On its way to the cathode the ions undergo charge exchange collision and also generate energetic neutrals. $N_2^+$ ions and energetic $N_2$ are the main active species in plasma nitriding (PN). Thus near the substrate surface by recombination of $N_2^+$ ions and dissociative recombination of energetic $N_2$ atomic nitrogen is effectively generated. The thermo-chemical diffusion of nitrogen atom in the surface of substrate causes the nitriding.

<table>
<thead>
<tr>
<th>Operating pressure</th>
<th>few mbar (1-5mbar)</th>
<th>$10^{-3}$ mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas mixtures</td>
<td>$N_2/H_2$</td>
<td>Ar/N$_2$ or O$_2$ or H$_2$</td>
</tr>
<tr>
<td>Treatment duration</td>
<td>Tens of hours</td>
<td>hours</td>
</tr>
<tr>
<td>Line of sight process</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Sample manipulation</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Temperature</td>
<td>400-560°C</td>
<td>Room temperature to 450°C</td>
</tr>
<tr>
<td>Substrate bias</td>
<td>high</td>
<td>low</td>
</tr>
</tbody>
</table>

Table 2.1 Comparison of operating conditions of plasma nitriding and thin film deposition
A high temperature is thus necessary so that nitrogen diffusion into the steel takes place. However, depending on the alloying element and stability of elements the nitriding temperature lies in the range of $250^\circ$C to $600^\circ$C [34]. The distance up to which nitrogen diffusion occurs is known as the diffusion zone and its depth is given by,

$$d = \sqrt[3]{\frac{kDt[N]}{[X]}}$$

(2.14)

with $[N]$ is the surface nitrogen content, $[X]$ is the original concentration of the nitride forming element and $D$ is the diffusion coefficient of atomic nitrogen [35]. The diffusion zone consists of nitrogen in solid solution as long as the temperature dependent solubility limit is not exceeded. If it is exceeded, the nitrides and alloy formation occur. Depending on the alloying elements and their amounts iron nitrides, alloy nitrides and mixture of both can be found either on the grain boundary or within the grain boundary. This layer is known as the compound layer and when it forms, the diffusion zone can be found below the nitride layer [36]. The compound layer generally consists of mono phase layer such as the $\gamma'$Fe$_2$N or $\varepsilon$Fe$_{2-1}$N or mixtures of both. The $\varepsilon$ layer is best for wear and fatigue application. The $\gamma'$ layer is somehow softer and wear resistant but is tougher and more forgiving in severe loading situation [36]. The formation of compound layer depends on the $N_2$ / $H_2$ gas composition as well as the treatment temperature. When the gas composition is such that nitrogen species are more, in that case treated surface contain multiphase layer ($\varepsilon + \gamma'$) known popularly as the white layer. Plasma nitriding can inhibit the formation of white-layer and if needed can form a mono phase layer which may be either $\varepsilon$ or $\gamma'$ nature.
As per requirements a diffused layer can be generated or a mono-phase layer can be made available on top of the diffused layer. The role of hydrogen in plasma nitriding is to increase the sticking coefficient [37] of atomic nitrogen formed near the cathode surface. Plasma nitriding achieves repetitive metallurgical results and complete control of the nitrided layers. This control results in superior fatigue performance, wear resistance and hard layer ductility.

Figure 2.16 The experimental set-up for DC pulsed plasma nitriding. Pulsed plasma nitriding is done at fixed duty cycle of 80% and frequency of 50 kHz.

Moreover, the process ensures high dimensional stability, eliminates secondary operations, offers low operating-temperature capability and produces parts that retain surface finish. As the PN operates at very high pressure compared to planar magnetron sputtering, therefore it
does not require diffusion pump. The schematic diagram of the plasma nitriding set up is
given in Fig. 2.16. The rotary pump (Make: Hind High Vacuum, Banglore, India; Model:
ULK-06) of suitable pumping speed (35m³/hr) is sufficient to acquire the base pressure (10⁻² mbar) and working pressure (1-5 mbar) required for PN. In practice, a conductance
control valve is connected between the rotary pump and the remaining system to reduce the
effective pumping speed and for this system the required flow rate to sustain 5 mbar
working pressure is 80 SCCM.

2.6 Summary

A DC planar magnetron set up is used to characterize the magnetron discharge plasma. The
fundamental aspects for the planar magnetron chamber design; such as pumping speed for
the pumps and flow rate to be kept for maintaining the operating pressure is calculated. The
details of the diagnostic tools to characterize the magnetron discharge plasma are given in
this chapter. The Langmuir probe I-V characteristics and optical emission spectrographs at
various operating conditions for the magnetron set up is achieved to determine the values of
plasma parameters. A description of plasma nitriding mechanism is discussed and the basic
differences between the two surface modification techniques are mentioned. The schematic
diagram of the plasma nitriding chamber is also given in this chapter.

References


[17] P. Hatta, and N. Sato, Prof. 5th Int. Conf. on Ionization, Phen in Gases, North Holland, Amsterdam, (1962).


