Chapter 3

Reactive Discharge Study
In Direct Current Cylindrical Magnetron Plasma
Chapter 3: Reactive discharge study

REACTIVE DISCHARGE STUDY IN DIRECT CURRENT CYLINDRICAL MAGNETRON PLASMA

3.1. Introduction

Direct current magnetron glow discharge process is used for sputter deposition of different compound films in a large number of technological fields [Grill 1994, Debal et al 1998]. Some of the examples are: multiple films on magnetic recording media or heads, metallic interconnects in microelectronics, thin film solar cells, various coatings namely optical, decorative or protective. It is also regarded as an environment friendly process since it fully avoids the use of various chemical reactants [Roth 1995]. Magnetron glow discharge systems differ from the conventional glow discharge systems by employing externally applied magnetic field, which is parallel to the cathode surface. The externally applied magnetic field traps the energetic electrons and effectively increases the ionization efficiency. This results in enhanced sputtering of the cathode resulting in high deposition rate at a relatively low pressure, thereby making it a favourable process for many manufacturing applications [Wendt et al 1988, Sheridan et al 1990, Wu 2005, Borah et al 2008b].

In many plasma processing applications, reactive sputtering in magnetron devices is actively used where metal oxides or metal nitride films are required for surface treatment. However, due to complex discharge behaviour of the molecular gases and complexity generated by the various plasma species under the influence of crossed magnetic and electric fields, the basic physical mechanism in reactive
magnetron sputtering is still a topic of interest for many researchers. Plasma collective behaviour is believed to play an important role in magnetron discharge and therefore, the delicate dependence of plasma parameters (density profile, temperature and energy distributions) on the sputtering efficiency as well as on the physico-chemical processes leading to quality film growth in reactive sputtering is undoubtedly a subject of investigation.

Titanium nitride (TiN) film is a suitable candidate for industrial applications because of its unique properties like high hardness, good wear and corrosion resistance [Arnell et al 1996]. Due to these properties, TiN has been used as a coating for cutting tools or as an anti-corrosive coating for turbines in aerospace industries. Further, it has good electrical, thermal, mechanical and chemical properties. In recent years, it is gaining more attraction of the scientific community for its applications in Nano-Electro-Mechanical Systems (NEMS) and in etching process of dielectrics as hard mask in Complementary-Metal-Oxide-Semiconductor (CMOS) device fabrication. In micro-electronics instrumentation, it also finds application for its electrical characteristics and for its diffusion barrier properties [Gicquel et al 1990, Glass et al 1992, Murarka et al 1993, Tarniow et al 1997, Szikora 1998, Dimitriadis et al 1999, Patsalas et al 1999, Niyomsoan et al 2002]. TiN has lustrous golden yellow colour due to which it has been used for decorative applications. The golden colour of the film is due to the high reflectance of TiN at the red end of the visible spectrum with low reflectance near the ultraviolet region.

In cylindrical magnetron device (also called as post magnetron device), the magnetic field $B$ is applied in the axial direction parallel to the cathode and is homogeneous throughout the system volume. The electric field $E$ lies in radial direction and hence, the charged particles in the cylindrical magnetron discharge
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plasma moves under the influence of the $E \times B$ field [Thornton 1978]. Due to the $E \times B$ effect, ionization rate is greatly enhanced in the vicinity of the cathode and high density plasma can be produced, hence, high sputtering rate can be achieved. Cylindrical magnetron is particularly useful for coating on the cylindrical bodies e.g. outer surface of wires or rods, inner surface of hollow cylinders, wave guides etc.

The plasma characteristics have an innately strong dependence on the applied magnetic field strength. It also depends on the material of the cathode which acts as the target in sputter deposition processes, the discharge power density, the sputtered species and gas pressure [Wu 2005]. A Langmuir probe is often used as a diagnostic tool in various types of plasmas including magnetron systems [Spatenka et al 1997, Passoth et al 1999]. It facilitates the local estimation of the plasma parameters like plasma density, electron temperature and electron energy distribution function (EEDF) in the plasma volume.

Emissive probe has been used for accurate measurement of plasma potential in direct current discharges for many years [Kemp and Sellen Jr 1966, Mravlag and Krumm 1990]. Several methods are employed to measure the plasma potential by an emissive probe, amongst which the floating potential method [Coakley et al 1978] and the inflection point method [Smith et al 1979] are in widespread use. However, the presence of magnetic field makes the plasma potential measurement complicated when electron Larmour radius is comparable or smaller than the probe radius. Despite these problems, the strongly emitting probe has been used to a good approximation (error is less than the voltage equivalent of electron temperature) in different magnetized discharges e.g. Quadruple devices [Bradley et al 1992], Tokamak edge plasmas [Diebold et al 1995] and Q machines [Mravlag and Krumm 1990]. Recently, Bradley et al have used emissive probe successfully in DC
magnetron with magnetic field strength up to 0.03 Tesla to measure the plasma potential [Bradley et al 2001]. Here, the emissive probe has been used for the measurement of plasma potential profiles between the cathode and the anode to study the cathode sheath and presheath behaviour.

In magnetron discharges with argon (Ar) and nitrogen (N\textsubscript{2}) gas mixture, atomic nitrogen species play a significant role in the surface nitriding processes [Debal et al 2001, Wautelet et al 1996]. The presence of ionic, atomic and molecular nitrogen, as well as ionic and atomic argon and also that of the cathode species can be detected with the help of optical emission spectroscopy (OES) [Debal et al 1998]. The numerous spectral lines, which are emitted by the different species, are the result of various collisional mechanisms. Moreover, the relation between the intensity of the emission lines and the densities of the corresponding species is intrinsically dependent on the sputtering conditions, namely, gas pressure, discharge current, gas flow rate as well as the geometry of the target. A qualitative analysis of the optical emission lines of the plasma composed of Ar-N\textsubscript{2} mixture has been done in this work. Such discharges in a reactive environment of argon and nitrogen gas are typically operated in two different stable modes, namely metallic mode and reactive mode. The reactive mode is due to maximum covering of the target material by the reactive nitrogen species at higher nitrogen partial pressure. Below a critical gas pressure of nitrogen, the discharge is in the metallic mode at which the sputtering rate of the metal target atoms is higher than the rate of formation of metal nitride on the metal target surface. The target surface remains metallic below this critical pressure of nitrogen when there is sufficient amount of sputtered metal atoms to react with all the nitrogen. However, at higher partial pressure of nitrogen gas in the plasma discharge environment, the metallic target surface is almost covered by it. This
reduces the metal atom density in the discharge by decreasing the sputtering rate resulting in the decrease in the formation of metal nitride. This state of the discharge is called the reactive mode. The ideal deposition condition is the point immediately before the transition from the metallic mode to the reactive mode. At this state of the discharge, both the sputtering rate and nitride formation rate is delicately balanced.

3.2. Experimental Setup and Diagnostics

The experimental cylindrical magnetron device is a stainless steel cylindrical chamber having dimensions of 30 cm inner diameter and 100 cm in length. A small titanium cylinder is placed co-axially inside the chamber which acts as the cathode. The length of the cathode is 25 cm and its outer diameter is 3.25 cm. Both ends of the cathode are terminated by stainless steel end reflectors of 5 cm in diameter. A schematic diagram of the experimental set up along with the probes and accessories is shown in figure 3.1. For generation of steady axial magnetic field, two coils of enamel-coated copper coils (SWG 9) are placed around the body of the chamber. Each coil having 1500 turns is mounted over rails, which covers a length of 20 cm on the chamber axis and fitted with castor wheels so that it can be easily moved along the axis of the chamber for adjustment of the distance between the coils. Direct current is passed through both the coils using DC power supply to produce axial magnetic field parallel to the cathode surface. The coils produce 0.0025 Tesla of magnetic field per ampere of DC current passing through it. The magnetic field is measured with the help of a Hall probe and found to be uniform within a length of ~40 cm at the central portion of the chamber. The radial variation of the magnetic field is within 5%.
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Figure 3.1: Schematic diagram of the experimental set up: E - Electric field, B - Magnetic field, ER - End reflectors, Lp - Langmuir probe, Ep - Emissive probe, MM - Magnetic field coils, QW - Quartz window, PS - Discharge power supply, PC - Personal computer, R - 200 Ω.

The vacuum unit consists of a rotary pump having a displacement rate of 350 l/min and a diffusion pump with an effective pumping speed of 700 l/sec. The base pressure of the chamber is brought down ~ 2 × 10^{-6} Torr. The partial pressure with the working gas mixture is maintained in the range of ~ (1-3) × 10^{-3} Torr. Argon and nitrogen gases are injected separately into the chamber through double valve system. The discharge power is supplied from a stabilized DC power supply (1500 V, 5 A) working in the voltage-regulated mode. Plasma is produced by applying DC voltage (350 V - 850 V) between cylindrical titanium electrode as cathode and the grounded chamber as anode. The axial magnetic field applied is 0.01 Tesla and the total argon
Figure 3.2: Current-voltage characteristics of Langmuir probe at different radial positions from the cathode. The total gas pressure is $2 \times 10^{-3}$ Torr at Ar:N$_2$ = 1:1. Magnetic field, $B = 0.01$ Tesla. Discharge voltage is 600 V and discharge current is 90 mA.

Nitrogen gas pressure is maintained at $2 \times 10^{-3}$ Torr. Typical discharge current is 50 mA to 450 mA. Plasma parameters are measured with a cylindrical Langmuir probe made of tungsten having diameter 0.05 cm and length 0.5 cm. Current – voltage ($I - V$) characteristics of the Langmuir probe at different radial positions from the cathode is shown in figure 3.2. Typical measured plasma parameters are: plasma density, $n_e \sim (10^8 - 10^{10})$ cm$^{-3}$ and electron temperature, $T_e \sim (2 - 6)$ eV. $n_e$ is calculated from the electron saturation current of the current – voltage characteristics and the corresponding $T_e$ value. The cylindrical Langmuir probe is a tungsten wire of
radius 0.025 cm which is smaller than the electron gyro-radius for B = 0.01 Tesla (~0.05 cm) and therefore, the electron saturation current is safely accounted for the density calculation. The ion saturation current, also, has been measured to confirm the validity of the measurement.

The radial plasma potential profiles are recorded with the help of an emissive probe ($E_p$), made of 1% thoriated tungsten wire of 0.005 cm in diameter and 0.3 cm in length [Kemp and Sellen Jr 1966, Boruah et al 2003, Pal et al 2004]. The probe wire is looped into a semi-circle and is suitably attached at the two ends with two supporting stainless steel rods (each 0.025 cm in diameter). The supporting rods are covered by ceramic tubes for proper insulation. The floating potential of a strongly emitting probe technique is used to determine the plasma potential profile radially towards the cathode. The filament wire is heated by a half wave rectified DC voltage source (0-4 V). The procedure for interpretation of emissive probe characteristics is based on the fact that electron emission can take place when probe bias is more negative than the local plasma potential [Kemp and Sellen Jr 1966]. It is known that the floating potential technique can give a reasonable approximation to the plasma potential provided the emission is strong enough [Hassal and Allen 1997]. The resistance used for floating potential measurement is 30 MΩ and the measured value is calibrated. The continuous measurement of plasma potential profile is done by moving the probe slowly (1 cm/min) using a motor driving system attached to the emissive probe shaft.

The optical emission spectra of discharge are recorded using BENTHAM M300 Monochromator through optical fiber cable. Focal length of the Monochromator is 30 cm and it is coupled with a photomultiplier tube (PMT) and a
programmable motor controller. The output signal from the PMT is transferred to a personal computer (PC) through an analog to digital converter.

3.3. Experimental results and discussion

3.3.1. Discharge current – voltage characteristics

Figure 3.3(a): Discharge current-voltage characteristics for different Ar-N\textsubscript{2} partial pressure ratios. The total gas pressure is 2 \times 10^{-3} Torr. Magnetic field, B = 0.01 Tesla.

The discharge current – voltage characteristics for different partial pressures of Ar-N\textsubscript{2} gas mixture are shown in figure 3.3(a). Throughout the experiment, the total gas pressure and magnetic field strength are maintained at 2 \times 10^{-3} Torr and 0.01 Tesla respectively. Discharge current (I) increases with increasing discharge voltage (V_d) satisfying the current - voltage relation, \( I \propto V_d^n \), \( n \) being an index of the performance of the system. This is an interesting relationship which holds in case of
cylindrical magnetron discharge first reported by Thornton and Penfold [Thornton and Penfold 1978]. The value of \( n \) for this device is found to be within 4.5 to 5.5. It increases with the introduction of \( \text{N}_2 \) into the \( \text{Ar} \) plasma. For DC magnetron discharges, this value is in the range from 4 to 10 and higher is its value, more efficient is the electron confinement [Yeom et al 1989a].

The discharge current is found to decrease with the increase of \( \text{N}_2 \) partial pressure in the gas mixture at constant discharge voltage. This is primarily because the ionization cross-section for \( \text{N}_2 \) by electron impact is about 40% lower than that of \( \text{Ar} \) [Massey and Burhop 1969, Lennon et al 1988, Itikawa 2006]. Another factor, the secondary electron emission coefficient can also affect the discharge. However, it has been shown that the secondary electron emission coefficient of titanium (cathode material) bombarded with \( \text{Ar}\)-\( \text{N}_2 \) ion mixtures at typical magnetron

![Discharge current-voltage characteristics at different magnetic fields.](image)

The total gas pressure is \( 2 \times 10^{-3} \) Torr at \( \text{Ar}:\text{N}_2 = 1:1 \).
sputtering ion energies has a marginal increase as N\textsubscript{2} pressure is increased [Lewis et al 1989]. This indicates that the increase in the secondary electron emission coefficient contribute to enhance the index of performance of the discharge.

The discharge current – voltage characteristics for different applied magnetic field strengths are shown in figure 3.3(b). The total gas pressure has been maintained at 2 × 10\textsuperscript{-3} Torr. With increasing discharge voltage, the discharge current increases satisfying the current - voltage relation, \( I \propto V_d^n \). When the magnetic field is increased, the discharge current is found to increase for a fixed discharge voltage showing that at higher magnetic fields due to higher confinement high density plasma is achieved at relatively lower discharge voltage. At a discharge voltage of 600 V, the discharge current is 64 mA at a magnetic field of 0.0075 Tesla and it rises to 345 mA at a magnetic field of 0.015 Tesla. The value of \( n \) ranges from 4.5 to 7 at magnetic field strengths between 0.01 Tesla and 0.0225 Tesla. This suggests that the system operates in the magnetron mode in the above applied magnetic field strength range. For lower and higher magnetic field strengths (0.0075 Tesla and 0.025 Tesla respectively), \( n \) has a value less than three (< 3).

3.3.2. Magnetic field effect on discharge characteristics

In figure 3.4, the variation of the discharge current and discharge voltage with the applied magnetic field are shown. The total Ar and N\textsubscript{2} gas pressure is 2 × 10\textsuperscript{-3} Torr. The discharge current gradually increases with the increase in the magnetic field and it is found to attain a maximum value of 322 mA at 0.02 Tesla. This is because more electrons are available for the discharge due to higher confinement and proper interaction with the gas species with the increase in the magnetic field. It then decreases slightly and almost becomes uniform with further increase of magnetic field strength. The discharge voltage, on the other hand, decreases with the increase
of magnetic field. Initially, when the magnetic field is very low, a very high potential drop across the cathode and the anode is required to generate the discharge. The discharge voltage gradually decreases to a lower value with the increase in the magnetic field. At higher magnetic fields, the discharge voltage is low in comparison to lower magnetic fields due to higher confinement of the electrons. For efficient sputtering in magnetron device, the primary requirements are high plasma density and higher cathode voltage. Plasma density is enhanced around the cathode by the use of

Figure 3.4: Variation of discharge current and discharge voltage with magnetic field / magnetic coils current. The total gas pressure is $2 \times 10^{-3}$ Torr at Ar:N$_2$ ~ 1:1.
magnetic field, however, for higher magnetic field the cathode voltage drop is smaller. In this device, most efficient sputtering is, therefore, achieved at magnetic field strength of \( \sim 0.01 \) T with discharge voltage \( \sim 600 \) V.

### 3.3.3. Dependence of plasma parameters on discharge parameters

#### 3.3.3.1. Plasma density

![Graph showing plasma density vs distance from cathode](image)

Figure 3.5: Radial profiles of plasma density for different Ar-N\(_2\) partial pressure ratios. The total gas pressure is \( 2 \times 10^3 \) Torr. Discharge voltage is 600 V and B = 0.01 Tesla. The discharge current varies from 74 mA (N\(_2\) only) to 130 mA (Ar only)

Measured radial profiles of plasma density for different ratio of partial pressure of Ar and N\(_2\) are shown in figure 3.5. Plasma density is measured from the electron saturation current of the cylindrical Langmuir probe. It is observed that the
plasma density near the cathode is relatively high (of the order of $\sim 10^{10}$ cm$^{-3}$) and it decreases with increasing distance from the cathode. Density decreases to $\sim 10^9$ cm$^{-3}$ at radial distance of 7 cm from the cathode. In magnetron discharge, there is significant ion loss to the highly negative cathode and emission of secondary electrons by ion bombardment occurs. The secondary electrons are accelerated away from the cathode by the sheath electric field and are trapped by the axial magnetic field. Trapping of the secondary electrons enhances the ionization efficiency, which is responsible for maintaining high plasma density near the cathode. In fact, the purpose of using a magnetic field in a sputtering system is to make more efficient use of the electrons to obtain higher ionization rate. The $E \times B$ field enforces a helical path to the
electrons that increases its path length enabling it to cause more ionization. As $E\times B$ field is stronger near the cathode, the discharge is confined to a core region around the cathode, which becomes narrower with increasing magnetic field. Plasma density decreases with increasing radial distance from the central cathode due to decrease in the rate of ionization. At larger distance $\sim 7$ cm from the cathode, $n_e$ decreases by one order of magnitude than near the cathode.

In figure 3.6, measured plasma density profiles for different discharge voltages at different probe positions are shown. The total gas pressure is $2 \times 10^3$ Torr at Ar:N$_2$ = 1:1 and the magnetic field strength is 0.01 Tesla. The plasma density increases with increasing discharge voltage. On the other hand, the plasma density decreases in radial direction away from the cathode for constant discharge voltage.

![Figure 3.7: Dependence of plasma density on magnetic fields at different probe positions. The total gas pressure is $2 \times 10^3$ Torr. Discharge voltage = 600 V.](image-url)
The measured plasma densities for different magnetic fields are shown in figure 3.7 with probe position as a parameter. The total gas pressure is $2 \times 10^{-3}$ Torr and the discharge voltage is 600 V. With increasing magnetic field, the electrons are confined closer to the cathode. The cyclotron frequency increases significantly and the diffusion coefficient reduces across the magnetic field which decreases the particle loss rate. On the other hand, due to the $E \times B$ drift, the lifetime and also the path length of the electrons around the cathode increases. This type of electron motion increases the collision probability between the electrons and the atoms, therefore the ionization rate increases. The resultant effect is that, the plasma density becomes very high in the vicinity of the cathode due to enhanced ionization rate and lower diffusion rate. As the plasma density increases, the current density at the cathode becomes higher and therefore, the sputtering rate also increases. Again, as most of the electrons remain entrapped within the vicinity of the cathode and only the low velocity electrons are present beyond this magnetic entrapment, the plasma density reduces at larger radial distance away from the cathode.

3.3.3.2. Electron energy distribution function (EEDF)

Electron energy distribution functions are computed by double differentiating the measured Langmuir probe current - voltage ($I$ - $V$) characteristics. This second derivative with respect to the probe voltage, is proportional to the electron energy probability function (EEPF), $f_r(\varepsilon)$ and is related to the EEDF as

$$g_r(\varepsilon) = \varepsilon^{1/2} f_r(\varepsilon)$$

(3.1)

where $g_r(\varepsilon)$ is the EDE. The EEPF is obtained from the Druyvesteyn formula: [Lieberman and Lichtenberg 1994]
\[ f_e(\varepsilon) = \frac{2 \sqrt{2 m_e}}{e^2} j_p''(V) \]  

(3.2)

where \( eV (=\varepsilon) \) is the electron kinetic energy and \( 'V' \) is the probe voltage with respect to the plasma potential. \( 'e' \) and \( 'm_e' \) are the electron charge and mass respectively, and \( j_p''(V) \) is the second derivative of the probe current density with respect to the probe voltage. The plasma potential is obtained from the minimum point of the absolute value of second derivatives of the probe \((I - V)\) characteristics which correspond to the probe bias where the first derivative of the \((I - V)\) characteristics is maximum.

Figure 3.8: Measured electron energy distribution function for different magnetic fields. Probe positions are (i) 1 cm, (ii) 2 cm, (iii) 3 cm and (iv) 4 cm. The total gas pressure is \(2 \times 10^{-3} \text{Torr}\) at \(\text{Ar:N}_2 = 1:1\). Discharge voltage is 600 V.
Electron energy distribution functions measured at different magnetic field strengths are shown in figure 3.8. Measurements are made at four different radial positions from the cathode surface e.g. 1 cm, 2 cm, 3 cm and 4 cm. The total gas pressure is maintained at $2 \times 10^{-3}$ Torr with Ar:N$_2$ = 1:1 and the discharge voltage is 600 V. Magnetic field is increased from 0.0075 Tesla to 0.0275 Tesla. Broad electron energy distribution indicating higher electron energy is obtained for lower magnetic field for all radial locations. This is because at low magnetic field when the electron density is low due to less confinement, the electrons suffer fewer collisions and hence, there is minimum loss of energy of electrons resulting in broader distribution with higher energy. With the increase in the magnetic field, there is an increase in the electron density due to increasingly efficient confinement of the secondary electrons.

![Figure 3.9: Measured electron energy distribution function for different Ar-N$_2$ partial pressure ratios. Probe position = 3 cm. The total gas pressure is $2 \times 10^{-3}$ Torr. Discharge voltage is 600 V and B is 0.01 Tesla.](image-url)
This will result in more number of collisions thereby leading to a decrease in the energy of the electrons as indicated by the narrower distribution function at higher magnetic field. The electron temperature which is a measure of the energy of the electrons decreases with the increase in the magnetic field. 

Measured EEDFs at radial distance of 3 cm from the cathode surface are shown in figure 3.9. N\textsubscript{2} gas is mixed with Ar keeping the total working pressure fixed and data are shown for different partial pressure ratios of argon to nitrogen. In case of pure Ar plasma, the energetic secondary electrons coming out of the cathode fall region relax energetically in the glow region of the discharge mainly by collision with Ar neutrals. The EEDF represents a steady effective temperature of ~ 2 eV. For pure Ar plasma the EEDF follows Maxwellian behaviour. With increasing N\textsubscript{2} concentration the shape of the EEDF changes from Maxwellian to Druyvesteyn type [Lieberman and Lichtenberg 1994, Seo et al 2005] and at pure N\textsubscript{2} plasma it very closely follows the Druyvesteyn nature. As N\textsubscript{2} has much lower ionization cross section for electron impact (nearly 40 % less) than that of Ar, the energy loss for ionizing electrons during ionizing collisions with N\textsubscript{2} decreases. This results in increase in the population of energetic electrons (because of higher residual energy after ionizing collisions) and decrease in electron density. The EEDF’s in nitrogen mixed plasma, therefore, becomes broader indicating rise in electron temperature with increasing N\textsubscript{2} concentration. In pure N\textsubscript{2} plasma, only electron-nitrogen ionizing collisions are dominant and EEDF shows a little higher temperature of ~ 4.3 eV. 

3.3.3.3. Electron temperature

The value of electron temperature at any discharge condition is determined from Langmuir probe (I - V) characteristics. The electron temperature is determined
from the slope of the ln($I_e$) vs $V$ curve of the Langmuir probe in the Maxwellian region by the equation: [Kakati et al 2007a]

$$T_e = \frac{\partial V}{\partial (\ln I_e)}$$ (3.3)

where ‘$I_e$’ represents the electron current collected by the Langmuir probe.

Figure 3.10: Radial profiles of electron temperature for different Ar-N$_2$ partial pressure ratios. The total gas pressure is $2 \times 10^3$ Torr. Discharge voltage is 600 V and B is 0.01 Tesla.

Measured electron temperature, ‘$T_e$’ at different radial distances from the cathode is shown in figure 3.10. Electron temperature is maximum near the cathode, typically for Ar-N$_2$ = 1:1, $T_e$ is ~ 4 eV and decreases to ~ 1 eV at a distance of 7 cm from the cathode surface. As discussed earlier, the ionization efficiency is maximum around the cathode, as most of the electrons emitted by the secondary emission are
trapped around the cathode and electrons gain energy from the cathode sheath electric field. The faster electrons have longer helical path-length and are better confined but the relatively slower electrons may escape this region and reach the anode or wall after suffering more number of collisions. Thus, the dominating transport mechanism is diffusion by electron–neutral collision. The uniform axial magnetic field reduces the net velocity of the electrons towards the wall (due to more number of collision on the way), so that wall recombination losses are reduced. The electron temperature profile, therefore, shows a decreasing trend toward the wall. With the increase in partial pressure ratio, the electron temperature increases due to the decrease in the energy loss by the electrons during ionizing collision with N₂ molecules as the ionization cross-section for N₂ is smaller than that of the Ar.

Figure 3.11: Electron temperature versus discharge voltage at different probe positions. The total gas pressure is $2 \times 10^{-3}$ Torr with Ar: N₂ = 1:1. B = 0.01 Tesla.
Electron temperature measured at different discharge voltages for different positions of the Langmuir probe is shown in figure 3.11. The magnetic field is 0.01 Tesla and the total gas pressure is $2 \times 10^3$ Torr. The electron temperature increases with the increase in the discharge voltage. At discharge voltage of 450 V, the measured electron temperature is ~ 2.9 eV which is found to increase to ~ 4.9 eV at discharge voltage of 700 V when the probe is at distance of 2 cm from the cathode. With the increase in the discharge voltage, the sheath electric field also increases. Therefore, the electrons constituting the plasma gain momentum due to the increase in the discharge voltage. This results in an increase in the thermal energy of the electrons which will thereby result in the increase of the electron temperature.

![Graph showing electron temperature versus magnetic field at different probe positions.](image)

Figure 3.12: Electron temperature versus magnetic field at different probe positions. The total gas pressure is $2\times10^3$ Torr. Discharge voltage = 600 V.
In figure 3.12, the variation of electron temperature measured at different magnetic fields for different positions of the Langmuir probe is shown. The discharge voltage is 600 V and the total gas pressure is $2 \times 10^{-3}$ Torr. The electron temperature is found to decrease from ~ 4 eV to ~ 1.8 eV with the increase of the magnetic field strength from 0.005 Tesla to 0.055 Tesla when it is measured at a distance of 2 cm from the cathode. When the magnetic field is increased, then it results in more number of electrons getting confined within the plasma and these electrons lose their energy to a greater extent due to ionizing collisions during their drift due to $E \times B$ effect. This leads to the decrease in the electron temperature value with the increase in the applied magnetic field strength. The electron temperature is higher near the cathode i.e. within the magnetic trap and it goes on decreasing radially away from the cathode as the electrons lose their energy in collision and ionization while travelling radially outward. Near the cathode surface, the electron temperature is high and it decreases away from it. The high value of the electron temperature within the $E \times B$ trap is due to the confinement of the energetic electrons by the magnetic field. Electron temperature decreases towards the bulk plasma region when one moves away from the cathode surface.

3.3.3.4. Floating potential

Figure 3.13 shows the corresponding variation of floating potential, $V_f$ measured by the Langmuir probe at different partial pressure ratio along the radial direction. Floating potential becomes less negative with the increase of distance from the cathode. This is supported by the observed decrease in electron temperature in radial direction and the recorded increase in electron temperature when $N_2$ is introduced. Lowering of floating potential is often essential in the case of film
deposition on insulated substrate to reduce the energetic electron bombardment during the film growth process.

Figure 3.13: Radial profiles of floating potential for different Ar-N$_2$ partial pressure ratios. The total gas pressure is 2 × 10$^{-3}$ Torr. Discharge voltage is 600 V and B is 0.01 Tesla.

The deposition of thin films is influenced by the floating potential. So, it becomes an important parameter during the thin film deposition process. In figures 3.14 and 3.15, the corresponding variation of floating potential measured by the Langmuir probe at different distances away from the cathode for different discharge voltages and magnetic fields respectively are shown. Floating potential takes less negative values with the increase of both the discharge voltage and the magnetic field. At constant discharge voltage, floating potential increases (less negative) with
increasing radial distance. Variation of $V_f$ follow the same trend with constant magnetic field.

Figure 3.14: Floating potential versus discharge voltage at different probe positions. The total gas pressure is $2 \times 10^{-3}$ Torr. $B = 0.01$ Tesla.

Figure 3.15: Floating potential versus magnetic field at different probe positions. The total gas pressure is $2 \times 10^{-3}$ Torr. Discharge voltage = 600 V.

3.3.4. Optical emission spectroscopic study of the discharge

Typical emission spectra of the discharge with different partial pressure ratio of Ar-N$_2$ obtained by using the Monochromator are shown in figure 3.16. The light
from the discharge is obtained through a quartz window and taken to the Monochromator using an optical fiber. In the wavelength range of 370 nm to 400 nm, the emission spectrum shown by ‘a’ in figure 3.16(i), is from pure Ar discharge.

Figure 3.16: Optical emission spectra for (a) Ar only, (b) Ar:N\textsubscript{2} ~ 1:1 and (c) N\textsubscript{2} only at total gas pressure of 2 × 10\textsuperscript{-3} Torr for different wavelength ranges: (i) 370 – 400 nm and (ii) 450 – 510 nm. Discharge voltage is 600 V and B is 0.01 Tesla.
With the introduction of N\textsubscript{2} (Ar:N\textsubscript{2} - 1:1) (spectrum 'b'), prominent peaks for molecular N\textsubscript{2} and N\textsubscript{2}\textsuperscript{+} bands appear at 380.5 nm and 391.4 nm. Intensity of these peaks maximize when discharge is made with N\textsubscript{2} only (spectrum 'c'). Figure 3.16(ii) contains spectral data for wavelength range of 450 nm to 510 nm, which shows a clear transition of spectral lines from Ar to N\textsubscript{2} discharge. In pure Ar discharge (spectrum 'a'), many of the Ar lines appear prominently (typical lines are at 451.07 nm, 476.48 nm, 488.1 nm). Few Ti lines also appear with moderate intensity (typically at 459.9 nm, 466.8 nm, 468.2 nm, 499.1 nm). When Ar:N\textsubscript{2} is 1:1, it is seen that intensity of the Ar lines decreases and new lines (typically at 493.51 nm, 500.2 nm and 500.5 nm) and band (typically at 470.9 nm) for N\textsubscript{2} appear along with the Ti lines (spectrum 'b'). When discharge is maintained with N\textsubscript{2} only, all the Ar lines disappear and only N\textsubscript{2} lines and band with increased intensity along with Ti lines are seen (spectrum 'c'). An important observation regarding the intensity of the observed Ti lines is that their intensity initially increases for Ar to N\textsubscript{2} partial pressure ratio 1:1. The intensity decreases when discharge is maintained only with N\textsubscript{2}. The transition of discharge from the metallic mode to the reactive mode is, therefore, appears to be at this partial pressure ratio of Ar and N\textsubscript{2} which is 1:1. This discharge mode transition is further evidenced from the intensity variation of TiN band spectrum.

Line intensity is estimated by measuring the area under the curve of the lines corresponding to particular species recorded in wavelength spectra of the discharge. Table 1 shows the prominent emission lines of different observed species along with their transition levels and relative intensity variations. Emission spectra confirm the presence of both Ti and N\textsubscript{2} species in the plasma. With the introduction of N\textsubscript{2}, though the electron density slightly decreases, the intensity variation of a particular line is dominated by the density of the concerned species. As expected, the intensity of the
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Ar lines decreases whereas that of the N₂ lines increases with the increase of N₂ partial pressure in the gas mixture.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength, λ (nm)</th>
<th>Transition</th>
<th>Intensity (a.u.) (Ar only)</th>
<th>Intensity (a.u.) (Ar:N₂ ~ 1:1)</th>
<th>Intensity (a.u.) (N₂ only)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>380.5</td>
<td>C³μ− B³μ ν'(0,1,2,3) − ν''(0,1,2,3,4) bands</td>
<td>0.02515</td>
<td>0.03745</td>
<td></td>
</tr>
<tr>
<td>N₂⁺</td>
<td>391.4</td>
<td>B²Σ⁺− X²Σ⁺ ν'(0,1,2,3) − ν''(0,1,2,3,4) bands</td>
<td>0.05399</td>
<td>0.1031</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>451.07</td>
<td>3s²3p⁵(3P)4s − 3s²3p³(3P)5p</td>
<td>0.02028</td>
<td>0.01334</td>
<td></td>
</tr>
<tr>
<td>N⁺</td>
<td>469.59</td>
<td>2s2p⁷(4P)3p − 2s2p⁷(4P)3d</td>
<td>0.000175</td>
<td>0.000947</td>
<td></td>
</tr>
<tr>
<td>Ar⁺</td>
<td>476.48</td>
<td>3s³3p⁵(4P)4s − 3s³3p³(4P)4p</td>
<td>0.02035</td>
<td>0.00756</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>493.51</td>
<td>2s²2p⁹(4P)3s − 2s²2p⁹(4P)4p</td>
<td>0.00101</td>
<td>0.00186</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>499.11</td>
<td>3d³(4F)4s − 3d³(4F)4p</td>
<td>0.0024</td>
<td>0.00307</td>
<td>0.00133</td>
</tr>
</tbody>
</table>

Table 1: Identified spectral lines of wavelength spectra. Only a selection of the most prominent lines is tabled.

With the introduction of nitrogen, different species e.g. N, N⁺, N₂⁺ etc. are formed due to dissociation of N₂ and subsequent ionization. The most dominant species is the N₂⁺ which is obvious from the above emission spectra. The dissociation energy of N₂ is 9.76 eV and the ionization energy of atomic nitrogen (N) is 14.53 eV. So a total of 24.29 eV will be required to form N⁺ due to electron impact dissociation of N₂ and ionization of N. The ionization energy of N₂ to form N₂⁺ is 15.58 eV which is slightly lower than that of Ar (15.76 eV) [Mallard and Linstrom http://www.webbook.nist.gov, Zavilopulo et al 2005]. Also the ionization cross section of N₂ is significantly higher than that of N. So the dominance of N₂⁺ is due to lower ionization potential and higher ionization cross-section of N₂.
3.3.5. Plasma potential profile and sheath parameter

Figure 3.17: Measured radial plasma potential profiles for different Ar-N₂ partial pressure ratios (a) Ar only, (b) Ar:N₂ ~ 3:1, (c) Ar:N₂ ~ 1:1, (d) Ar:N₂ ~ 1:3 and (e) N₂ only. Total gas pressure is maintained at $2 \times 10^{-3}$ Torr. Discharge voltage is 600 V and B is 0.01 Tesla. Zero in the abscissa represents the surface of the cathode.

The measured radial plasma potential profiles between the cathode and the anode wall for different Ar-N₂ compositions are shown in figure 3.17. Near the anode wall, plasma potential is zero. In Ar discharge (trace ‘a’), plasma potential profile suffers a drop of nearly 10 V in the region 8-6 cm from the cathode. The region is considered to be the boundary of the intense ionization region covering the
cathode visible by naked eye. Plasma potential takes a steady negative value within
this region (signifying electron enhancement) followed by a sharp fall in the cathode
sheath. With increasing Ar-N\textsubscript{2} ratio (traces ‘b’, ‘c’ and ‘d’), the potential drop in the
boundary region of the intense ionization region decreases. Finally, with N\textsubscript{2} only, a
smooth presheath drop from the anode wall to the cathode sheath is seen. This
observation indicates a modification in the ionization process as well as the plasma
transport mechanism in presence of N\textsubscript{2}. The sheath thickness is measured from the
plasma potential profiles from semi-logarithmic plot of the plasma potential versus
distance. The intersection point of the tangents drawn one in sharp fall region of
potential closer to cathode and the other in constant plasma region in the bulk plasma
is taken as the measure of sheath.

![Graph showing variation of sheath thickness and discharge current]

Figure 3.18: Variation of sheath thickness and discharge current with
increasing N\textsubscript{2} partial pressure at total gas pressure of 2 \times 10\textsuperscript{-3} Torr.
Discharge voltage is 600 V and B is 0.01 Tesla.
Chapter 3: Reactive discharge study

Figure 3.18 represents the variation of sheath thickness with N\textsubscript{2} partial pressure as a parameter. The sheath thickness is 0.86 cm in pure Ar plasma and it increases to 1.08 cm in pure N\textsubscript{2} plasma. This indicates modification in space charge density, which influences the current density at the cathode. The corresponding variation of discharge current with increase of N\textsubscript{2} partial pressure is also shown in figure 3.18. The measured discharge current decreases with the increase in the N\textsubscript{2} partial pressure in the gas mixture. As plasma density decreases with increasing N\textsubscript{2} partial pressure in the gas mixture, the cathode sheath expands to collect more number of positive ions so that the effect of cathode sheath electric field on the plasma can be shielded out, hence sheath thickness increases. In other words, the space charge density in the cathode sheath decreases and the current density to the cathode also decreases when N\textsubscript{2} concentration is increased. With the increase in sheath thickness, the strength of the sheath electric field decreases which in turn will lead to the lowering of the energy of the ions bombarding the cathode and hence low rate of sputtering.

3.3.6. Optimum condition for high rate titanium nitride formation

In figure 3.19, the position of the expected TiN band in the emission spectra corresponding to the wavelength 613.9 nm is shown for different ratios of Ar-N\textsubscript{2} partial pressures. However, peak observed for TiN band at this wavelength is not prominent. This is due to low level emission intensity corresponding to this transition. Since, discharge is maintained at a low value of total pressure of the gas mixture ~ 2 \times 10^3 \text{Torr} while recording the emission spectrum data, so, to a good approximation, the corresponding emission intensity can be considered to be a qualitative representation of that particular species density in the discharge. The intensity of the TiN band spectrum obtained at wavelength value of 613.9 nm for
Figure 3.19: Optical emission spectra of TiN band for different Ar-N$_2$ partial pressure ratios (a) Ar only, (b) Ar:N$_2$ ~ 3:1, (c) Ar:N$_2$ ~ 1:1, (d) Ar:N$_2$ ~ 1:3 and (e) N$_2$ only at total gas pressure of $2 \times 10^{-3}$ Torr for wavelength range: 610 nm – 630 nm. Discharge voltage is 600 V and B is 0.01 Tesla.

Different Ar-N$_2$ partial pressure ratio is shown in Table 2. Initially, with the increase in the N$_2$ partial pressure, the TiN formation rate increases. It is observed that the most intense TiN transition occurs for Ar to N$_2$ ratio of 1:1. At this composition of the gaseous mixture of argon and nitrogen in the discharge, the density of TiN is the highest. Here, the sputtering rate is balanced by the reaction rate between titanium and nitrogen ions. As a result, almost all of the sputtered titanium atoms react with nitrogen to form titanium nitride. With further increase in the N$_2$ partial pressure, there is decrease in the electron density, which gradually decreases the ionization rate.
and hence, the sputtering rate. At lower nitrogen partial pressure, the rate of TiN formation will be low. There will be excess Ti atoms in the discharge and therefore, the deposited film will contain a proportion of metallic titanium with TiN. So, to have a metallic titanium free pure TiN film, the nitrogen partial pressure in the discharge should be above a certain value. However, when the N₂ concentration in the gas mixture becomes too high (above 1:1), the ionization rate decreases and also the sheath electric field decreases. The density reduction will lead to the decrease of ion flux to the cathode and reduction of electric field will in turn reduce the energy of the bombarding ions. The resulting effect is the reduction of the flux and energy of the ions hitting the cathode and hence the rate of titanium sputtering. So, the TiN formation rate will also become lower. Therefore, a balanced composition of argon and nitrogen should be maintained in the discharge for deposition of TiN and to obtain a high deposition rate.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Wave length λ (nm)</th>
<th>Transition</th>
<th>Intensity (a.u.) (Ar only)</th>
<th>Intensity (a.u.) (Ar:N₂ ~ 3:1)</th>
<th>Intensity (a.u.) (Ar:N₂ ~ 1:1)</th>
<th>Intensity (a.u.) (Ar:N₂ ~ 1:3)</th>
<th>Intensity (a.u.) (N₂ only)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>613.9</td>
<td>2π - X²Σ⁺ 0-0 band</td>
<td>0.000175</td>
<td>0.000194</td>
<td>0.000162</td>
<td>0.000143</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Observed TiN band spectral intensity at different argon and nitrogen partial pressures at wavelength of 613.9 nm.

3.4. Conclusion

This experimental study on the discharge characteristics of the direct current cylindrical magnetron plasma system shows that the transition of the discharge to the magnetron mode occurs with the increase in the magnetic field. Plasma density is found to increase with magnetic field due to higher confinement and enhanced
ionization. A strong radial density gradient is recorded with decreasing density away from the cathode. The EEDF has been measured at different radial distances from the cathode for different magnetic fields and also at different Ar:N₂ partial pressure ratios. It is found that electron temperature \( T_e \) is maximum (~ 4 eV) near the cathode and it decreases at larger distances (~ 1 eV). A temperature gradient is also observed for increasing magnetic field which is a characteristic of such devices. The high value of the electron temperature within the \( E \times B \) trap is due to the confinement of the energetic electrons by the magnetic field. Electron temperature decreases towards the bulk plasma region when one moves away from the cathode surface.

Further, this experimental observation provides a detailed understanding on the influence of nitrogen on plasma properties in a cylindrical magnetron reactive sputtering system. It has been observed that nitrogen gas slows down the overall ionization process, as a result the plasma density and therefore, the discharge current reduces. Electron temperature is found to increase with nitrogen concentration, since the ionization cross section of nitrogen is less than that of argon. Argon-nitrogen gas mixture can also lower the floating potential which influences the titanium nitride deposition rate. Nitrogen plasma chemistry also influences the cathode sheath structure, which expands as discharge current decreases with the increase in nitrogen concentration. Argon and nitrogen gas mixture with partial pressure ratio 1:1 is found to provide the most balanced condition of the reaction rate between the two gas species for the formation of titanium nitride under the present deposition condition.