IN THE NAME OF ALLAH, THE MOST BENEFICENT, THE MOST MERCIFUL

ALL PRAISE BE TO ALLAH, WHO IS FULL OF KNOWLEDGE AND WISDOM, GIVES KNOWLEDGE AND WISDOM TO WHOM OVER HE WISHES
A research thesis submitted to the University of Peshawar in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

IN

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APPROVED BY

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EXTERNAL EXAMINER
Dr. Muhammad Salahuddin
Dedicated to

My loving mother and caring father
Publication in Abstracted Journals


5. M. Abrar, A. Qayyum, A. W. Khan, A. Saeed, M. Zakaullah, “Nitrogen dissociation and parametric study in a magnetic pole enhanced inductively coupled Ar-N\textsubscript{2} plasma (MaPE-ICP)”, European Physical Journal of Applied Physics DOI:10.1051/epjap/2013120324


7. A. Saeed, A. W. Khan, F. Jan, M. Abrar, M. Zakaullah, “Effect of active screen cage on nitriding of AISI 304 stainless steel in 50 Hz pulsed dc discharge”, Plasma Science and Technology, PST (Under review)


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*This thesis is based on work contained in the papers listed
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### ACRONYMS

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<th>Description</th>
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<tr>
<td>TRG-OES</td>
<td>Trace rare gas optical emission spectroscopy</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
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<td>Carbon nanotubes</td>
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<td>Multi wall carbon nanotubes</td>
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<tr>
<td>QUB</td>
<td>Queen's University Belfast</td>
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<tr>
<td>EDMS</td>
<td>Energy dispersion mass spectrometry</td>
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<tr>
<td>VUV</td>
<td>Vacuum ultra Violet</td>
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<td>RIE</td>
<td>Reactive ion etching</td>
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<td>Chemical vapour deposition</td>
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Trace rare gas optical emission spectroscopy (TRG-OES) is carried out to investigate the excitation temperature, relative densities of active species \( (N, N_2^+) \) and nitrogen dissociation in inductively coupled helium admixed nitrogen plasma for different rf power \((50, 100, 150 \text{ W})\), pressure \((0.2 \text{ – } 0.5 \text{ mbar})\) and helium percentage \((10\text{–}90\%)\) using Ar as an actinometer \((4\%)\). The excitation temperature is obtained from Boltzmann plot method using emission intensity of several argon lines. The dissociation of nitrogen has been investigated by both the actinometry method and the ratio \( (I_{N}/I_{N_2}) \) of the atomic nitrogen line emission intensity at \((746.83 \text{ nm})\) to the vibrational band \((0\text{-}0)\) of the \(N_2\) second positive system at \(337.1 \text{ nm}\). The excitation temperature increases with the increase in power and helium percentage and decreases with increase in fill pressure. The nitrogen dissociation as well as the relative densities of \([N]\) and \([N_2^+]\) increases with the increase in helium percentage.

Optical emission spectroscopy and Langmuir probe are used to diagnose the low pressure inductively coupled \(\text{Ar-N}_2\) plasmas for different discharge parameters such as rf power \((10\text{–}100\text{W})\), filling pressure \((0.02\text{–}0.4 \text{ mbar})\) and argon content \((5\text{–}95\%)\) in nitrogen discharge. Both diagnostic tools are used to obtain the plasma parameters including the excitation temperature, the density of active species \((N,N_2)\) in ground electronic state, dissociation fraction, electron temperature, electron number density and electron energy probability functions (EEPFs) in \(\text{Ar-N}_2\) plasmas. It is noticed that the actinometry is an efficient and reliable technique to calculate the densities of nitrogen species. It is also observed that the active species generation, dissociation fraction and electron temperature significantly depend on discharge parameters and may be used to optimize the plasma reactor.

Mixture of single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) are treated for different treatment time \((0\text{–}120\text{min})\) at optimum discharge conditions. Changes induced in the elemental composition, surface morphology, crystallographic structure, and structural disorder in the plasma irradiated CNTs are analyzed by EDX, FTIR, SEM, XRD and Raman spectroscopy, respectively. Ar-\(\text{N}_2\) mixture plasma treatment of CNTs leads to significantly increase the electrical conductivity, modify the microstructure and induce structural disorder and a transition of crystalline phase from well crystalline to an amorphous structure.
CHAPTER 1
INTRODUCTION

1.1. Plasmas

Plasma is a quasi-neutral ionized gas composed of charged particles such as electrons, ions, either positive or negative and neutral particles that show a collective behavior. Plasma is present everywhere in the universe like stars, sun, stellar coronas; lightning and fire. Long and attentive efforts have been made for the creation of laboratory plasmas. It can be created artificially by applying electrical energy, and are used in industrial applications [1].

Plasmas are divided into two groups on the bases of temperature i.e. first one is the cold plasma and second is hot plasma. The subcategories of the cold plasmas are thermal cold plasma and non-thermal cold plasma. The temperature of electrons and ions in thermal cold plasma lies in the range of \((T_e \approx T_i \approx T \leq 2 \times 10^4 K)\) and for non-thermal cold plasma \((T_i \ll T_e \leq 10^5 K, T_i \approx T \approx 300 K)\). For cold plasma the degree of ionization of the particles is very low, almost 1% or less than 1%. The hot plasma is completely ionized plasma having higher electron energy and ion temperature than cold plasma i.e. \((T_i \approx T_e \geq 10^7)\).

The fundamental principle of the plasma generation is to transfer enough energy from energetic electrons to the molecules present in the gas to ionize and dissociate them through inelastic collisions. These all processes finally lead to the formation of the plasma state.

1.2. Literature Review on Plasma Diagnostics

In thermal equilibrium (TE), most of the plasma species have the same temperature such as electrons, ions, and neutral species. Non local thermodynamic equilibrium (non-LTE) plasmas are characterized by the plasma species having different temperature. In low temperature non-LTE plasmas, electrons have higher energy than ions i.e. the temperature of the electron lie from 1 to 10 eV [1]. Plasmas have a number of applications in many disciplines of science, technology and industries. Microelectronics industry is an important field of application. In this field, the plasmas are employed as
etching agent of metallic surfaces as well as for coating as thin films. Similarly plasmas are extensively utilized in processing of materials such as high performance ceramics, surface coating, sparkling and pre-treatment of outer layer of the different materials. Plasma technology is rapidly covering world market predictable over trillions of dollars annually due to its heavy use in the industry such as waste reprocessing, microelectronics, flat panel displays, high power switches, sputtering, ion implantation, etching and plasma torches etc. [2].

So far, the study has been focused on the advancement on a variety of plasma sources, diagnostic and analytical tools for examination of plasma parameters and for industrial purpose. Summary of the work that has been performed by different research scientist for the evaluation of various plasmas, are employed for different engineering purposes, are briefly discussed here.

Optical emission spectroscopy (OES) is widely used to determine the parameter of plasma such as excitation temperature($T_{exc}$), carrier concentration in ground electronic state, dissociation fraction, electron temperature ($T_e$)and electron number density ($n_e$). Another important diagnostic tool is a Langmuir probe that is extensively used to determine these plasma parameters [3, 4]. The effectiveness and the efficiency of rf and DC discharges depends on these plasma parameters [5]. The knowledge of these parameters helps to optimize the plasma used for material processing.

Khan et al.[6] investigated the changes induce due to the addition of Ar in nitrogen plasma powered by rf source. They obtained the dissociation fraction of nitrogen molecule up to 18% by the addition of 70 % Ar in nitrogen plasma at the pressure of the gas and applied rf power of 0.5 mbar and 300W, respectively. They also studied the discharge parameters ($T_e, n_e$) by using OES and Langmuir probe. They also studied the abundance of active species($N, N_2^+$and$N_2^{3+}$) and dissociation of nitrogen molecules.

Naveed et al.[7], used the OES to study the changes induced by He on the $n_e$and $T_e$in nitrogen discharge powered by pulsed dc source. They showed that the electron temperature is enhanced up to 0.67 eV by the addition of 90 % He in nitrogen discharge keep pressure and power constant at5 mbar and 300 W, respectively. Park et al. [8]
investigated the correlation between excitation temperature and electron temperature in capacitively coupled argon plasma. They reported that $T_e$ can be deduced from $T_{\text{exc}}$. Hope et al.[9] studied the electron temperature in Ar-O$_2$ as a function of filling pressure generated in a parallel plate dry etcher. They compared the results of OES and Langmuir probe and it is found that they are in good agreement with each other. They assumed that the plasma is defined by corona equilibrium model and line ratio Boltzmann plot technique is employed to calculate electron temperature. Boivin et al.[10] investigated the electron temperature ($T_e$) using helium spectral lines in rf generated helicon plasma system. In this work, the authors examined the number of helium transitions and selected a suitable pair of transitions. They calculated $T_e$ of about 10 eV by comparing two lines with method of line ratio and compare the results with theoretical model. They found good agreement between the results obtained experimentally and theoretically. They also studied the various transition levels of He and picked the suitable transition for lines ratio method to determine the plasma parameters. In 2003, Joshi and his group [11] calculated the variation in the temperature by using modified Boltzmann plot method in the plasma generated by a spray torch. The emission intensities of Ar atoms are used to calculate the temperature. They reported the temperature can be obtained without performing an Abel inversion at the central axis of the plasma column. Crolly et al.[12] investigated electron temperature ($T_e$) in rf generated argon and nitrogen. The comparative study of $T_e$ is performed by two types of Langmuir probes (i.e. single & double). They also compared the results with OES along with energy dispersive mass spectrometry (EDMS). Using OES technique, the ratio between atomic to ionic spectral line is utilized to calculate the $T_e$. They found the OES results are in accordance with the results of Langmuir probe. The densities of flux of single and double charged Ar ions are evaluated by using line ratio technique by employing EDMS technique. Once again the outcome of the electron temperature is in accordance with Langmuir probe results. Bibinov et al. [9] used the Langmuir probe and OES for the evaluation of electron energy distribution function (EEDF) in N$_2$ and N$_2$/He plasmas. They reported that the results obtained by both the techniques are inside the range of the experimental errors. The dissociation fraction of N$_2$ molecules is estimated and found to be minute because of strong N–N bonding [13].
From literature it is observed that the rate of dissociation fraction is enhanced by mixing the noble gases (He, Ne, Ar) in to the N$_2$ discharge by using different techniques. Such as, Saloum et al. [14] determined the dissociation fraction by using OES in rf generated argon admixed N$_2$ plasma. They concluded that the rate of dissociation is increased with the increase in Ar content in nitrogen plasma. They found a higher value of dissociation at a filling pressure of 5 Pascal with 50%Ar in nitrogen plasma. Czerwiec et al. [15] have investigated the nitrogen dissociation by Ar addition using mass spectrometry and actinometry method in rf generated nitrogen plasma. They observed that the dissociation of nitrogen molecules is increased by the addition of Ar; highest dissociation is obtained at 10% Ar in the argon admixed nitrogen plasma. Nakano et al. [16] measured the rate of dissociation fraction of nitrogen molecules in rf generated ICPs by using vacuum ultra violet (VUV) spectra. They observed that the dissociation fraction is increased from 5 % to 20 % with increasing rf power (30 W - 100 W) at filling pressure of 0.665 Pa. Shin et al.[17] measured the degree of dissociation in ICP using OES and found that the dissociation rate decreases slightly with increasing power. Liu et al.[18] observed that the addition of Ar may increase the rate of dissociation fraction and ionization of N$_2$ molecules. It is also observed by them that the factor of increase in dissociation is much higher than that of ionization. The observed factor of dissociation in mixture nitrogen plasma is four times the pure nitrogen plasmas. Voulot et al. [19] achieved the dissociation fraction of nitrogen molecule from 10 to 40 % for ICP sources for molecular beam epitaxy (MBE). Itagaki et al.[20] reported the degree of dissociation is maximum ($I_N/I_{N_2} \sim 0.48$) at the rf power of 1.5kW and filling pressure of 0.27 Pa, using 915 MHz electron cyclotron resonance (ECR) Ar-N$_2$ plasma. Liu et al. [18] reported the nitrogen dissociation and ionization mechanism using OES operated at 10 kV in Ar/N$_2$ Flue plasma. The dissociation rate of nitrogen is increased by adding Ar \( 0.06 \frac{m^3}{h} - 0.9 \frac{m^3}{h} \) in to the N$_2$ plasma. The maximum increase is 4.3 and this value increases with the increase of nitrogen in the discharge. They also measured the density of ionization by adding argon in N$_2$ discharge. The ionization density is increased with the addition of Ar (0.1 m$^3$/h to 1.5 m$^3$/h) in N$_2$ discharge. Nisha et al. [21] studied plasma parameters in rf
generated Ar plasma using OES and Langmuir probe. They measured $T_e$ and $n_i$ by varying the input power. The electron temperature is exponentially decreased and $n_i$ linearly enhanced with rf power. Kimura et al. [22] reported that the EEDF in CF$_4$/O$_2$ ICPs plasmas at filling pressure of 8, 15, and 25 moor powered rf source. The value of $n_e$ is observed to decrease by increasing the oxygen content in CF$_4$ discharge lower than 20% and higher than this value is almost linear. They reported that the electron temperature obtained from these plasmas, it is not very much sensitive to the oxygen percentage in the CF$_4$ plasma.

Langmuir probe is used to determine the EEDF which is an essential plasma parameter. The knowledge of EEDF is necessary for the theoretical modeling of physical and chemical processes occurring in the plasmas. The shape and different sections of EEDF describe various behaviors of plasmas; these includes diffusion coefficient having dependence on the EEDF bulk area and tail gives the knowledge about the excitation and ionization rates coefficients. Tuerner et al. [13] calculated the EEDF by using Langmuir probe in Ar plasma powered by rf source. They compared the results with theoretical modeling using the particle in cell method. A good agreement is achieved between theoretically and experimentally measurement of EEDFs in the pressure range from 20 to 200 mTorr. Fischer et al. [23] investigated the EEDF of pure helium at low-pressure in electron-cyclotron resonance plasmas. They observed the Druyvesteyn-like shape of EEDF and a decrease in the electron energy is observed with the raising the gas pressure in the discharge while electron number density increases from 0.13 to 1.33mbar at current of 100 mA. Paranjpe et al. [24] measured the concentration of charged particles and EEDFs in Ar-SF$_6$ plasma using a tuned Langmuir probe. The characteristic of this Langmuir probe is that the distortion induced by the rf to Langmuir probe was reduced by adding a simple passive circuit. Bai et al. [25] reported the measurement of EEDF in inductively coupled N$_2$/He, Ar, Xe mixtures plasmas to obtain different plasma parameters. They measured the ion species (N$_2^+$, N$^+$) and also calculated the ion ratio using mass spectrometry. They reported that the ratio of ion number density ($N^+$/N$_2^+$) is strongly dependent on electron temperature. Godyak et al. [26] has reviewed different features of probe technique by using EEDF in the plasmas discharge. They reported the
measurements of EEDF in a 13.56 MHz capacitive coupled radio-frequency discharges. The measured EEDF is departed significantly, at pressure 0.03 Torr, the shape of EEDF is bi-Maxwellian. At 0.3 Torr the EEDF is Druyvesteyn-like. Important variation is observed in $n_e$ and $T_e$ from different parts of the probe characteristics curve. Dilecce et al. [27] investigated the He-N$_2$ rf generated plasma at 27 MHz with gas pressure of 0.1-2 Tor and input power of 10-50W. They used the Langmuir probe to determine EEDF and the results confirmed the non-Maxwellian behavior of plasma. Electron temperature and electron densities were obtained from recorded EEDFs. The comparison of results showed that in Ar discharge, the average energy is much lower than the helium discharges while the value of $n_e$ is increased due to higher cross sections and lower-energy thresholds in Ar than in He. The average energy is reduced with power and the charge density is enhanced in both He and Ar discharges.

1.3. **Introduction and Significance of Carbon nanotubes**

Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, which is significantly larger than any other material. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers, approximately 1/50,000th of the width of a human hair, while they can be up to 18 centimeters in length. CNTs have extraordinary properties that make them the emerging candidate for application in diverse fields [28].

Since 1952, different scientists reported the formation of some nano sized structures of carbon. In 1952, Radushkevich and Lukyanovich [29] published a paper in the Soviet Journal of Physical Chemistry. In this paper, the formation of hollow graphitic carbon fibers of 50 nanometers in diameter was reported. In 1960 Bollmann and Spread borough [30] studied the frictional properties of carbon due to rolling sheets of graphene. Graphene is the single layer of graphite structure. Electron microscope images of these samples clearly showed that structure resembled the multiwall carbon nanotubes discovered later on. In 1976 Oberlin, Endo and Koyama [31] reported the growth of nanometer-scale carbon fibers by the method of Chemical Vapor Deposition. In 1991,
Sumio Iijima at NEC [32], discovered the carbon nanotubes in the soot of arc discharge. In the same year, nanotubes were discovered by the CVD method by Al Harrington and Tom Maganas of Maganas Industries. In 1993, Groups led by Donald S. Bethune at IBM and Sumio Iijima at NEC [33] independently discovered single-wall carbon nanotubes and methods to produce them using transition-metal catalysts.

Elemental carbon exists in nature in different crystalline forms or is found as amorphous carbon. Its crystalline forms contain diamond and graphite. In diamond, each carbon atom is sp$^3$ hybridized. Graphite is composed of different layers, which are stacked up over each other. These layers are interconnected through the Vander Waals forces. These are week forces so layers can slip over each other. Each individual layer is called a graphene sheet. In a graphene layer, each carbon atom is sp$^2$ hybridized, and is attached to three other carbon atoms in the same graphene layer. Carbon atoms are linked together forming a hexagonal lattice. Basic building unit of CNTs is the same graphene sheet. This sheet is rolled up in a cylindrical tube to form CNT. This tube has diameter on the nano scale level that’s why it is called a nano tube. There are different types of CNTs. In single walled CNTs, graphene sheet is rolled up only once while in double walled CNTs, it has two turns. In multi walled CNTs, graphene layer is rolled up in different layers that form concentric cylinders of increasing diameter [34].

![Graphene Sheet to CNT](image)

Figure 1-1 Rolling up of graphene sheet to form carbon nanotubes [35]
CNTs have surprising properties on the basis of their unique chemical bonding and nano scale structure. Carbon atoms are sp² hybridized in CNTs. These bonds are stronger even than the sp³ bonds of diamond. On the basis of this strong bonding network between the atoms, CNTs have the extraordinary mechanical strength. Young’s modulus of CNTs is about 1000 GPa that is 5 times higher than that of steel. Tensile strength is up to 63 GPa, 50 times higher than that of steel. It makes them mechanically very strong. Diamond is considered to be the hardest material among all. Carbon is sp³ hybridized in diamond, while in CNTs, it is sp² hybridized. Chemical bonding based on the sp² hybridized orbital, is stronger than that of sp³ hybridized orbital. Bulk modulus of CNTs is (462-546) GPa, surpassing the value of 420 GPa for the diamond. On the basis of bonding strength, CNTs are found to be harder even than the diamond. CNTs have tubular hollow interior structure, due to which these are not strong enough under the compression stress [28].

CNTs have a very high aspect ratio, and large surface area. It is the ratio of their length to the diameter, found to be approximately 1000:1. Length of CNTs is very large as compared to their diameter; this makes the CNTs one dimensional. CNTs have a variety of electric properties. They show semiconducting and metallic nature on the basis of their structure and type. MWCNTs with inner shells interconnected, can also show the superconductivity. CNTs also own the good field emission properties, which is the emission of electrons from the surface of CNTs when exposed to the applied electric field. Electrons are emitted from the tips of the tube and the defective sites at the surface of the wall. CNTs are good thermal conductors. These are also thermally stable in vacuum up to 2800 °C and in air up to 750 °C [28]. CNTs can be easily functionalized. Functionalization of CNTs is the attachment of any element, molecule or the organic functional group to the carbon atoms. This process increases their chemical reactivity.

1.3.1 Literature Review on Plasma Processing of Carbon Nanotubes

Plasmas have been extensively utilized in materials applications that includes plasma nitriding, coating and etching, fabrication of integrated circuits and flat-panel displays, because of their high densities and spatially homogeneous profiles of reactive species
including excited atoms, free radicals and ions [36, 37]. Such plasmas are produced with high electron number density \((10^{10} - 10^{12}) cm^{-3}\), small surface damage and highly uniform source of radicals, to meet the industrial/commercial requirements [38, 39]. Moreover, inert gas admixed nitrogen plasmas have significant scientific and industrial role in the application such as polymer surface activation and alteration, nitriding of metal and steel, plasma sterilization of medical tools and production of semiconductors materials[2, 40]. Especially, with the increase of Ar content in \(N_2\) discharge is useful for easy production of stable and uniform discharge. The addition of argon may also cause a change in the shape of the EEDF, \(T_e\) and consequently in the electron number density \([25, 41]\).

Iijima et al.[32] discover the carbon nanotubes in 1991 after that a significant study is carried out on their structures. Research results explored the astonishing properties of CNTs and their different possible types. Plasma treatment of CNTs is found to be an effective technique to enhance their properties and to modify their structure. CNTs have good conductivity and field emission properties. Field emission is the emission of electrons from the surface of CNTs by the application of electric field. It makes them excellent candidate for use in the electronic devices.

In recent years, plasma treatment of carbon nanotubes became an important topic of research specifically with the variation of different discharge parameters having significant job to enhance the field emission properties and the modifications of microstructures [42]. In addition, plasma treatment has been applied to modify chemical, mechanical and electrical properties of CNT [43]. Different works are reported [42, 44, 45] for the processing of CNTs to modify the field emission properties and microstructure in the mixture plasmas. Effect of different plasma gas chemistry, working pressure and flow rate on CNTs was also observed. Yu et al.[46] treated the carbon nanotubes in rf generated hydrogen plasma at gas pressure, rf power and time duration of 2-5mbar, 200-300W and 15-20 min, respectively. They reported that the field emission and structural properties of carbon nanotubes are changed and active sites on the surface are increased by plasma treatment. Feng et al.[47] reported the effect of gas mixture
plasma processing on structural and electrical properties of CNTs. The plasma treatment was carried out in the mixture of gases (H₂, N₂ and NH₃) at gas pressure, rf power and processing time of 1.5 mbar, 200–300 W and 0–40 min, respectively, with gas flow rate of 10 sccm. They reported that the defect density of plasma processed samples is increased and field emission properties are improved by three orders of magnitude. They reported that there is not any chemical bonding present between CNTs and plasma species. Nitrogen and hydrogen radicals are interacted with carbon nanotubes only physically and affect their field emission properties.

Hou et al.[42] reported the effect of Ar, O₂, CHF₃, and SF₆ plasma treatments on the morphological, structural, elemental compositions and working of CNT films electrodes in a reactive ion etching (RIE) system powered by rf source. According to their results, Ar-CHF₃-SF₆ and O₂/Ar processing are the better option for the improvement of electrical properties and gas ionization, respectively. In 2003 Yu et al.[46]also processed CNTs for field emission properties. CNTs manufactured by catalytic CVD process are treated in H₂ plasma, generated by capacitively coupled radio frequency source of frequency 13.56 MHz. Surface morphological changes are observed in treated CNTs. Surface of untreated CNTs is rough and tidy. While after treatment, surface morphology is totally changed. Surface defects are created and CNTs surface is reconfigured. CNT’s walls became open like palpus structure. Structural disorder and electrical conductivity of CNTs are found to be enhanced by plasma treatment. In untreated CNTs electrons are emitted from the tips of tubes only. While in the treated CNTs, surface microstructure is reconstructed, and active sites on the surface are increased. Now electrons are also emitted from every available active sites of the surface. Emission site density was increased so the electrical properties were also increased. Finally the hydrogen plasma was found an efficient method to enhance the electrical properties of CNTs. In the same year, another group, Zhang et al. [45] also reported the effect of plasma processing of screen printed CNTs (SPCNTs)to study the surface morphology and field emission properties. Motivation behind his work is that SPCNTs based field emitters could replace the well aligned CNTs based emitters, being low cost and larger surface area. SPCNTs are treated in nitrogen, ammonia, and hydrogen plasma generated by radio frequency
etching system. Hydrogen and nitrogen did not react with carbon of CNTs structure. Surface morphology of CNTs is changed and their microstructure is reconfigured. Some nano structures like nano-nodes appeared on the surface. While field emission properties of CNTs are enhanced in all plasma treatments due to enhancement of emission site density. It implied that the improvement of the field emission of CNTs is in fact independent of the chemical interaction of the hydrogen or nitrogen with the CNTs. Rather physical modifications occurred in the CNTs structure are sufficient to increase their electrical properties. In untreated CNTs the field emission occurred from the tips of the tubes while in the treated CNTs electrons are emitted from the nano buds developed at the surface of CNTs. So plasma ion bombardment is found to be a useful tool to enhance the electrical properties as well surface morphology of carbon nanotubes

On the basis of different experiments carried out for the plasmas treatment of CNTs, those results in the enhanced field emission properties, it became a field of interest. Yan et al.[48]studied the changes induced by plasma irradiation on field emission of CNTs and their applications. They concluded that CNTs had good field emission properties and generated very intense electric field even on the application of small voltages. CNTs based electrode set up used for the gas ionization reduced the applied voltage required for the ionization of a gas. CVD grown CNTs are treated in argon plasma generated in radio frequency ion etching system. It is observed that the Surface morphology and electrical properties of CNTs is changed by the plasma irradiation. Due to which an electrode based on the plasma treated CNTs developed a strong electric field on applying voltage, leading to the lowering of the ionization voltage of the gases like helium, oxygen, and argon.

It is concluded from the previous work that Chemical activity of CNTs could be enhanced by increasing the active sites on its surface by surface treatment of CNTs. Plasma treatment is considered to be useful way to reconfigure the surface morphology of carbon nanotubes. Bittencourt et al.[49] reported the deposition of metallic nano particles on plasma treated CNTs in 2006. They observed that electrical and chemical properties of CNTs could be tailored by addition of suitable nano structures. Deposition of nano structured metals on as synthesized and plasma treated CNTs are studied and compared. Interaction of metal clusters with CNTs is dependent on surface morphology of CNTs
that is modified by plasma treatment. CNTs synthesized by arc discharge and CVD are treated in oxygen plasma generated using ICP radio frequency discharge. In plasma treated CNTs, surface defects are created that increased the available active sites. Due to which the deposition of metal layer is very dense and uniform on treated samples. Concentration of active sites is smaller on treated CNTs synthesized in arc discharge than the synthesized in CVD. It is also observed that the chemical interaction between Ni particles and CNTs can modify their electrical and chemical configuration.

CNTs have unique thermal, chemical, and electrical properties. These are used as adhesive material for formation of polymer composites. Unpurified CNTs contain a layer of amorphous carbon on its surface, which reduces their reactivity. Purification of CNTs can improve their reactivity and potential for application in polymer composition. Xu et al.[50] reported his work based on purification of CNTs by plasma treatment in 2007. CNTs were treated in ICP generated oxygen plasma in two modes. In first mode, CNT powder was exposed to plasma directly. Here surface morphology is changed even at lower power and smaller exposure time. Amorphous carbon was removed from the surface and oxygen was attached to CNTs. Ion bombardment created surface defects such as vacancies and interstitial sites at the surface. But higher power and longer exposure time damaged the CNTs’ structure. In second mode CNT powder was placed inside a rotating barrel between the two electrodes to have a uniform plasma exposure. Higher power and larger exposure time was required to change the surface morphology and chemistry of CNTs. Plasma treatment was found to be very effective source of quick purification of CNTs and their chemical and surface morphological changes.

Basic building unit of CNTs is the graphene layer. Graphitic carbon surfaces are good choice for developing the electrochemical sensors. The sp² bonded carbon in graphite is chemically stable and very good conductor. Surface treatment of graphitic carbon improves its electrochemical properties. Deslandes et al. [51] reported the plasma treatment of highly ordered pyrolatic graphite (HOPG) in 2009. HOPG was treated in methane plasma generated in ICP mode. Effect of different operating parameters like exposure time, power and pressure was examined. Surface morphology of graphite was changed; new growth sites were formed on the surface. Hydrogen was incorporated on
the surface of graphite. When the exposure time was increased beyond 60 minutes, a dense hydrogen film was deposited on surface of HOPG. But hydrogen layer increased its resistivity which was not the desired effect for their use in electrochemical sensors. So plasma treatment of graphite layer within the optimum conditions increased its conductivity and chemical activity.

On the basis of their unique properties, CNTs are widely used in the field of medicine, medical engineering and drug delivery. Kalbacova et al.[52], reported their work in 2011. There work is based on the use of functionalized CNTs in the field of medicine. They studied that Plasma treated CNTs based substrates are used to increase adhesion and proliferation of osteoblasts cells. Osteoblastic cells are the human cells that form the bones. Their mutual adhesion is very important for their functioning such as proliferation and the protein synthesis. CNTs can be utilized as holder for the osteoblasts cells development and the proliferation. CNT films were treated in oxygen plasma generated by rf source. Plasma treatment introduced the structural defects on the surface of CNTs. Presence of these defects was confirmed by Raman spectroscopy. Reactive sites were increased and the oxygen was attached on the surface. Prolonged plasma treatment damaged the CNTs. Osteoblasts cells were grown on both the pristine and the treated CNTs. It was concluded that the surface morphology of CNTs was changed and oxygen was attached on the surface. Adhesion and the proliferation of osteoblasts cells was increased on the treated CNTs based substrates.

It is concluded that plasma treatment of CNTs is an efficient technique that can be used for purification of CNTs. It can be used to functionalize the CNTs that increase their chemical reactivity. Plasma treatment induces significant changes in the surface morphology of CNTs that leads to some very interesting and new properties in CNTs.

1.4. Plasma Generation

Plasmas are formed by providing enough energy to the gas particle to generate charged species i.e. positive and negative ions by electron attachment, electrons, and neutral species. Positive and negative charged particles are formed by transforming large amount of energy, this energy is utilized rapidly before it is vanished to the surroundings and this
energy is maintained in order to keep in the plasma state. Plasmas are generated in many way and different sources are used to produce it. These sources include rf generator of fixed and variable frequencies, DC and Pulsed DC source, microwave and dielectric barrier discharges etc.

### 1.4.1. Direct Current (DC) Discharges

DC glow discharges are usually produced in a vacuum sealed wall container consist of two metallic electrodes. The inter electrode distance is very small of the order of few centimeter. These electrodes are connected to a battery by wires through a switch and a variable resister. The anode and the cathode are connected to the positive and negative terminals of the source, respectively. When a sufficiently high voltage is applied through a variable resistor, an electrical discharge occurs between the electrodes. During this process the gas is transformed into a plasma state. As a consequence, a DC current move from side to side of steady state discharge as give in figure 1-1. These parameters i.e. Current and voltage between the electrodes are used to study the plasma behavior inside the tube.

The phenomena of breakdown of the gas may be explained as under: a small number of electrons are ejected from the surface of the electrode due to the universally existing cosmic rays. These electrons are emitted without applying any voltage but these are not capable to maintain the discharge. On the other hand, when the voltage is applied, the
electric field speeds up the electrons in front of the cathode. These electrons strike with the atomic species in the gas. The most significant impacts are the inelastic collisions that results with the excitation and ionization of the discharge. With de-excitation of the species photon are emitted with typical frequencies. These characteristics of excitation and de-excitation are responsible for the creation of plasma called ‘glow’ discharge. These whole processes cause the creation of new electrons and ions by ionization. The ions present in the plasma are accelerated toward the cathode by the electric field, where these ions produce ion-induced secondary electrons. These secondary electrons experience further collisions, creating new ions and electrons. The glow discharge self-sustaining is made by this emission of electron at the cathode and ionization in the plasma. A uniform potential difference is applied between the electrodes, a constant current move in the discharge when a uniform voltage is applied across the electrode. This current will result a discharge called a direct current (DC) glow discharge. As shown in figure 1-3, some significant electrical discharges appeared while changes the current and voltage across the electrode. The discharge known as Townsend discharge is sustained independently describe by a small discharge current. The change from sub-normal to normal glow discharge is characterized with the decrease in voltage as a function of current. It is observed that an abnormal glow discharge is generated with further increase in the current. At the end the plasma goes to arc region at large amount of current.
Figure 1-3: The dependence of voltage upon current for various kinds of DC discharges

1.4.2. Pulsed DC Glow Discharge Plasma

If we look at the figure 1-3, the abnormal glow discharge appears after normal glow discharge. At this region thermionic emission starts from the cathode due to highly energetic particles. This process transforms the plasma from the normal glow to the arc discharge that results everlasting damage to the electrodes. Pulse dc discharges are used to reduce this effect and to avoid this transition from glow to the arc region.

The principle of the pulsed DC glow discharge, the applied potential continues after regular pulses with definite frequency and duty cycle according to the necessities of industries [53]. This discharge can be controlled according to requirement by using these pulsating voltages. At any time positive ions are just about to raise the temperature to the significant value that may cause thermionic emission due to which transition in the discharge may take place in to the arc region. To avoid this effect a biasing voltage applied to the cathode is switched off for a specific interval of time so that the ions cooled down and their heating effect is reduced. So the temperature of the cathode is reduced. In such a case few of the ions having sufficient energy are reached to the cathode. Now, at this stage when the power supply is switched off, the plasma species are slow down and finally the discharge is gradually ended.
Advantages of pulsed sources are as following:

- Pulsed DC discharge can be operated at high power and pressure
- It is possible to prevent the arc discharge by using a resistor in series in pulsed DC discharge
- On the other hand, for a short interval of time before the glow to-arc transition takes place, the discharge can be interrupted. The discharge can be broken up before it is re-lighted again.
- More activities are maintained by a changeable duty cycle of dynamic plasma regime and plasma afterglow.

1.4.3. Radio Frequency (rf) Discharges

In RF (radio frequency) discharges, alternating electric field is used having frequency range from few Hz to \(10^2\) MHz. Any value of this range of frequency can be used logically. The signal of resonance is generated if the frequency of the generator are utilized in plasma production then setup matches with the frequency of any adjacent radio receiver. These resonance signals cause noise in surrounding of radio receiver. The standard value for the generation set up of radio frequency plasma is 13.56 MHz for the whole world. This value is also suitable for the processing experiments of cold plasma. The suitable care of the setup is necessary which cannot reverberate (resonate) with the other radio receiver if some other frequency is used.

1.4.3.1. Capacitively Coupled Plasma (CCP)

Capacitively driven radio frequency (rf) discharges are usually utilized for material coating and their treatment for different industrial proposes. A schematic diagram that describe the setup of CCP that have two parallel plate electrodes with small distance as shown in figure 1-3. These plates are powered by rf generator to produce the plasmas inside them. This type of system is known as capacitively coupled due to the resemblance of electrodes configuration with the capacitor. Usually, capacitors consist of two electrodes with opposite polarities having small distance between them filled with dielectric material. These electrodes are switching their polarity comparative to one another with a specific frequency. The conductive medium of plasma between the
electrodes is used to separate them. The charge carriers oscillate periodically between the electrodes in capacitively coupled plasma (CCP); their movement obtains relatively randomized instantly when the polarity is reversed. Due to which the inelastic collisions are enhanced. It is also resulted due to quite random motion and constituent species strike with one-another relatively fast. So that at a particular power, degree of ionization in CCP discharges is greater than the DC discharge. Similar ionization rate may be obtained in rf generated CCP as compared to the DC discharge with low pressure, low power and low breakdown voltage,

![Figure 1-4: Capacitive rf discharges in plane parallel geometry](image)

By considering these properties, the plasma produced by radio frequency (rf) sources in CCP’s are beneficial as compared to the DC plasmas sources. Even at the low pressure, this kind of plasma having a greater degree of ionization and sustaining the discharge is free from impurities.

1.4.3.2. Inductively Coupled Plasma (ICP)

Inductively coupled plasmas (ICPs) are extensively utilized as a source of plasma processing. ICPs are developed in order to overcome the weakness of CCP’s, namely, the difficulty in independently controlling the particle density and energy due to their operation and design. The charged particle density of ICPs can be as high as $10^{12} \text{cm}^{-3}$. However, the density regime fall in the range $10^{11} \leq n_o \leq 10^{12} \text{cm}^{-3}$ for proficient
inductive discharge process, is still normally ten times larger than for rf powered CCP discharges at similar conditions of pressure $\sim 1\ Pa$. In ICPs, the energy of the oscillating electric field cannot directly interact with the discharge volume. In 1884, Hittrof first time proposed the idea of ICPs; he enclosed a solenoid around the tube filled with the gas. An alternating current is allowed to flow through the solenoid and energy is coupled inside the tube to generate the discharge. In 1942, Babat et al. established the construction of inductively coupled discharge at atmospheric pressure.

![Figure 1-5: The simplest configuration of inductively coupled plasma discharges](image)

- **Working of ICP:**

The working ICPs are based on the basic principle of induction. In order to generate ICP, a time varying electric field is applied through the coil and generates a time varying magnetic flux ($\varphi_B$) which penetrates into the plasma. The power transferring mechanism of ICPs is same as that of transformer. The phenomena of electromagnetic induction is applied in ICPs;

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

the time varying axial magnetic flux density induces an azimuthally electric field and induced current as shown in [figure 1-7](image). The free electrons are accelerated and sustained the discharge by this field [54]. By varying the current passing through a loop, the amount of the induced electromotive force (emf) is given by

$$\varepsilon = -\frac{d\varphi_B}{dt}$$

1.1
Where $\varepsilon$ and $\varphi_B$ are the electromagnetic force and linking magnetic flux, respectively. If the coil through which current is flowing has N number of turns then the induced emf will be given as

$$\varepsilon = -N \frac{d\varphi_B}{dt}$$  \hspace{1cm} 1.2

An induced current will flow through the circuit due to the induced electric field generated by induced emf.

In the equation 1.2, the negative sign represent that the direction of flow of the induced current is opposite to the direction of change in $\varphi_B$(magnetic flux) through the circuit.

![Figure 1-6: Basic set up for planar inductively coupled plasma discharge](image)

**Figure 1-6: Basic set up for planar inductively coupled plasma discharge [55]**

In this process the energy of electric field is transferred to the particles of gas such as electrons and ions. The charge particles are accelerated and transmit their energy through inelastic collisions. These inelastic collisions cause the ionizations of the atoms and molecules of the gas and are also responsible for more excitations of atoms and molecules to result the plasma in the tube. In this way there is no direct communication present between the applied field and the gas particles. The ICP discharges have two major configurations according to the structure based on the inductive element i.e. the planar configuration and the cylindrical configuration (see figures 1-5, 1-7).

In the planar configuration the inductive element is a coil that is wound in a spiral shaped plane. Planar coil is constructed upon the upper side of the dielectric window that is placed on the plasma chamber. The dielectric windows act as coupling media and also
used to prevent a direct connection between the planar coil currents and the gas chamber [55, 56].

Figure 1-7: Working of the planar coil configuration in Inductively coupled plasma setup [56]

If we consider the first part of the ac voltage signal, current flows all the way through in the clockwise direction through each turn. Due to this effect a magnetic field is generated in the direction determined by right hand rule. The magnetic field lines are directed in the upward direction at the center of the innermost turn and in the downward direction at outside of the outermost turn. A stronger field is produced due to overlaps of magnetic field lines of all the turns that linked with the plasma through the quartz window. Since an alternating voltage is applied a time varying magnetic flux is linked with plasma chamber. According to Faraday’s induction law, an electric field is induced with the chamber emf to produce induce current in the discharge [54, 56, 57].

This type of configuration is beneficial to decrease the losses in the plasmas and enhanced the rate of production of ions; a disadvantage is the enhancement of contamination of sputtered species, damage cause by ultra violet radiations and heating effect cause by the neutral particles on the substrate

➢ Cylindrical Geometry

In this type of configuration, a coil wound across the plasma tube in the shape of a helix. This type of ICPs works on the basis of Faraday law of electromagnetic induction. In this
type of setup an indirect coupling mechanism is used to transfer applied rf power to the
discharge gas particles. Mainly, an alternating current is flow through the solenoid that is
placed over the plasma chamber. In this type of geometry a uniform energy is transferred
resulting uniform plasma inside the chamber along its cylindrical axis.

![Diagram of cylindrical inductively coupled plasma discharge](image)

**Figure 1-8: Basic set up of the cylindrical inductively coupled plasma discharge**

### 1.4.4. Dielectric Barrier Discharge (DBD)

This type of source was first time introduced with the concept of ozone production by
Von Siemens in 1857 [58]. DBD are described by the existence of dielectric or insulating
layers (one or more than one) in the path of current between metallic electrodes, in
addition to discharge air gap. The main feature of this dielectric layer covering one or
both of electrodes is to prevent the transition of plasma discharge to an arc discharge. An
electric arc produces ongoing plasma in which current density is very high. Sometimes
electric arc becomes uncontrolled and may become destructive. Dielectric barrier
discharges are also called silent discharges as it produces no sparks due to local
overheating.

The materials used for dielectric barrier includes ceramics, quartz, polymer or other
materials of low dielectric loss and high break down strength. Metal electrodes can also
be coated by a dielectric. As an example, steel tubes coated by enamel layer can be
effective in dielectric barrier discharges. Thickness of dielectric layer covering electrode
should be small so that efficient power could be transferred through the dielectric to
cause break down of gas. In most cases, thickness of dielectric material is kept about 0.8mm.

![Figure 1-9: Dielectric barrier discharges in volume discharge configuration](image)

Dielectric barrier discharges cannot be excited through direct current due to presence of dielectric layer on the electrode. So, it must be excited through alternating current (AC) having amplitude of 1-100 kV and frequency ranges from only some Hz to MHz. Dielectric barrier discharges can be operated at rang of pressures, typically from 0.1 atm. to 1 atm.[59]. Dielectric barrier discharges can also be operated equally well in open atmosphere at atmospheric pressure. The type of gas used in dielectric barrier discharges depends upon application. The distance between two electrodes may vary starting 0.1 mm (for plasma display panels) to several centimeters. In the case of ozone production, inter-electrode gap distance is usually kept 1mm.

The most important feature of dielectric barrier discharges is the breakdown of working gas is initiated as large number of independent current filaments of nano-second duration, called micro-discharges. Proper understanding of micro-discharges is the key to the understanding of dielectric barrier discharges.

The two basic configurations of dielectric barrier discharges are volume discharge (VD) and surface discharge (SD). Other configurations of dielectric barrier discharges depending upon application are also exist. These configurations are combination of two basic configurations, such as co-planer arrangement which is utilized FPDs and packed bed reactor, which are utilized in the plasma chemical reactors.

The VD contain of couple of parallel plates as shown in the figure 1-8. One electrode is covered up with the dielectric layer. With the application of input power, micro
discharges are developed in the region between these two electrodes and cover up the whole volume in the gap. In this case; the micro-discharges occur in slim channel that passes gas of the discharge and arbitrarily dispersed above the surface of electrode. The amount of micro-discharges is directly related to the amplitude of applied AC supply.

**Figure 1-10 Configuration of surface barrier discharge**

On the other hand, Surface discharge consists of an electrode covered up with a dielectric layer and a number of surface electrodes are placed on this dielectric layer as shown in the figure 1-10. It is clear from here that no well-defined discharge gap is produced. So in this case micro-discharges only occur in a fine film on the surface of dielectric material that is observed over definite distance. The discharge area over the dielectric material can be enhanced by increasing the applied voltage [60].

In DBD, within few seconds after break down of gas, charges built up at the surface of the dielectric and as a result electric field at the position of micro-discharges is reduced to degree so the flow of current is interrupted at that place. Due to short interval of discharge, the transportation of charge is very small and energy loss, it may result in slight gas heating. But overall temperature of gas remains close to room temperature. A large fraction of energy of electrons inside a micro-discharge can be utilized for exiting molecules or atoms of background gas to initiate necessary chemical reactions. The energetic electrons in micro-discharge collide with the atoms and molecules of background gas producing ions, excited species and ultraviolet radiation which initiate chemical reactions.

Dielectric barrier discharges have large number of applications. Most of the applications of DBD are linked to the industry. Applications of dielectric barrier discharges include, industrial scale ozone production, plasma coatings, thin film deposition, treatment of
polymers, in cleaning and activation of substrates, plasma treatment of textiles, for deriving CO$_2$ high power laser, sterilization of surfaces and materials, in pollution control and in large area FDPs.

1.5. **Plasma Applications in the Industry**

Technology is playing key role in industrial development. The history of developed nations is based on the development of the new and appropriate technology to solve the specific problems and adapting the imported technologies to suit the local conditions. These countries possess an international technological dynamism that contributes a steady stream of technical improvements to their industrial production. This flow of technological changes generated a continual increase in the efficiency of industrial development. The increasing opportunities for employment and growth in turn, created improvements in living standards of their citizens.

Plasmas are very important from industrial point of view because they possess at least one of two important characteristics. There characteristic is high power or energy density. For examples, DC electrical arcs or rf inductive plasma torches, in which the plasma power density can range from 100W/cm$^3$ to above 10kW/cm$^3$. Such types of plasmas are in thermal equilibrium and are preferably used for thermal plasma processing. These plasmas are able to melt and even evaporate bulk materials and are used industrially for welding, plasma flame spraying, arc furnaces and other high temperature materials processing applications.

Since, the plasmas consist of free electrons, ions and excited neutrals due to which they can respond positively to any externally applied electromagnetic field and force. These applied fields may transport energy and momentum to the plasma particles. The fluid behavior of the plasmas are enabled by plasma species by inner self consistent electric and magnetic fields that cause in combined result similar to flow and waves. All the particles inside the discharge have their own energy distribution function and it is not necessarily be in equilibrium with each other. The sum of all interior energy is consisting of thermal, electric, magnetic field and radiative field. Their magnitude allows the plasma to be exists in an excited state. Plasma processing (PEP) exploits plasma as an industrial
tool. As an example of knowledge based postindustrial technology, it is environmentally clean, energy efficient with very little effluents and emissions. Its ability to integrate multiple process steps leads to high outputs and increased efficiency. Multitasking in a single reactor results in a faster response to changing market demands and lower capital cost. Control is quick, precise and amenable with computers improving its reliability.

A variety of transformations of the materials such as physical, chemical and metallurgical transformations takes place when materials are exposed and the plasmas are generated. The plasma material interaction phenomena with the manufacturing process are integrated by PEP. PEP technology changes the properties of conventional materials and makes new types of materials. The economic impacts of plasma enabled processing can be measured with the help of a number of indices. A trivial measure is the market for plasma processing equipment and products, which by conservative estimates, runs into hundreds of billions of dollars. Lifecycle enhancement of products such as engineering tools and components through plasma assisted modifications of surface and near surface properties is an important index of the economic impact. Improving the quality of environment by treating industrial emissions using the non-equilibrium plasma chemistry decarbonisation which reduces the negative economic impact of carbon pollution through treatments at the source is yet another measure. Finally, the economic significance of the contribution of plasma processing to consumer products, ranging from antireflection ophthalmic coating to giant plasma display panels for high definition television, cannot be forgotten.

This indicate a number of important applications of plasma including the hardening of tools, arresting fermentation (pasteurization) in foods, plasma based space propulsion systems, ecological cleanup, for lighting and lasers due to gas discharges, ornamental laminations, high definition television, separation of isotope, electrical power switching, technology of welding, cutting technology, and sterilization of medical products. Hence plasma technology has deep influence on our daily life. High efficiency lighting is perhaps the best example. Basically there are two types of plasma based light sources: fluorescent lamps and high intensity arc lamps. Fluorescent lamps have widespread use in
homes, industry and commercial settings. Inside every fluorescent lamp, it is plasma which converts electrical power into ultraviolet light that in turn, causes the lamp’s phosphor coating to produce the light that we can see. High intensity sources are widely used in industry and commercial settings as well as for outdoor and security lighting near homes and public areas. Another best example of plasma product is the Pentium chip in which 500 million micron sized transistors, capacitors, resistors and diodes are formed on silicon substrate and wired together to form a circuit in approximately a one square cm area [61]. These devices power home computers, televisions and electronics. Now plasma display panels are slowly replacing the bulky cathode ray tube displays in the television. These panels consist of millions of pixels made from tiny gas discharge plasma sources. The construction has two glass plates, each containing parallel electrodes, sealed to form an envelope filled with a neon and xenon gas mixture. Gas discharge plasma is created by applying an electric field between the electrodes. Each pixel consists of three sub pixels, one each of red, green and blue. By combining these primary colors at varying intensities, all colors can be formed.

New methods for surface cleaning and the technique of freeing food and medical instruments from microbes, and other applications are also made possible by plasma systems. In contrast to heat sterilization, which is very slow, and causes damage to materials, this new plasma technology has been shown to kill bacteria on various surfaces within seconds. In addition to kill bacteria, the other micro-organisms like viruses, fungi and spores are also destroyed by such plasma system, besides providing an environmental friendly method for pre- treating surfaces. Plasma can mediate in producing wear and corrosion resistant hard coatings on engineering tools, increasing tool life and enhancing productivity. Small plasma reactors are placed in the exhaust of automobiles for removal of the harmful nitrogen oxides emitted by the diesel/petrol burning engines. These types of reactors can also clean emissions from coal burning power stations.

Traditionally, plasma is studied in the context of astrophysics, power generation and thermonuclear fusion research. The major motivation towards the growth of plasma sciences came from the search for conditions under which the $^1\text{H}^2$ and $^1\text{H}^3$ nuclei fuse together to form $^2\text{He}^4$. This would yield nuclear energy. Likewise nuclear reactions create
the stars to burn up and act as powerful source of energy. On the earth, many conditions are required to release this energy and these conditions must be simultaneously fulfilled.

The low density plasma can be confined and heated in magnetic traps using a variety of energy sources like intense RF (radio frequency) fields or energetic neutral beams or the large currents. The Tokomak, invented by Russian scientist, Igor Tamm and Andrei Sakharov is the most successful of such traps. Tokomak has a donut shaped vacuum vessel. This vacuum vessel is filled with mixture of \(^2\text{H}\) and \(^3\text{H}\) at a low pressure. A toroidal magnetic field is produced by the magnetic coil which is wounded around the chamber. The current flowing in the toroidal plasma heats the plasma by ohmic dissipation. A poloidal magnetic field is also produced by this current. The conjunction of poloidal magnetic field with the external toroidal magnetic field produces confining magnetic surfaces to which the plasma particles stick. Tokamak Fusion Test Reactor at Princeton, USA has demonstrated the scientific feasibility of fusion through experiments in which \(^2\text{H} - ^3\text{H}\) plasmas were burned to produce thermonuclear neutrons, even though at low power levels of the order of a few megawatts. It is a major break through towards the goal of power producing reactors in the ITER (International Tokamak Experimental Reactor).

Plasmas of industrial interest have not only improved quality of our life but have also provided equally new challenges to scientists. With the use of plasma technology in industry, higher quality and sometimes cheaper products can be obtained. Properties of plasma such as high temperature, energetic e\(^-\) (electrons) and e\(^+\) (ions), existence of plasma in very wide range of densities, pressure and temperature provide the positive use in industry. An additional advantage of plasma technology is that, it is environmentally clean technology as compare to conventionally exist other chemical industries. Due to non-equilibrium conditions of plasma, it can improve some chemical and material industry.

The most important application of plasma in these days is the production of large scale micro-electronic circuits or micro-chips, which are used in almost every electronic device such as personal computers and cell phones. Probably, we would not have computers and
cell phones like we have now, without plasma processing. Plasma processing of materials surely affects a lot of manufacturing industries, including defense, automobiles, biomedicines, computers, hazardous wastes, aerospace and telecommunication.

In order to improve surface properties of material without changing their bulk properties, plasma technology is very useful. Surface of materials such as metals, alloys, semiconductors, ceramics, insulators and polymers can be modified using plasma technology. The refractory (difficult to melt) metals are best deposited using sputtering or PACVD (plasma assisted chemical vapor deposition). Plasma is used to start chemical reactions in gas with electric discharges. In case of standard vapor deposition, the interaction between substrate and vapor occur at high temperature. Sometimes, the substrate is damaged by these high temperatures. By using PACVD the ions are attracted towards the substrate from plasma, which can be kept at very low temperature as compared to conventional chemical vapor deposition (CVD).

Plasma polymerization (PP) is another way to deposit thin films of organic substances like polymers. For example, when tetraflouroethelene gas is injected into plasma, Teflon like film is deposited on the substrate. Plasma turns the starting gas into fragments which may nucleate into a polymer film at the surface of substrate or polymerize into chain of clusters. So plasma processing may produce thin films of polymers necessary in many applications like coating on other materials, multiple layers for magnetic recording tapes or disks and plastic wrapping materials. Here, magnetic recording industry is also multi-billion dollar enterprise.

One of the major problems facing mankind all over the world is the disposable of hazardous waste materials. Many billions of tons wastes exist around the world. Plasma can be used as better and cheaper means of “clean-up” of many of waste materials like concentrated liquid organic hazard wastes, wastes from manufacturing processes, low level radioactive wastes, municipal solid wastes and hazardous chemicals in gas media. When waste material passes through arc plasma either in the form of liquid spray or fine powder, then chemical bonds can be broken to decompose the hazardous wastes by using the plasma processing. The undesired wastes can be decayed into non risky components
by heating the plasma to a very high temperature. Other industrial applications of plasma include plasma sprays, plasma arcs for welding and cutting, plasma space propulsion, plasma display panels and plasma lighting.

Last but not least, research on high temperature plasmas for fusion to get energy to meet energy requirement of growing world is going on.

1.6. Layout of the Thesis

In summary, the thesis encompasses the following chapters: First chapter has three parts, first part include the definition of the plasma, and classification and generation of different type of plasmas. The second part of the chapter provides the literature review for the understanding of plasma parameters including electron temperature, electron number density, excitation temperature, dissociation fraction, EEPF etc. A historical background of plasma processing of carbon nanotubes and their applications in industry is discussed. In third part, a review of most commonly used laboratory plasmas is presented and identifying which type of non-Maxwellian plasmas is important for material processing. In last, this chapter includes the plasma applications in the industry. In second chapter, a detailed discussion is made on plasma diagnostics and tried to explore the proper statistical model for low pressure inductively plasmas. This chapter includes the different coupling schemes used for the representation of atomic transitions occurring between two states. It also explains different type of levels, including translational, vibrational and rotational energy levels along with selection rules. In the same chapter, a detailed discussion is made on the plasma statistical model and calculation of excitation temperature. It also includes the comprehensive study of actinometry and calculation of concentration of active species in their ground electronic state and dissociation fraction using actinometry. The experimental set up and the characterization techniques are explained comprehensively in chapter # 3. These characterization techniques include the Raman spectroscopy, XRD, SEM, EDX, FTIR, and DC electrical resistivity. Synthesis, purification and procedure for pellets preparation of carbon nanotubes are also discussed in detail. Fourth chapter contains the experiment conducted for the characterization of rf generated He-N₂-Ar plasmas. Boltzmann plot is
employed to calculate the excitation temperature with effect of He content in N\textsubscript{2} mixture keeping argon as a trace gas. Actinometry is used to study the effect of helium mixing on ground state densities of active species and nitrogen dissociation in inductively coupled plasma. Fifth chapter deals with characterization of rf generated Ar-N\textsubscript{2} inductively coupled plasma by using Langmuir probe and OES. Electron temperature and excitation temperature is obtained by using Langmuir probe and OES, respectively. Other plasma parameter such as electron number density, floating potential plasma potential, concentration of active species and dissociation fraction are obtained using above mentioned diagnostic techniques. Sixth chapter include treatment of carbon nanotubes in the mixture of rf generated inductively coupled Ar/N\textsubscript{2} plasmas. Different characterization techniques are used to explore the changes induced in the carbon nanotubes by plasma treatment. Finally all the results are concluded in chapter 7 along with suggestion of future work.
CHAPTER 2
PLASMA DIAGNOSTICS

2.1. Introduction

Plasma diagnostics are used to study the physical and chemical processes occurring inside the discharge. These processes may strongly affect the discharge parameters. Appropriate and reliable diagnostic tool is necessary to study the internal behavior of the plasma and processes occurring in it. The diagnostic techniques can be categorized into ex-situ (offline) and in-situ (online) techniques. The first method is used to characterize the contents of plasma reactor and transfer fragment of the contents outside the reactor for examination. The in-situ is an online diagnostic technique with further classification of intrusive and non-intrusive techniques. The most used plasma diagnostic techniques are mass spectrometer, electric probes and optical emission spectroscopy.

2.2. Optical Emission Spectroscopy (OES)

Optical emission spectroscopy (OES) has been widely used to characterize the plasma due to its non-intrusive nature. It is used for the investigation of various plasma parameters such as electron energy distribution function (EEDF), electron number density ($n_e$), electron temperature ($T_e$) and excitation temperature ($T_{exc}$) due to its non-perturbing nature [3, 4]. OES can be used to study the other mechanisms occurring in the plasma like excitation and de-excitation processes, dissociative excitation and recombination etc.

- Plasma spectroscopy

When sufficient energy is provided to an atom by a suitable energy source, this energy is utilized by the electrons to excite to from lower to higher energy level. There is a natural tendency for the excited electrons to make a transition or drop back down to the ground state. When an electron makes a transition from a higher energy level to a lower energy level, electromagnetic radiation or photons are emitted. Both the absorption and emission of energy are quantized with certain allowed transitions. An electron may drop all the way back down to the ground state in a single step (emitting one photon), or may drop down in smaller steps (emitting a photon with each step). In either case, the energy of the
emitted photon is equal to the difference in energy between the upper state and the lower state. The unique energy levels are present in each atomic system. The electromagnetic interaction among various bound electrons and the nucleus are used to determine these unique energy levels [62, 63].

2.3. Atomic and Molecular Spectroscopic Terms

Many fairly accurate theories are presented to compute the atomic energy levels. Currently, the energy levels of many atomic systems are identified and tabulated in the form of Grotrian diagram. One way to designate the various energy levels in the Grotrian diagram is called LS (also known as Russell-Saunders) coupling. However, it should be noted that the LS coupling scheme does not necessarily specify each energy level uniquely, thus one should be careful about using LS coupling scheme. According to this scheme, each state is denoted by its orbital and the spin angular momentum along with each electron’s configuration state [64].

2.3.1 L-S Coupling

The approximation in which the residual electrostatic interaction between electrons is assumed to be large compared with the spin orbit interaction is called LS coupling and is important for light atoms. When more than one electron contributes orbital and spin angular momenta, the total angular momenta \( J \) is the vector sum of these individual momenta. The usual pattern for all but the heaviest atoms is that the orbital angular momenta \( l_i \) of the various electrons couple together into a single resultant \( L \). Similarly, the spin angular momenta \( s_i \) are also coupled together to a single resultant \( S \). The momenta \( L \) and \( S \) then interact via the spin-orbit effect to form a total angular momentum \( J \). This scheme is called LS coupling, can be summarized as follows [64, 65].

\[
L = \sum l_i, \quad S = \sum s_i
\]  
\[
J = |L \pm S|
\]

So total orbital angular momentum \( J \) will be

\[
J = |L \pm S|
\]

Permitted values of \( J \) given by a Clebseh-Gordon CG series are
In summary, the designation of atomic energy levels can be done using the spectroscopic designation of an atomic state for \( L - S \) coupling, given by \([65, 66]\).

\[
J = |L + S|, |L + S - 1|, \ldots, |L - S|
\]

Whereas, \( n \) is principle quantum number, \( w \) is the number of electrons in the \( l^{th} \) shell, \( L \) is the orbital angular momentum, \( 2S + 1 \) is the multiplicity and \( J \) is total angular momentum.

The multiplicity is equal to \( 2S + 1 \) in the usual situation, where \( L > S \), since \( J \) ranges from \( |L + S| \) to \( |L - S| \).

For \( S = 0 \), the multiplicity = 1, singlet state

\( S = \frac{1}{2}, \) the multiplicity = 2, duplet state

\( S = 1, \) the multiplicity = 3, triplet state

In a configuration for which \( S > L \), the multiplicity will be \( 2L + 1 \).

### 2.3.2 \( J - J \) Coupling

For atoms with large \( Z \), the spin-orbit effect is much stronger than the electrostatic interaction between electrons. It is appropriate here to couple the spin and orbital angular momenta of each electron separately to give resultant angular momentum \( j_i \). The total angular momentum \( J \) forms the resultant angular momenta of each electron \( j_i \) \([67]\).

\[
j_i = |l_i \pm s_i|
\]

So

\[
J = \sum_{N} j_i
\]

For \( jj \)- coupling scheme, the basis function is denoted by

\[
[(l_1, s_1)j_1, \ldots, (l_N, s_N)j_N]
\]

So it may be written in the spectral term as

\[
(j_1, j_2) J
\]

So that
\[ |j_1 - j_2| \leq J \leq |j_1 + j_2| \]

For a given electron configuration the total number of levels with a definite value of \( J \) will be the same for the \( LS \) coupling and for \( jj \)-coupling schemes.

### 2.3.3 The \( j_cK \) Coupling

Consider the argon atom with one electron excited to some higher excited energy level. Then the spin-orbit interaction in the atomic core is much stronger than the interaction between core electrons and the excited electron of the atom [68]. In this situation, the interaction is described by an intermediate coupling scheme, called \( j_cK \) coupling. In this coupling scheme, the spin angular momentum and orbital angular momentum of the core electron(s) couple with each other, resulting the total angular momentum \( j_c \) of core electron(s). i.e., for a singly excited argon atom:

\[
j_c = |l_1 \pm s_1| \tag{2.10}
\]

The electrostatic interaction between the excited electron and the atomic core electron will give

\[
K = |l_2 \pm j_c| \tag{2.11}
\]

The spin of the excited electron will couple with \( K \), giving

\[
J = |s_2 \pm K| \tag{2.12}
\]

As a result, the energy level of the atomic particle is characterized by a set of quantum numbers [68].

\[(LSjlKJ)\] \tag{2.13}

The term for the \( j_cK \) coupling is written in following way

\[2s+1Ljnl[K]_J \quad \text{or} \quad nl[K]_J\] \tag{2.14}

Where \( n \) is the principal quantum number of the valence electron.

The scheme may be summarized as a chart, given in figure 2-1.
Figure 2-1: Schematic diagram of the $j, K$ Coupling

For, singly excited argon atom (Ar-I) i.e.3p$^5$4s, the term may be calculated as follows.

\[
l_1 = 1, l_2 = 0
\]
\[
s_1 = \frac{1}{2}, s_2 = \frac{1}{2}
\]
\[
j = |l_1 \pm s_1| = |1 \pm \frac{1}{2}| = \frac{1}{2}, \frac{3}{2}
\]

When $j = \frac{1}{2}$

\[
K = |l_2 \pm j|
\]
\[
K = |0 \pm \frac{1}{2}| = \frac{1}{2}
\]

When $j = \frac{3}{2}$

\[
K = |0 \pm \frac{3}{2}| = \frac{3}{2}
\]

For $K = \frac{1}{2}$

\[
J = |s_2 \pm K|
\]
\[
J = |\frac{1}{2} \pm \frac{1}{2}| = 0, 1
\]
For $K = \frac{3}{2}$

$$J = |s_2 \pm K| = \left| \frac{1}{2} \pm \frac{3}{2} \right| = 1, 2$$

The spectral terms for $3p^5 4s$ will

$4s \left[ \frac{1}{2} \right]_{0, 1}$ and $4s \left[ \frac{3}{2} \right]_{1, 2}$

### 2.4. Molecular Spectroscopy

If we consider the case of molecules, the spectrum arises due to simultaneous transition between different energy levels. These molecular transitions are associated with atomic (within a molecule), vibrational and rotational energy levels, all of which are quantized. The atomic energy levels responsible for optical emission spectra are $\sim 1 - 10 eV$, whereas molecular vibrational energy levels are $\sim 0.1 - 1 eV$ and the rotational energy levels are $\sim 1$ milli $eV$. When molecules emit or absorb visible or ultraviolet light, band spectra occur. The spectra arising due to transition of electronic, vibrational and rotational levels of specimen, give rise to the band spectra [68].

A diatomic molecule may be considered as a two body mass-spring system, with many quantized vibrational energy levels [68]. The most convenient theory by which the electronic energies of molecule can be predicted is the molecular orbital theory (MOT). It assumes that the valence electrons in a molecule occupy orbitals which are not confined to a single atom but rather extend over the entire molecule. The molecular energy can be represented by:

$$eE = eE_e + eE_v + eE_f$$  \hspace{1cm} 2.15

Where $eE_e, eE_v$ and $eE_f$ are the energy associated with electronic, vibrational and rotational energy level.

#### 2.4.1 Electronic Energy Levels of Molecules

A molecule is formed or bonded by combining two or more atoms in such a way that the total energy is lower than the sum of energy of the constituents. The bonds are normally of ionic or covalent in nature. Many molecules of interest have somewhat different behavior of electronic energy levels. If we consider the diatomic molecules, it becomes
easier to elaborate the study of different state of the molecules. On the other hand, polyatomic molecules are significantly complex, because they are three-dimensional.

Diatom molecules are always linear, and the $z$ coordinate is chosen to align inter nuclear axis as shown in **Figure. 2-2**, with inter nuclear spacing $R$. The spacing $R$ certainly change, but it is confined by potential field that is developed by the molecular electronic orbitals. The value of $R$ at the minimum of the potential well defines an equilibrium at inter nuclear spacing $R_e$. The nuclei vibrate about $R_e$ and rotate about the center of mass.

![Figure 2-2: Diatomic molecule](image)

The situation for a molecule is somewhat similar to that for an atom. However, there is an important difference due to presence of an electric field along the inter-nuclear axis. The orbital angular momentum $L(= \Sigma l_i)$ precesses very rapidly about the direction of electrostatic field and only axial component of $L$ is a constant. The individual components along this axis are quantized. However, it is the resultant that is significant rather than the components. The axial component or the projection along the inter nuclear axis is characterized by the quantum number $M_L$, where

$$M_L = L, L - 1, \ldots, -(L - 1), -L$$  \hspace{1cm} 2.16

When $M_L = 0$, the molecular orbitals (MO) are symmetric for rotation about the internuclear axis and hence called $\sigma - orbitals$. when $M_L = \pm 1$ orbitals are known as $\pi \pm orbitals$. The $\pi \pm MOs$ are antisymmetric for rotation about the molecular axis, that
is, if we rotate the molecular orbitals by $180^\circ$, they change sign. Similarly $M_L = \pm 2, \pm 3$ etc. represent $\pm \delta, \pm \phi \pm$ etc.

![Figure 2-3: The vector diagram for coupling of $L$ about the electric field along the inter-nuclear axis producing the axial component $A$](image)

Since internuclear field is electrical in nature, therefore, energy is not changed by the exchange of $M_L \leftrightarrow -M_L$. The absolute value of $M_L$ is designated by the symbol $\Lambda$. For quantum number $\Lambda = |M_L| = 0, +1, +2, +3, ..., L$ symbols $\Sigma, \Pi, \Delta, \Phi$ etc are used respectively [69].

All of these states are doubly degenerated except $\Sigma$ states because of the condition $M_L \leftrightarrow -M_L$ symmetry. It is worth noting that the ground state (often labeled by the symbol X) of most diatomic molecules exhibits maximum symmetry. The multiplicity is given by $2S + 1$, whereas $S(= \sum Ls_l)$ is the total spin angular momentum and is used as prefixed superscript. For $\Lambda > 0$, magnetic field will be produced due to orbital motion of the electrons along the bond axis and $S$ presses about the magnetic field direction as shown in figure 2-4 [69].

The spin $S$ has quantized magnetic component $M_s$ having value $\hbar M_s$. The quantum number $M_s$ is designated by the symbol $\Sigma$ and the allowed states for $\Sigma$ are $(S, S - 1, S - 2, .... - S)$ that take $2S + 1$ values. For the molecular state $\Sigma (\Lambda = 0)$, there is no resultant magnetic field and therefore $M_s$ is not defined, so these states have only one component, whatever be the multiplicity.
Electronic configuration of a diatomic molecule can be derived by filling the electrons in molecular orbitals. Essentially same rules apply to their filling as the filling of atomic orbitals. That is,

- The electrons occupy the available molecular orbitals one at a time, the lowest energy orbitals being filled first (Aufbau principle).
- Each MO can accommodate a maximum of two electrons provided their spins are opposite (Pauli’s exclusion principle).
- No pairing of electrons in orbitals of equal energy will take place unless there is at least one electron in each of them (Hund’s rule of maximum multiplicity).

Another quantum number $\Omega$ is used to designate the total angular momentum of the diatomic molecule, analogues of $LS$ coupling for atoms, whereas

$$\Omega = \Lambda + \Sigma, \Lambda + \Sigma - 1, \ldots \ldots \Lambda - \Sigma$$

The quantum number $\Omega$ is used as subscripts. So the spectroscopic designation of a molecular state is $nlw^{2S+1}\Lambda_{g,u}^{\pm,-}$ [66].

In molecular spectroscopic term, to describe whether the wave function is symmetric or anti symmetric upon inversion with respect to the molecular axis, $g$ (gerade or even) or $u$ (ungerade or odd) are used as subscript. This is referred as parity in a homonuclear diatomic molecule; the overall parity is equal to the product of individual parities. If two occupied orbitals are gerade their product is also gerade (g), if the two occupied orbitals are ungerade (u), their product is also (g). However, the product of one gerade and one ungerade (u) orbital will be ungerade [70], i.e.

$$g \times g = g, u \times u = g, g \times u = u$$

Similarly, the ‘+’ or ‘−’ are used as superscript to denote whether the wavefunction in symmetric or antisymmetric with respect to a reflection plane through the internuclear axis [68, 69].
The energy level diagram of a diatomic molecule with two electrons, i.e. molecular hydrogen, is shown schematically in figure 2-5.

The two electrons cause a splitting into a singlet and a triplet system. In molecules, the energy levels are usually abbreviated by upper and lower case letters, where \( X \) is the ground state (as a rule). The corresponding spectroscopic notation is shown in figure 2-5 for the \( X \) and \( b \) states [66, 71].

Let us consider the ground state of term symbol for \( \text{N}_2 \) molecule having configuration.

\[
N_2(14) = (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2
\]

As the completely filled molecular orbitals contribute nothing to the total orbital angular momentum and the total spin angular momentum and the overall parity is \( g \), we have to
consider the contribution of \((\sigma_g 2p)^2\) orbitals only. The following configuration is possible.

For \((\sigma_g 2p)^2\) state

\[
\lambda_1 = 0, \lambda_2 = 0
\]

As \(\Lambda = \sum \lambda_i\)

So \(\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0\) Hence \(\Sigma\) state

As both electrons are in same molecular orbitals they must be paired. Thus

\[
S = s_1 + s_2 = (\frac{1}{2}) + (-\frac{1}{2}) = 0
\]

So, Multiplicity = \(2S + 1 = 2(0) + 1 = 1\) (Hence singlet state)

![Molecular orbital energy diagram for N₂ diatomic molecule](image)

Figure 2-6: Molecular orbital energy diagram for N₂ diatomic molecule

The product of two gerade \((g \times g = g)\) gives us \(g\) parity since electrons are in \(\sigma\) orbital superscript will be +. Therefore, terms symbol for \(N₂\) diatomic molecules is \(1\Sigma_g^+\)
2.4.2. Vibrational Energy Level

If we consider a diatomic molecule, then each atom of the diatomic molecule can oscillate or vibrate along the line joining from the center of the atoms. For a harmonic oscillator, the vibrational frequency is \( \propto \sqrt{\frac{k}{m}} \) and for a diatomic molecule, the vibrational frequency is \( \propto \sqrt{\frac{k}{m_R}} \), where, \( m_R \) is the reduced mass of the system. The vibrational energy level is given by [71].

\[
e E = h\nu_o \left( \nu + \frac{1}{2} \right), \quad \nu = 0,1,2, \ldots \ldots
\]

Where, \( \nu \) is the vibrational quantum number, \( h \) is Planck’s constant and \( \nu_o \) is the frequency of vibration.

The energy gaps of vibrational states are separated by \( \sim 10^{-1} \) eV and are in infrared region with wavelengths of \( 10^{-6} \) m to \( 10^{-4} \) m. The higher vibrational states of a molecule do not obey above equation because the parabolic approximation to its potential-energy curve becomes less and less valid with increasing energy. As a result the spacing between
neighboring energy levels of high \( v \) is less than the spacing between low \( v \), which is presented in the figure 2-7. Therefore, the energy is almost the same, but the spacing does decrease with increasing vibrational quantum number due to the anharmonic motion of the molecule. The lower and higher energy levels are typically labeled as \( \tilde{v} \) and \( \tilde{\tilde{v}} \), respectively, as shown in figure 2-8.

The oscillating dipole can only absorb energy \( \Delta E = \hbar \nu_o \) at a time, in such a case the energy increases from \( (v + \frac{1}{2})\hbar \nu_o \) to \( (v + \frac{1}{2} + 1)\hbar \nu_o \). It can also emit \( \Delta E = \hbar \nu_o \) at a time, in that case its energy decreases from \( (v + \frac{1}{2})\hbar \nu_o \) to \( (v + \frac{1}{2} - 1)\hbar \nu_o \). Hence the selection rule is \( \Delta \nu = \pm 1 \).

### 2.4.3. Rotational Energy Level

The molecular energy states occur from the rotational, vibrational and electronic motion of the molecule. Rotational states are separated by quite small energy gaps usually of the order of \( 10^{-3} \) eV. The spectrum that arises from transitions between these states corresponds to the microwave spectrum (\( 10^{-4} \)-\( 10^{-2} \) m). The lowest energy levels of a diatomic molecule take place from rotation about its center of mass. The rotational energy level of diatomic molecule is given by [63]

\[
E_J = J(J + 1) \frac{\hbar^2}{8\pi^2 l} = B_o J(J + 1)
\]

Where \( J \) represents the rotational quantum number and \( E_J \) is the rotational energy. Therefore, the energy spacing increases with increasing rotational quantum number as shown in figure 2-9. Again, the lower energy level is typically labeled as \( J \) and higher energy level is labeled as \( J' \), as shown in figure 2-8. Note that X denotes the ground state, while A represents an excited state[63].
The rotational spectra occur from transitions between rotational energy states. Only certain molecules having electric dipole moments can absorb or emit electromagnetic photons in such transitions. For this reason non-polar diatomic molecules such as H₂ and symmetric polyatomic molecules such as CO₂ and CH₄ do not have rotational spectra. However, transition between rotational states in molecules like H₂, CO₂, and CH₄ can take place during collisions. Even in molecules with permanent dipole moments, the transitions between all rotational energy levels are not allowed. In the case of atomic spectra, certain selection rules summarize the conditions for a radiative transition between rotational states to be possible. For a rigid diatomic molecule the selection rules for rotational transition is $\Delta J = \pm 1$

2.4.4. Selection Rule for Molecular Transitions

For practical applications, the following (approximate) selection rules are given for molecular transitions [71]:

- Change in orbital angular momentum: $\Delta \Lambda = \pm 1$
- Change in spin angular momentum: $\Delta S = 0$
The selection rule for $\nu'$ to $\nu''$ be: $\Delta \nu = \pm 1$

The selection rule for $J'$ to $J''$ will be: $\Delta J = \pm 1$

In addition, for transitions between $\Sigma$ states, the only allowed transitions are $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$ and for homonuclear molecules, the only allowed transitions are $g \rightarrow u$ and $u \rightarrow g$.

2.5. Statistical Plasma Models

The plasma state exists everywhere in the universe except some planets like our earth and plasmas can be produced in the laboratory according to the required conditions. The plasma is composed of charged particles (ions, electrons) and neutrals that may cover a very large range of electron number densities $n_e (1 - 10^{20} \text{cm}^{-3})$ and electron temperature $T_e (10^{-2} - 10^5 \text{eV})$. Taking into account these wide ranges, the plasmas are classified into to several categories i.e. a. complete thermodynamic equilibrium (CTE), b. local thermodynamic equilibrium (LTE), and c. Non-LTE [72, 73].

Inside the plasma, the interaction among ions, electrons and photons lead to many complex processes. These plasma processes include excitation, de-excitation, and ionization of atoms and re-combination of free electrons with the ions. Statistical plasma models provide an easy way to understand these processes. This section presents and compares various plasma models. A comparative study of these models allow us a quick selection of a suitable plasma model for the investigation of plasma parameters [73].

2.5.1. Complete Thermodynamic Equilibrium

Complete Thermodynamic equilibrium (CTE) is a state in which all particles (neutral atoms, molecules, ions, and electrons) are at the same temperature in the plasma i.e.

$$T_g = T_{ion} = T_{exc} = T_e = T_r$$

Where $T_g$, $T_{ion}$, $T_{exc}$, $T_e$ and $T_r$ are the gas temperature, the ion temperature, the excitation temperature, the electron temperature and the radiation temperature, respectively. Indeed, a high pressure involves in many collisions in the plasma, leading to an efficient energy exchange between the plasma species, and hence, equal temperatures. In case of a complete TE (ideal case) the radiation and particles present in the plasma
implies a balance between forward processes and their inverse processes. That is, each type of process should be directly compensated by a corresponding inverse process.

Secondly, it is assumed that distribution of population densities of electrons is determined completely by collisional processes. A system will be in thermodynamic equilibrium when there is an overall balance due to these collisional processes (elastic as well as inelastic) among plasma species and also reactions occurring in the plasma. CTE plasmas exist only in star’s core or during the short interval of a strong explosion.

Plasma is in complete thermodynamic equilibrium (CTE) if it follows the following four distributions/laws: i.e. Maxwell distribution, Boltzmann distribution, the Saha’s ionization equation and Planks radiation law [74].

a) **Maxwell Distribution**

The number of free electrons within the velocity range $v_e$ and $v_e + dv_e$ can be found by using the Maxwell distribution law as:

$$dn_e = 4\pi n_e \left( \frac{m}{2\pi k_B T_e} \right)^{\frac{3}{2}} \exp \left( - \frac{m v_e^2}{2 k_B T_e} \right) v_e^2 dv_e$$

Where, $n_e$ is the total electron number density, $T_e$ is the electron temperature, $k_B$ is the Boltzmann's constant and $m$ is the electron mass.

b) **Boltzmann Distribution**

If the plasma is in thermodynamic equilibrium, then the energy distribution of the particles is given by Boltzmann's distribution law.

$$n_i = n_o g_i A_e \frac{E_i}{k_B T}$$

Whereas $n_i$ the total number of particles in unit volume having energy $E_i$ and the statistical weight $g_i$.

c) **The Saha’s Ionization Equation**

The Saha equation is used to describe the degree of ionization of the atom and molecules as a function of the density, temperature and ionization energies. The Saha equation is only valid for weakly ionized plasmas having large Debye length. In case of ionization
and thermal equilibrium, \( T_{gas} = T_e = T_i \) \( (T_i \) is the ions temperature), the Saha’s ionization equation is obtained:

\[
\frac{N_e N_i}{N_a} = \frac{g_e g_i}{g_a} \left( \frac{mT}{2\pi \hbar^2} \right)^{\frac{3}{2}} \exp\left(-\frac{E_i}{k_B T_e} \right)
\]  \(2.23\)

In this relation, \( E_i \) is the ionization potential, \( g_a, g_i \) and \( g_e \) are the statistical weights of atoms, ions, and electrons, \( N_a, N_i \) and \( N_e \) are their number densities; and \( m \) is the electron mass. The Saha equation describes the ionization equilibrium \( A^+ + e \leftrightarrow A \), which corresponds to a detailed balance of electron impact ionization and three-body recombination: \( e + A \leftrightarrow e + e + A^+ \).

d) Planck’s Law:

The propagation of photons in the plasma is an important characteristic whose energy distribution \( (N_{\nu}) \) is given by Planck’s radiation law. If particles and radiation present in the plasma have same temperature \( T \) under thermodynamic equilibrium, then, according to the Bose-Einstein statistics.

\[
N_{\nu} = \left( \exp\left( \frac{\nu}{K_B T} - 1 \right) \right)^{-1}
\]  \(2.24\)

An important significance of Planck’s distribution law is that plasma radiation under thermal equilibrium has a continuous spectrum coinciding with that of blackbody radiation (black light). The spectral density of radiation \( \rho(\nu, T) \) at equilibrium is described by Planck’s radiation law [75]:

\[
\rho(\nu, T) = \frac{8\pi \nu^3}{c^3} \left( \exp\left( \frac{\nu}{K_B T} \right) - 1 \right)^{-1}
\]  \(2.25\)

With the increase of temperature, radiation becomes more and more important and dominates the energy exchange. At high temperatures, that exceed \( 10^6 K \), the thermodynamic properties of the plasma are completely determined by radiation and not by the collisions and in this case, in order to obtain the complete TE, all radiation emitted must be re-absorbed with same rate [73].
2.5.2 Local Thermodynamic Equilibrium (LTE)

The applications of plasma chemistry and plasma processing require a clear understanding and distinction between the concepts of CTE and LTE. Complete thermodynamic equilibrium is difficult to achieve in the plasma sphere because the temperature of radiation ($T_r$) at the edge of the plasma is not equal to the temperature in plasma bulk. However, local thermodynamic equilibrium can be achieved by considering certain laboratory condition in a small plasma volume which is of the order of mean free path [73]. Since, laboratory plasmas are mostly obtained in a cylindrical configuration and are limited in dimension. In such plasmas, an escape of radiation and gradients of number density and temperature are observed. The possibility of escape of photons is higher than material particles that strongly affect the Plank’s distribution. The energy exchange is so effective among materials particles (atoms, ions and electrons) such that locally the Boltzmann law, the Saha equation and the Maxwell distribution are not affected so that the temperature of material particles becomes equal. This phase of equilibrium under such a condition is called as Local thermodynamic equilibrium [75].

The condition for LTE is that the excited states must be populated and depopulated by electron collisions, rather than by radiation. This condition requires high electron number density which is sufficient to ensure a high collision rate. The corresponding lower limit of electron number density is given by the McWhirter criterion [76]:

$$n_e \geq 1.6 \times 10^{12}T^{1/2}(\Delta E)^3$$

Where $\Delta E$ (eV) and $T$ ($K$) are the energy difference between the two states and electron temperature, respectively. This condition is a necessary but insufficient for LTE. It is, however, difficult to satisfy for the low-lying states, where $\Delta E$ is large.

2.5.3 Non-LTE

Plasma is said to be non-LTE, if the population distribution of atoms/molecules in excited energy levels is determined by radiative processes (absorption and emission of photons). In non-LTE situation, the de-excitation of atoms/molecules is dominated by the radiative processes over the collisional processes. The collisional processes are almost negligible as compare to radiative processes in the excited state, in such a case; the population
density does not necessarily follow the Boltzmann distribution. Low pressure plasmas in the pressure range \(10^{-4}\) to \(10^{-2}\) KPa are categorized as non-LTE plasmas [77].

In non-LTE plasmas the electrons temperature is higher than the temperature of heavy particles. It is because the energy exchange by inelastic collisions between the electrons and the heavy particles are not very much effective due to the small mass ratio \((m/M)\). The electrons temperature lies in the range of one to ten electron volts while \(T_g\) (the temperature of the gas), can be as low as room temperature. Therefore, such plasmas are called as cold plasmas.

### 2.5.3.1 Corona Equilibrium Model (CE)

Optically thin plasmas achieve corona equilibrium (CE) in low density regime \((n_e \leq 10^{10} cm^{-3})\) where the radiative processes are much faster than the collisional processes. In that case, the excited levels are populated by direct excitation by electron impact from the ground state and depopulated by spontaneous radiative decay only. The radiative processes are dominant over electron impact de-excitation and electron impact recombination due to the low electron density. Some excited levels are also depopulated by radiative decay in cascade [2], which means that some lower-lying levels are populated by radiative decay from higher-lying levels. This cascade contribution to the population of the lower-lying excited levels is however negligible compared to the contribution of collisional excitation from the ground state as shown in **figure 2.10**. In **figure 2.10**, light and dark gray arrows represent the collisional and radiative processes, respectively, and their width is proportional to their importance in the population and de-population mechanism of a level.

Also in CE, the collisional de-excitation rate is rather small in comparison with the spontaneous decay, therefore the population of the ground state is very high with respect to the population of the excited levels tend to one and zero, respectively. Some excited levels are depopulated by radiative decay from higher lying levels. This cascade is however negligible as compared to collisional excitation from the ground state.

In particular, this model is suitable for spectroscopic analysis of radiation which originates from low lying levels of atoms and ions in plasmas. In corona model,
Collisional excitation ↔ radiative decay
Collisional ionization ↔ radiative recombination

Figure 2-10: schematic of the dominant population and depopulation processes in corona equilibrium

2.5.3.2 Collisional Radiative (CR) Model

For the electron density range $10^{10} \text{cm}^{-3} < n_e < 10^{18} \text{cm}^{-3}$, the excited levels exist neither in LTE nor CE. This state of plasma is different from coronal model plasma because collisional depopulation processes and stepwise collisional processes affect the population distribution. They are in a middle regime where the radiative as well as collisional processes are taken into account during the population and depopulation mechanisms. This situation is frequently encountered in laboratory plasmas in various regimes of electron density and temperature.

Generally, a rate equation is used to determine the population densities of each state of particles. Since this model balances the radiative as well as collisional processes, such model is called a collisional radiative (CR) model.

The population balance of the quantum levels $(i, k)$ are given by the differential equation as [73].
\[
\frac{dN_i}{dt} = \sum_k (N_k v_{ki} - N_i v_{ki}) + \sum_a S_{\alpha,i} + T_{ri}
\]

2.27

Where \( v \)'s are the frequencies of transitions for collisional and radiative processes between the given states, \( S \) is the source function describing the creation and annihilation (\( \alpha \)) of the particles \( N_i \) along with different chemical processes (chemical reactions, ionization, recombination and others). Transportation of the particles is represented by the term \( T_{ri} \).

The basic assumptions of the CR model are as under [78]:

1. The free electrons have a Maxwellian velocity distribution.
2. Ionization can proceed from any bound level and is partially balanced by three-body recombination:
3. The electron-induced excitation and de-excitation transitions take place between bound levels.
4. Radiation results from transitions between bound levels and from radiative recombination.
5. The plasma is optically thin.

2.5.4 Evaluation of Plasma Parameters

Optical emission spectroscopy is a valuable plasma diagnostics tool for the determination of various plasma parameters such as plasma temperature, electron temperature \( (T_e) \), excitation temperature \( (T_{exc}) \), electron number density \( (n_e) \), dissociation fraction and concentration of plasma species.

2.5.4.1 Boltzmann Distribution and Excitation Temperature

In plasmas, neutral atoms, ions, molecules and electrons are distributed over many energy levels. In non-LTE plasma, the average energy of these species, in general, is not the same. Therefore, each species may be considered at its own temperature. Electrons are responsible for atomic and molecular (rotational and vibrational) excitations. The analysis of the atomic and molecular spectra is associated with the electron’s average
energy (temperature). Boltzmann plot (described at the end of this section) method is commonly used to determine the temperature. It is found that in non-LTE plasma, the temperature determined from molecule’s rotational, vibrational and atomic spectrum associated with electronic transition are different with one another, and different with electronic temperature determined by the Langmuir probe. These temperatures approach to the same value when the plasma approaches to LTE conditions. Therefore, in the case of non-LTE plasma, the temperatures obtained by the analysis of atomic/molecular spectra are called excitation temperature, rotational temperature and vibrational temperature, respectively.

Consider two excited energy levels, $i$ and $j$ with energies $E_i$ and $E_j$ and the population densities of $n_i$ and $n_j$, respectively, having common lower energy level $k$. If an electron makes a transition from higher energy state $E_i$ to lower energy state $E_k$, a photon of energy equal to the energy difference between the two states is emitted.

$$\Delta E_{ik} = E_i - E_k = h\nu_{ik} \quad 2.28$$

The emitted photon has a characteristic frequency which is given by

$$\nu_{ik} = \frac{E_i - E_k}{h} \quad 2.29$$

Where $h$ is the Plank constant.

The determination of the temperature as mentioned above are based on the assumption that the distribution of electrons is Maxwellian and the population of the radiative states obeys the Boltzmann distribution. The population density of atoms occupying the states $i$ and $j$ with energy $E_i$ and $E_j$ will be given as.

$$n_i = g_i e^{-\left(\frac{E_i}{k_B T_e}\right)} \quad 2.30$$

$$n_j = g_j e^{-\left(\frac{E_j}{k_B T_e}\right)} \quad 2.31$$

Where $g$ and $k_B$ are the statistical weight and Boltzmann constant, respectively. From these two equations we can write as.
The emission intensity of the spectral line is proportional to the population density of the corresponding emitting state and given by [79].

\[
\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-\frac{(\Delta E)}{k_B T_e}} \tag{2.32}
\]

Where \( v_{ik} = \frac{c}{\lambda_{ik}} \) is the radiation frequency.

\[
l_{ik} = n_i A_{ik} \nu_{ik} \tag{2.33}
\]

\[
l_{ik} = n_i A_{ik} \frac{c}{\lambda_{ik}} \tag{2.34}
\]

Figure 2-11: Emission from excited levels to common lower level

From these two equations the population density ratio is given by
By using equations 2.32 and 2.36, we get

\[
\frac{n_i}{n_j} = \frac{I_{ik} \lambda_{ik} A_{ik}}{I_{jk} \lambda_{jk} A_{ik}}
\]  

2.36

\[
g_i / g_j e^{-\Delta E / k_B T_e} = \frac{I_{ik} \lambda_{ik} A_{ik}}{I_{jk} \lambda_{jk} A_{ik}}
\]  

2.37

\[
\ln \left( \frac{I_{ik} \lambda_{ik} A_{ik} g_i}{I_{jk} \lambda_{jk} A_{ik} g_i} \right) = -\left( \frac{\Delta E}{k_B T_e} \right) + C
\]  

2.38

Since, in non-LTE plasmas \( T_e \neq T_{exc} \), in such a case, Boltzmann equation provide an excitation temperature rather electron temperature i.e.

\[
\ln \left( \frac{I_{ik} \lambda_{ik}}{g_i A_{ik}} \right) = -\frac{E_i}{k_B T_{exc}} + C
\]  

2.39

The values of \( \ln \left( \frac{I_{ik} \lambda_{ik}}{g_i A_{ik}} \right) \) are plotted versus the energy of the upper level \( E_i \) for each considered transition and slope of the line provide the corresponding temperature.

### 2.6 Trace Rare Gas Actinometry

Actinometry is a well-known OES technique that may be used for qualitative and sometimes quantitative determination of atomic densities in the plasma by the addition of a small amount (1-4%) of rare gas (e.g. Ar). It was first proposed by Coburn *et al.*[80] in 1980 and in more comprehensive form by Agostino *et al.*[81]. This technique is the most widely used diagnostic in low pressure plasmas for understanding the role played by active species in the discharge. This technique is also used to calculate the dissociation fraction of molecular gas in the discharge.

Although actinometry is a straightforward technique, but the validity of this method is based on the following assumption!

- Excited states are generated by electron collisions and lost by radiative emission.
- Electron impact excitation cross-sections of the actinometer and the gas to be examined have the same shape and similar threshold.
- Quenching processes and all other loss processes of the excited states are negligible as compared to spontaneous emission.
2.6.1. Relative Concentration of Reactive Species

Generally, the emission intensities of a particular type of atom/molecule are not simply related to their concentration in the ground state. The actinometry allows us to monitor the concentration of those species in the ground state. For example, the electronic excitation cross section of nitrogen (a reactive gas) of some energy levels is quite similar to some energy levels of argon (an actinometer gas). For those levels:

\[ I_{ik} = n_i A_{ik} h \nu_{ik} \]

\[ = n_o n_e k_{oi} A_{ik} h \nu_{ik} \tau_i \]

Where \( n_i \) = population density of excited state \( i \)

\( A_{ik} \) = transition probability from \( i \) to \( k \)

\( \nu_{ik} \) = frequency of radiation from \( i \) to \( k \),

\( n_o \) = population density of ground electronic state

\( n_e \) = electron number density or concentration of electrons

\( \tau_i \) = radiative life time of the emitting state \( i \)

The rate constant of excitation by electron impact from the ground electronic state to the excited state is given by \( k_{oi} \).

\[ k_{oi} = < \sigma_{oi} \nu > = \sqrt{ \frac{2e}{m} } \int_{0}^{\infty} f(\epsilon) \sigma_o(\epsilon) \epsilon^{1/2} d\epsilon \]

Where \( \sigma_o \) = size of the excitation cross section of the atom or molecule

\( \epsilon \) = excitation threshold of the emitting states

\( f(\epsilon) \) = electron energy distribution function

In accordance with above equation, the emission intensities of the actinometer (i.e. argon, the value with index Ar) and the reactive gas (i.e. nitrogen, the value with index N) will be given as:
\[ I_{Ar} = [Ar] n_{e} k_{Ar} A_{Ar} h \nu_{Ar} \tau_{Ar} \tag{2.42} \]

And

\[ I_{N} = [N] n_{e} k_{N} A_{N} h \nu_{N} \tau_{N} \tag{2.43} \]

From these two equations, the ratio between emission intensities of actinometric gas and reactive gas is given by.

\[
\frac{I_{Ar}}{I_{N}} = \frac{[Ar] k_{Ar} A_{Ar} \nu_{Ar} \tau_{Ar}}{[N] k_{N} A_{N} \nu_{N} \tau_{N}} \tag{2.44}
\]

\[
\frac{I_{Ar}}{I_{N}} = \frac{[Ar] \sqrt{\frac{2e}{m}} \int_{\varepsilon_{Ar}}^{\infty} f(\varepsilon) \sigma_{Ar}(\varepsilon) \varepsilon^{1/2} d\varepsilon A_{Ar} \nu_{Ar} \tau_{Ar}}{[N] \sqrt{\frac{2e}{m}} \int_{\varepsilon_{N}}^{\infty} f(\varepsilon) \sigma_{N}(\varepsilon) \varepsilon^{1/2} d\varepsilon A_{N} \nu_{N} \tau_{N}} \tag{2.45}
\]

The exact solution of this equation encounter principal difficulty associated mainly with the electron energy distribution function \( f(\varepsilon) \). However, these difficulties can be overcome if the conditions of actinometry are fulfilled as discussed above (i.e. \( \sigma_{Ar}(\varepsilon) \equiv \sigma_{N}(\varepsilon) \) and \( \varepsilon_{Ar} \equiv \varepsilon_{N} \)). By considering these conditions, the above equation can be written as.

\[
\frac{I_{Ar}}{I_{N}} = C_{1} \frac{[Ar]}{[N]} \tag{2.46}
\]

In this equation \( C_{1} \) is a constant that depends only on the properties of specific atoms. Thus, the concentration of reactive species (N) in the ground electronic state is given by.

\[
[N] = C_{1} \frac{I_{N}}{I_{Ar}} [Ar] \tag{2.47}
\]

Similarly, the concentration of molecular nitrogen in the discharge can be written as:

\[
[N_{2}] = C_{2} \frac{I_{N_{2}}}{I_{Ar}} [Ar] \tag{2.48}
\]

Where \([N_{2}]\) and \(I_{N_{2}}\) are the concentration and emission intensity of the molecular nitrogen, respectively.
2.6.2 Dissociation Fraction of Molecules

In molecular gases, inelastic collision between electrons and molecules often lead to dissociation of molecular gas into its fragments, and the fragments may be neutral or charged particles (positive or negative ions). These play a fundamental role in plasma processing because of their chemical reactivity. They may react in the plasma volume or at the surfaces (reactor wall or the substrate), sometimes lead to etching, deposition and fabrication of materials [82]. The possible reactions for electron impact dissociation of molecule will be given as:

\[
e + A_2 \rightarrow A + A + e
\]

2.49

\[
e + AB \rightarrow e + A + B
\]

2.50

The dissociation of a molecule will occur only if an electron has sufficient energy to break the bond i.e. above a threshold value. For example, for H\(_2\) and N\(_2\) molecules, the threshold values are 8.8±0.2eV and 9.5±0.5eV for the formation of their fragments, respectively [74, 82].

As an example, the dissociation of nitrogen (N\(_2\)) molecules in the discharge is considered. The dissociation fraction is defined as the ratio between the number of nitrogen atoms\([N]\) to the initial number of nitrogen molecules \([N_2]_i\) [17, 83].

\[D = \frac{[N]}{2[N_2]_i}\]

2.51

Using equation 2.46, the dissociation of nitrogen molecule can be written as.

\[D = C_3 \frac{I_N}{I_{Ar}} \frac{[Ar]}{[N_2]_i}\]

2.52

Where, \(C_3\) is a constant, which depends upon excitation rate coefficients and the spectroscopic data [14, 15].
CHAPTER 3

EXPERIMENTAL SETUP AND CHARACTERIZATION TECHNIQUES

3.1. Introduction

In this chapter, the experimental arrangement and the characterization techniques are described briefly. The experimental setup consists of rf generated magnetic poled enhanced inductively coupled plasma. The characterization techniques include the Raman spectroscopy, XRD, SEM, EDX, FTIR, and DC electric resistivity measurement. Synthesis, purification and procedure for pellets preparation of carbon nanotubes are discussed in detail.

3.2. Experimental Setup

3.2.1. Magnetic Pole Enhanced Inductively Coupled Plasma (MaPE-ICP)

The schematic diagram of experimental setup used for the plasma generation having diagnostic systems is shown in the figure 3-1. Plasma source used in our experiment is MaPE-ICP powered by rf source through matching network. The MaPE-ICP 200 system is manufactured for the plasma etching and coating process. Its ignition behavior is good for Ar, CH$_4$ and O$_2$. Pressure range for this system is dependent on the gas type, while it is stable within the pressure range of $1 \times 10^{-3}$- $5 \times 10^{-1}$ mbar. This chamber is cylindrical in shape and is made up of the stainless steel. The dimensions of the setup are 472mm×400mm×296mm. It is composed of two concentric cylinders having a small gap between them. A cooling arrangement is used to keep the temperature of chamber within the safety limits. For this purpose chilled water with pressure flow should be in the range of (3-60) bar, minimum water flow must be 3litre/min and temperature in the range of (15-20)$^\circ$C. Purified and distilled water is used for cooling purpose. Radio frequency generator (PFG-RF-13.56 MHz-1600 W) is connected to the system through the coaxial cable and the impedance matching network to ignite the plasma. It should be protected against the dust and mishandling. There are different ports used to make the connections for different devices like pressure gauges, the optical emission spectrometry, Langmuir probe, vacuum pumps and cooling water pipes. OES is carried out through one viewing port having quartz window. For this purpose a computer controlled McPherson–2061
monochromator is used having a grating of 1200 grooves/mm, resolution of 0.01 nm, attached with photo-multiplier tube (PMT-R928). It also contains an auto-ranging Pico-ammeter (Keithley-485). The entrance slit has the width of 5 μm and focal length of the monochromator of 1 m. An rf-compensated Langmuir probe is inserted just opposite side of viewing port used for OES. The Langmuir probe (Smart probe, Scientific System) having a cylindrical tip made from tungsten having diameter and length of 0.38 mm and 10 mm, respectively that is utilized to study the discharge parameters. The EEDFs are obtained by Druyvesteyn method. The electron energy distribution function is evaluated by taking double derivative of value I-V characteristics. Flow meters are used to read the flow rate of gases into the chamber. Penning and Pirani gauges are employed to read the value of gas pressure in reactor having the range (10^{-2}-10^{-7}) mbar and (10^{-3}-1) mbar, respectively.

Figure 3-1(a): A schematic diagram of the experimental setup and diagnostics

The MaPE-ICP set up is consisted of planar coil configuration, along with a magnetic core. In this setup a ferrite core is used, that surrounds the coil from all sides. This core concentrates the magnetic field generated by the coil to the plasma chamber and increases the field intensity. It also provides the mechanical strength to the dielectric window. This system consists of a planar coil that is used horizontally on the upper surface of the
dielectric window is used to prevent direct communication and acts as coupling media between the planar coil and the plasma chamber. It also works as a vacuum seal for the discharge that is physically powerful to withstand between the ambiance pressure and the pressure inside the chamber.

Figure 3-1(b): A snap shot of MaPE-ICP system with diagnostic tools

Alternating voltage is applied to the coil through an rf source and alternating current flows in the turns of coil. Magnetic field is generated around the turns of the planar coil as shown in figure 3-2. This magnetic field is linked with the gas mixture through the dielectric window. Since AC voltage is used so that the magnetic flux produces around the coil varies with time linking with the gas present in the discharge chamber. According to the Faraday’s law of electromagnetic induction, the electric field is induced in the gas reactor that cause induce emf resulting induce current in the discharge chamber. The ICP’s having planar coil configuration has a major drawback. Since the self-inductance is generated across the coil that increases with the increase in diameter of the coil. Because of this self-inductance, the magnetic field generated by the coil inside the plasma is non-uniform. Magnetic field is the strongest at the center and the plasma density also becomes non-uniform having a peak at the central region. In order to overcome this problem, a
magnetic pole is used around the coil. This pole is in fact a core made up of some magnetic material. It concentrates the magnetic field uniformly to the plasma [54, 56].

![Planar coil configuration of inductively coupled plasma discharge](image)

**Figure 3-2: Planar coil configuration of inductively coupled plasma discharge** [56]

Another important component of the MaPE-ICP is the impedance matching network. Impedance of plasma and the RF generator can differ from each other. Due to this mismatch, input rf power is not efficiently transferred to the plasma reactor causing a reflection in back path. Impedance matching network is utilized to transfer the maximum input power to the plasma keeping the reflection minimum. L type matching network is basically used that contains two units, the tuning unit and the control unit. Tuning unit contains components that are variable capacitors and inductors.

### 3.3. Characterization Techniques

Different characterization techniques were utilized to observe the effect of plasma treatment on carbon nanotubes. Basic working principles along with the operation of these techniques are described briefly as follow.

#### 3.3.1. Raman Spectroscopy

Raman spectroscopy is a technique, used to detect and identify the presence of various elements and compounds in different materials. Each molecule in organic and inorganic compounds can execute vibrational and rotational motions. Type of motion and its amplitude depends on the energy of the molecule. Molecules can vibrate and rotate in different ways, each distinct way called a mode of vibration or rotation. These modes require a specific amount of energy for their activation. Molecules can make transitions
between different modes by emitting or absorbing specific amount of energy. These modes and the energy required to activate them is purely the characteristic of the different types of molecule present in the material. Raman spectroscopy is the analysis of the sample on the basis of study of its vibrational and the rotational modes. A monochromatic beam of light in visible, infrared or the ultraviolet region is made incident on the sample. Laser beam can interact with the sample in two different ways. It includes Rayleigh scattering and the Raman scattering that is further divided into two types, Stokes scattering and the anti-Stokes scattering. At room temperature, almost all the molecules are present in their ground states except some energetic molecules that are in higher energy states.

![Diagram of different modes of interaction of incident photon with molecules](Image)

**Figure 3-3: Different modes of interaction of incident photon with molecules**

Let us take a sample in which the molecules have different vibrational and rotational energy levels. Incident laser beam activates the vibration or the rotation modes depending upon its energy. Rayleigh scattering is in fact the elastic scattering of incident photons from the molecules. Let a photon beam of energy \( h\nu \) is made to incident on the sample as shown in figure 3-3. It excites a molecule from energy state \( E_1 \) to any higher energy level\( E_i \). Molecule de-excites back to the same state\( E_1 \), emitting energy \( h\nu \). There is no change in the energy of photon, it is just scattered back from the molecule. Rayleigh scattered photons do not provide any information about modes of molecules, as these are
exactly same as the incident photons. These photons are filtered away from the signal coming out from the sample using a properly designed filter.

Incident photons can also be scattered in-elastically. In this case, photons transfer their energy to the molecule resulting in the Raman scattering. In inelastic scattering molecule absorbs the photon energy and is excited from $E_i$ to any higher energy level $E_f$. De-excitation in to the same ground state is not necessary for all the molecules; it can also de-excite to some other lower energy level in accordance with the selection rules of transition. Let us assume that it de-excites to $E_2$. It is stokes scattering, here the amount of energy emitted is less than the energy absorbed from incident photon. Remaining energy is absorbed by the molecule. Another way of inelastic scattering is the anti-Stokes scattering. Molecule is excited from $E_2$ to any higher energy level $E_f$, while is de-excited to even a lower level than $E_1$. In this case emitted energy of the incident photon is greater than the absorbed energy. Additional energy is emitted at the cost of energy of molecule itself. In anti-Stokes scattering molecule emits a net amount of energy. Specific energies emitted or absorbed by the molecules during the transitions between different energy levels are characteristics of the vibration and the rotation modes. Spectrum obtained from the output light signal gives the identification of nature of different molecules present in the sample.

![Figure 3-4: Schematics of experimental setup of Raman spectroscopy](image)
Experimental set up used for Raman spectroscopy consists of laser that emits a well-focused and monochromatic light beam. This beam of photons is made to incident on the sample, where it interacts with the molecules. Light signals emitted from the sample are collected back and are deflected by a reflecting mirror towards the filter. The filter absorbs the photons emitted due to Rayleigh scattering. Signals of Stokes and anti-Stokes scattering are forwarded to the detector. It analyzes these signals on the basis of their energies. Vibration and the rotation modes are identified that lead to the information of the type of molecules present in sample. The schematic diagram of the experimental setup of the Raman spectroscopy is shown in figure 3-4.

Raman spectroscopic analysis of plasma processed CNTs was carried out using Raman spectrometer available at Plasma Physics Laboratory, Quaid-i-Azam University Islamabad.

3.3.2. X-Ray Diffraction (XRD)

The XRD is an effective technique to study the crystalline structure of different materials. It can also give the identification and the quantitative analysis of the crystalline compounds present in the sample. XRD is a nondestructive technique to study the crystal structure, phase analysis of different compounds and the detection of the crystal imperfections. It is based on the diffraction of the incident X-rays from the crystals of the sample. Information about the crystal structure is obtained from the diffraction pattern obtained. In crystalline materials the atoms are linked together in regular and periodic arrangement. These atoms form a series of parallel planes separated from each other by equal distance “d” called the inter-planar spacing. Value of “d” and the arrangement of atoms on each plane depend on the nature of crystalline structure of the sample. In order to obtain diffraction pattern of the crystalline materials, it is necessary that the wavelength of the incident radiation should be comparable or smaller than the interatomic spacing of the crystal. X-rays, neutrons and high energy electrons meet this condition.

Diffraction is simply the bending of the radiation from the obstacle coming in path of its propagation. X-rays made incident on the sample are diffracted from the atoms of the crystalline planes. Diffraction pattern, called the diffractrogram is obtained due to the
interference between the diffracted beams. Formation of the diffraction pattern is governed by the Bragg’s law. Let’s assume that two X-rays beams are made incident on the sample as shown in figure 3-5. Ray 1 is diffracted from the first plane of the crystal; ray 2 penetrates into the crystal and is diffracted from atoms of the second plane. Rays 3 and 4 are the diffracted ones; these can interfere with each other depending upon the path difference between them. They have a path difference of \(2dsin\theta\); \(d\) is the inter-planar spacing and \(\theta\)is the angle of incidence of the incident ray with the surface of the crystal.

\[2dsin\theta = n\lambda\]  \hspace{5cm} 3.1

If the above condition is not satisfied then the interference is destructive. A Schematic of the XRD set up is shown in the figure 3-6 that consists of a source of monochromatic X-rays, a sample holder to mount the sample and a detector.

X-rays are diffracted from the material to be analyzed and detected by the computer controlled detector. Sample and the detector both are adjusted on a goniometer, over which both can rotate at any angle. Rotation of sample is carried out to obtain angle of incidence of X-rays on the sample.
Figure 3-6: Schematics of X-ray diffraction spectroscopy

Detector is rotated to analyze the sample from different directions. In this way, XRD is found to be an effective technique to identify and study the crystallographic features of the sample. The X-ray diffraction (XRD) spectra used in our experiment are acquired by using (JEOL JDX-3532, CuK\(_\alpha\) radiation, 1.54 Å) working voltage of 40 kV having current of 30 mA in the range 10°-60° (2θ) with a step size of 0.01 and a time per step of 1s. This system is installed in Centralised Resource Laboratory (CRL), University of Peshawar, Pakistan.

3.3.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) as shown in figure 3.7 is one of the most efficient characterization techniques used for the study of surface morphology, topography and the chemical composition of different type of materials. It provides high resolution images of the sample due to which it is widely used in research and industry [84]. The resolution of electron microscope and its depth of focus are much better than optical microscope. The electron microscope takes the images of a material to be analyzed by scanning its surface through an energetic electron beam. It interacts with the sample and makes them to generate such signals that provide information about the surface morphology and elemental composition of the sample [85].
The principle of the SEM is simply based upon the interaction of the electron beam with atoms and molecules of the sample. Energetic electron beam from a source is focused on the sample. These electrons interact with the atoms present at and near the surface and can also penetrate through it depending upon their energy and the density of the sample.

In SEM, electron beam is used for imaging instead of the ordinary light. Incident electrons interact with sample atoms both elastically and inelastically. This interaction results in various types of signals generated including: secondary electrons, back scattered electrons and the emission of characteristic X-rays. Different types of detectors are required to detect and analyze these signals. Commonly used SEM contains the secondary electron detectors, for surface morphology and EDS/WDS detectors for elemental analysis [86].

![Figure 3-7: Basic schematics of scanning electron microscope](image)

In the inelastic scattering of incident electrons, their energy is transferred to the loosely bound electrons of atoms at the surface. These electrons are emitted from the atoms and are collected by the corresponding detectors. Density and the energy of the emitted electrons are highly influenced by the topography and the morphological features of the surface of the sample. There exists a local variation in the intensity of the secondary
emitted electrons. This provides a high resolution imaging of the surface morphology of the sample [85].

Inelastic scattering may also result in the emission of the characteristic X-rays. In order to detect and analyze these X-rays, EDX detector is used. EDX detector gives the qualitative and the quantitative analysis of the chemical composition of the sample. Working of EDX detector is described briefly in section 3.3.4. In elastic scattering, the energy of the incident electrons is not changed; rather they are reflected back from the surface of the sample. These backscattered electrons are collected by the corresponding detector. The number of the backscattered electrons is directly dependent on the atomic number \( (Z) \) of materials. Atoms with greater \( Z \) reflect large number of electrons. Variation in the intensity of the backscattered electrons gives the information about the chemical nature of atoms and their distribution along the sample surface [85].

Electron beam of energy (0.5 eV - 30 K eV) is obtained from a thermionic electron gun used as electron source. It mainly consists of a heated tungsten filament. Thermionic emission of electrons takes place from this filament. In a typical SEM, a tungsten filament is used; it has the highest melting point among all the metals, allowing it to be heated for electron generation. Also its low cost makes it a preferable candidate. A positive potential is applied to the emitted electrons to attract them towards the column. A group of condenser and electromagnetic lenses are equipped to deflect and focus the electron beam towards the sample. Electron beam interacts with the sample and the emitted signals are collected and analyzed by the corresponding detectors [87, 88].

Traditionally the SEM requires a conductive sample or at least a conductive surface to perform the analysis. It is necessary to make sure that incident electrons are conducted away to the ground. If the sample is not conductive, then the incident electrons are accumulated on the surface of sample and form a space charge. It deflects the incoming electrons, and degrades the SEM images. In order to overcome this problem, a layer of some conductive material is coated on the sample surface. Generally gold, platinum, gold palladium alloy, tungsten and iridium are used for coating. It prevents the accumulation of static electric charge on the sample surface during the electron beam irradiation.
3.3.4. Energy Dispersive X-Ray (EDX) Analysis

The EDX is a chemical microanalysis technique. It identifies the elemental composition of the material examined, for all the elements with an atomic number greater than Boron. It can detect the elements even with the concentration of 0.1%. Basic working principle of EDX is the observing the characteristic X-rays produced from the constituent elements of the sample on the application of a beam of energetic particles [89, 90]. Generally an electron beam of energy E is made incident on the sample. It interacts with all the elements present in the sample and transfers its energy to the atoms of the elements. Some deep seated electrons are knocked out from the lower orbit of the atoms. Let’s assume that an electron is knocked out from the first orbit that is the K shell of energy $E_0$ of some atom as given in figure 3-8.

![Figure 3-8: Emission of electron from an atom on the application of electron beam.](image)

Any electron from some higher orbit can jump down to fill this vacancy. During this orbital transition of electrons, during X-ray photon are produced this phenomena to give up the energy. These X-rays are called the characteristic or the discrete energy X-rays. If electron jumps from the L shell to the K shell to fill the vacancy then emitted X-rays are called the K$_\alpha$ line. Electron can also jump from the M shell emitting the K$_\beta$ line. Similarly other types of X-rays are emitted depending on the orbits between which the electrons’ transition takes place.
Figure 3-9: Basic experimental set up of energy dispersive X-ray spectroscopy

Each element in the periodic table has its characteristic energy levels, so emitted X-rays are the characteristic of the elements present in the sample material as shown in figure 3-9. Electron beam is made incident on the sample, where it gives rise to the emission of X-rays. Emitted X-rays are collected by the detector. Incident X-rays striking the detector, create an electrical pulse proportional to their energy and abundance. These electrical signals are amplified and are sent to the computer, where the data are collected and graph is plotted between the intensity of the emitted X-rays versus their corresponding energies. These X-rays have typical energy are utilized to obtained the information about the chemical nature of the elements present in the sample and their intensity gives the idea of concentration of the element. Accuracy of the EDX measurements is affected by many factors. It cannot detect the elements with the atomic number less than that of Boron. X-rays of these elements are of very low energy. These are usually absorbed by the windows of the detectors and cannot reach the detector. So presence of these elements goes unnoticed in EDX. Measurement of the relative concentration of the elements may also contain some errors, in the case when elements with atomic number less than the Boron are present in the sample. Concentration of an element is determined on the basis of the intensity of the X-rays reaching the detector. Likelihood of an X-ray photon, escaping the sample and reaching the detector depends on the energy and amount and density of the material it has to pass through before reaching the detector. It is quite possible that all the X-rays of some particular element are not completely collected by the detector. So in this way, EDX can report the concentration of the elements lower than the actual value.
3.3.5. Fourier Transform Infra-Red (FTIR) Spectroscopy

The FT-IR is used to analyze the material by recording infrared spectrum of absorption, emission, photoconductivity Raman scattering. In this type of spectroscopy, the infra-red spectral radiations are passed through the sample that is to be analyzed. In this procedure a small number of IR radiations are absorbed and remaining radiations are transmitted through it. The molecular absorption and transmission spectra are recorded by the computer control software, generating a molecular finger print of the material. This molecular finger print is always a unique signal producing the same IR spectrum for every material. This property of the FTIR makes them a valuable tool for various type of analysis.

Figure 3-10: The layout diagram simple FTIR setup

The basic motivation behind the development of FTIR spectroscopy is to remove the restrictions encountered with dispersive apparatuses. The slow scanning process of older instruments makes them more difficult to utilize. A method was needed for computing almost all the IR frequencies at the same time, rather than separately. An infrared spectrometer was developed for purpose which produces a unique type of signal and all al IR frequencies are encoded. These signals may be observed simultaneously in a short
interval of time with a few seconds or so. Therefore, the time for the scanning of the material is decreased to a matter up to few seconds.

The IR spectrometer contains a beam-splitter that is used to split the incoming beam into two parts. One part of beam is reflected back by a mirror placed in front of it and second part of the beam is also reflected off from another mirror moving back and forth. These two beams are then recombined after reflecting back from respective mirror results a path difference at the beam splitter. Since the path of first beam is fixed while the second beam is continuously changing due to moveable mirror. This cause interference between two beams produces a signal is called an interferogram. This signal will define each and every IR frequency that is arriving from source. This single is unique and distinctive due to its typical frequency. This makes the interferometer as extremely fast analyzer. These signals are not directly readable and must be decoded. This decoding is performed by using a mathematical technique called Fourier transformation. This technique is carried out by the computer and then presented in the form of spectrum that is readable by users.

The advantage of *FT-IR spectroscopy*

- It is used to recognize anonymous samples
- It is used to determine the worth or reliability of a material
- It is used to find out the quantity of content present in the sample
- FTIR spectroscopy is *Fourier transform infrared spectroscopy* is favored upon other technique for various reasons
  a. It is not dispersive, non-destructive technique, fast speed analyzer, increased sensitivity and simple in operation.
  b. It is used to measure accurate values that do not need any external calibration. It is self-calibrating system used He/Ne laser as internal wavelength calibration.

### 3.3.6. DC Electrical Resistivity

Electrical properties of Carbon nanotubes have considerable interest because of a lot of their application in the nano devices. The CNTs are almost ideal 1-D conductors in which a number of attractive mesoscopic phenomena at low temperatures has been observed such as single-electron charging, resonant tunneling through discrete energy levels and
proximity-induced superconductivity. To measure the electrical resistance of the materials mostly two methods are used i.e. two-point and four-point probe methods. Since the electrical resistivity of carbon nanotubes is high so it is difficult to use four probe method because it is mostly used for those sample that have low resistance [97]. The use of this method is also not appropriate at higher temperature because of instability of Ag paste used for joints. Whereas the two point probe method is appropriate for the CNTs because these have higher resistivity at higher temperature. Two probe method is employed to measure the electrical resistivity of CNTs in the temperature range of 300-675 K.

The DC electrical resistivity setup was constructed to calculate various electrical properties such as electrical resistivity, electrical conductivity and activation energy at high temperature range (300-675 K). A shown in schematic diagram (figure 3-11) that a heater (H) was used to heat the materials that is hold tightly contained by a hollow ceramic pots.

The heater can sustain maximum temperature up to 773 K. A thermocouple is attached with a multimeter (Uni, UT-55) to examine the temperature that can be obtain in the range of 73 to 1473 K with an accuracy of ±0.01K. A triac control (B) was established in series with the heater to heat the material with slow rate. The sample holder was

![Block diagram representing the resistivity apparatus.](image-url)
constructed as per necessity of two-probe setup. Two metal strips (P1 and P2) were used for this purpose. The upper strip (P1) was connected to the lower strip (P2) at the ends and ceramic beads were inserted between them to avoid the short circuiting. There were two holes in the middle of the strips and two screws were used to hold the sample. The constant voltage was applied by a Keithley source meter-2400 to the sample (S) and the change in current (A) was measured as a function of temperature. This Multimeter can measure the current from 1µA to 400A with an accuracy of ±0.0001A.

![Figure 3-12: Temperature dependence of electrical resistance measured by the apparatus described in section 3.4.](image)

Resistance of sample was calculated by using Ohm’s law:

$$R = \frac{V}{I} \quad \text{3.2}$$

Where, $V$ is constant voltage applied to the sample and $I$ is the corresponding current. Using resistance, resistivity of pellet of sample was calculated as:

$$\rho = R \frac{A}{L} \quad \text{3.3}$$
Where, $L$ is the height of pellet of sample and $A$ ($A = \pi r^2$) is the area of pellet of sample. The electrical resistance of CNTs as function of temperature measured by the above mentioned apparatus is shown in figure 3-12.
CHAPTER 4
EFFECT OF HELIUM MIXING ON PLASMA PARAMETERS IN
INDUCTIVELY COUPLED Ar-N₂ PLASMA

4.1. Introduction

Inductively coupled plasmas (ICPs) are extensively used for material processing including coatings on different type of materials [91, 92]. For many years, high pressure inductively coupled nitrogen plasmas have been intensively studied for their numerous applications in analytical chemistry and spectroscopy [93, 94]. The ICPs operating at low pressure, producing non-local thermal equilibrium (non-LTE) plasmas, have been developed to meet requirements in plasma processing as high density, low damage and high uniformity source of radicals for cleaning and etching, especially in microelectronic processing. Most attractive feature of these discharges is the inductive coupling of the rf power to the plasma across a dielectric window or wall by transformer action, rather than by direct connection to an electrode inserted in the plasma [95, 96].

Optical emission spectroscopy (OES) is the most widely used tool for investigation of various plasma parameters such as electron energy distribution function (EEDF), electron number density \(n_e\), electron temperature \(T_e\) and excitation temperature \(T_{exc}\) due to its non-perturbing nature [3, 4]. The effectiveness and the efficiency of inductively coupled rf plasmas depends on these plasma parameters [5]. In non-LTE plasma, electron energy distribution function (EEDF) plays noteworthy job in excitation and ionization processes and consequently, production of different active species. Electron impact excitation promotes a small fraction of these species into upper electronic states which decay and emit radiation in the visible-near-UV region. At sufficiently low pressure (<1 mbar) and low electron number density \(\sim10^{8} - 10^{11} cm^{-3}\), the plasma is generally non-LTE, and the corona equilibrium model may be considered appropriate if the excited states are mainly populated by electron impact, and the radiative decay is dominant over collisional de-population [4]. Under these conditions, optical emission from rare gas can be used to measure excitation temperature \(T_{exc}\) by using Boltzmann plot method. If the
collisonal excitations and de-excitation processes then excitation temperature $T_{\text{exc}}$ may be equated to electron temperature $T_e$, under such conditions the plasma will be in local thermodynamic equilibrium (LTE). These conditions exists at very high-electron density (typically $\sim 10^{16} \text{cm}^{-3}$ or greater) and high pressure ($\sim 1.33 \text{ mbar}$ or greater). However, the applicability has to be checked carefully to diagnose plasmas which require different models including the plasma kinetics in appropriate manner [4, 66].

The degree of dissociation in the nitrogen plasma is important for improving the plasma processes because the number density of active specie of N atoms is associated with the adsorption/diffusion on the surface of different materials. Generally it is difficult to obtain high dissociation efficiency of N$_2$ due to its high bonding energy (the N–N bond strength is 9.76 eV) and some inert gas is mixed to increase the dissociation rate through Penning effect [97]. There are not enough studies available on dissociation of nitrogen by the effect of helium addition. However, some articles are available on the dissociation of nitrogen in Ar admixed plasma [15, 98, 99]. Czerwiec et al. [15] have investigated the nitrogen dissociation by Ar mixing using mass spectrometry and actinometry method. It is shown that the nitrogen dissociation fraction can be enhanced by argon addition; a maximum is observed for 10 % of argon in the Ar-N$_2$ gas mixture. Nakano et al. [16] measured the dissociation degree of N$_2$ in inductively coupled plasma by using vacuum ultra violet (VUV) emission spectroscopy. They observed that the dissociation fraction increased from 5 % to 20 % with increasing the rf power from 30 W to 100 W, keeping pressure constant at 0.665 Pa. Itagaki et al.[20] have reported high degree of dissociation degree for nitrogen molecule ($I_N/I_{N_2} \sim 0.48$) at the input power and gas pressure of 1.5 kW and 0.27 Pa, respectively. They used 915 MHz electron cyclotron resonance (ECR) Ar-N$_2$ plasma. Voulot et al.[19] achieved dissociation fraction from 10 to 40 % for ICP nitrogen atom sources for molecular beam epitaxy (MBE).

Khan et al.[6] investigated the change induced by Ar addition on the nitrogen dissociation in CCP by using 13.56 MHz rf source. They obtained the dissociation fraction up to 18% by addition of 70 % Ar in nitrogen plasma at filling pressure of 0.5
mbar and rf power of 300W. They also investigated the changes induced in plasma parameters \( (T_e, n_e) \) by using modified Boltzmann plot and Langmuir probe and consequently abundance of active species \( (N, N_2 \text{ and } N_{2}^{++}) \). Naveed et al.\[7\], used the optical emission spectroscopy to investigate the effect of He on electron temperature in nitrogen plasma generated by 50 Hz pulsed dc power source. They showed that the electron temperature is enhanced up to 0.67 eV by addition of 90 % He at a filling of 5 mbar and 300 W power.

![Figure 4-1: Schematic diagram of the experimental setup](image)

In plasma processing reactors, the plasma characteristics may fluctuate. For reliable processing, some online monitoring of the plasma properties will be necessary. Although, the resolution of present day compact spectrometers may not be good, specially, when the required sensitivity is quite high, but these spectrometers are reasonably fast and may be helpful in online monitoring. The aim of this work is to investigate the effect of He mixing on \( T_{exc} \) and the consequently generation of active species in \( N_2 \) plasma keeping Ar as trace gas. The excitation temperature is estimated from the slope of the Boltzmann plot using different argon spectral lines. The effect of helium on the nitrogen dissociation and relative population density of reactive species by using actinometry is also investigated. It is observed that the nitrogen dissociation fraction can be enhanced by He addition;
maximum dissociation is observed for 90 % of He in nitrogen plasma. By doing so, the dissociation fraction up to 26 % is obtained at filling pressure of 0.5 mbar and rf power of 150 W in ICP N₂ plasma.

The plan of this chapter is as follows. The experimental set-up and the spectral observation with reaction scheme occurring in the plasma are described briefly in sections 4.1 and section 4.2, respectively. Section 4.3 contains the discussion related to the Boltzmann’s plot for the determination of excitation temperature. Attention is paid to the discussion on actinometry and investigation of dissociation fraction of nitrogen is presented in section 4.4 and section 4.5 respectively. Results and discussion are presented in section 4.6.

4.2. Experimental Setup

The schematic diagram of the experimental setup with diagnostic system [OES] is shown in figure 4-1. The chamber consist of two coaxial stainless steel cylinders having a small gap between them through which cold water is pumped from the chiller to control the temperature. The diameter and height of plasma chamber are 31 cm and 24 cm respectively. It consists of four main vacuum tight ports; two of them are rectangular in shape having width of 3.2 cm and length of 13 cm, closed with stainless steel plates. The third and fourth ports are circular in shape having diameter 9.8 cm. Third port is used as a view window to monitor the status of the plasma. The fourth port is used for optical diagnostics by using Ocean spectrometer (HR4000 CG-UV-NIR USB 2000) with grating having groove density of 300 lines per millimeter and resolution of 0.5 nm (FWHM) to characterize the plasma. Apart from these four main ports, there are some additional ports used for the injection of working gases via flow meters and pressure measurement using different type of gauges. To resolve the spectral lines,narrow range of spectra are obtained using computer controlled McPherson2061 monochromator having a 1200 grooves/mm grating with a spectral resolution of 0.01 nm coupled to a photomultiplier tube (PMT-R928) and an auto-ranging Pico-ammeter (Keithley-485). The width of the entrance slit and focal length of the monochromator were 5 mm and 1 m, respectively.
The plasma chamber is evacuated by using a diffusion pump backed by a rotary pump. Operating gas pressure inside the chamber is controlled by adjusting mass flow meters. In this experiment 13.56 MHz rf power supply with automatic impedance matching network is used for the generation of plasma at various powers (50 W to 150 W) while keeping the corresponding parameters constant. The effect of filling pressure (0.2 – 0.5 mbar) and He fraction (10 – 90 %) is investigated keeping argon concentration fixed at 4 % in $N_2$ plasma. The reflected rf power is continuously monitored and is kept below 2 % with the help of automatic impedance matching network.

![Emission spectrum recorded from a mixture (10% He, 4% Ar, 86% N2) at filling pressure 0.5 mbar and rf power 150 W.](image)

**Figure 4-2**: Emission spectrum recorded from a mixture (10% He, 4% Ar, 86% N2) at filling pressure 0.5 mbar and rf power 150 W.

### 4.3. Spectral Observations

Characteristic emission spectra in the wavelength range of 200 nm to 1100 nm are recorded from a 13.56 MHz rf plasma in He-$N_2$ mixture with argon as trace gas, for filling pressure varying from 0.2 mbar to 0.5 mbar and rf power varying from 50 W to 150 W. Prominent spectral lines and bands in the spectrum are identified and labeled as given in **Figure 4-2**. The main processes involved in the excitation and de-excitation
of \( \text{N}_2(\text{C}^3\Pi_u) \), \( \text{N}_2^+\text{(B}^2\Sigma_u^+) \) and \( \text{N} - \text{I} \) states along with available rate coefficients are given in the table 4-1. The wavelength of the spectrometer (Ocean optics) is calibrated using a mercury lamp before the experiment. The recorded emission intensities of the spectral lines are integrated and then normalized by using the spectral response curves of the spectrometer, optical fiber, optical lens and quartz window provided by the manufacturers. The relative intensities of the spectral lines are used for the spectroscopic analysis. The measurements of spectral lines are time-integrated over interval of 1000 msec (integration time=1000 msec) and mean of 10 successive measurements (average=10) was calculated.

Table 4-1: Main reactions involved in the excitation and de-excitation of plasma species

<table>
<thead>
<tr>
<th>No.</th>
<th>Transitions/ Reactions</th>
<th>Rate constant/ Transition probability</th>
<th>Ref:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + e \rightarrow \text{N}_2(\text{C}^3\Pi_u) + e )</td>
<td>( k = 6.42 \times 10^{-15} \exp\left(-\frac{9.87}{T_e}\right) \text{ m}^3\text{s}^{-1} )</td>
<td>[22]</td>
</tr>
<tr>
<td>(R2)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + e \rightarrow \text{N}_2(\text{A}^3\Sigma_u^+) + e ) ( \text{N}_2(\text{A}^3\Sigma_u^+) + e \rightarrow \text{N}_2(\text{C}^3\Pi_u) + e )</td>
<td>( k = 1.22 \times 10^{-14} \exp\left(-\frac{7.34}{T_e}\right) \text{ m}^3\text{s}^{-1} )</td>
<td>[22] [7]</td>
</tr>
<tr>
<td>(R3)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + \text{He}_m \rightarrow \text{N}_2(\text{C}^3\Pi_u) + \text{He} )</td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>(R4)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + e(E &gt; 18.7eV) \rightarrow \text{N}_2^+(\text{B}^2\Sigma_u^+) + 2e )</td>
<td>( k = 2.8 \times 10^{-14} \exp\left(-\frac{18.56}{T_e}\right) \text{ m}^3\text{s}^{-1} )</td>
<td>[22]</td>
</tr>
<tr>
<td>(R5)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + e \rightarrow \text{N}_2^+(X^2\Sigma_g^+) + 2e ) ( \text{N}_2^+(X^2\Sigma_g^+) + e \rightarrow \text{N}_2^+(\text{B}^2\Sigma_u^+) + e )</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>(R6)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + \text{He}_m \rightarrow \text{N}_2^+(\text{B}^2\Sigma_u^+) + \text{He} )</td>
<td>( k = 7.1 \times 10^{-11} \text{ cm}^{-3}\text{s}^{-1} )</td>
<td>[100]</td>
</tr>
<tr>
<td>(R7)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + \text{He}^+ \rightarrow \text{N}_2^+(\text{B}^2\Sigma_u^+) + \text{He} )</td>
<td></td>
<td>[100]</td>
</tr>
<tr>
<td>(R8)</td>
<td>( \text{N}_2(\text{C}^3\Pi_u) \rightarrow \text{N}_2(\text{B}^3\Pi_g) + \text{hv} )</td>
<td>( \tau = 2.74 \times 10^7 \text{s}^{-1} )</td>
<td>[101]</td>
</tr>
<tr>
<td>(R9)</td>
<td>( \text{N}_2^+(\text{B}^2\Sigma_u^+) \rightarrow \text{N}_2^+(X^2\Sigma_g^+) + \text{hv} )</td>
<td>( \tau = 66 \text{ ns} )</td>
<td>[100]</td>
</tr>
<tr>
<td>(R10)</td>
<td>( \text{N}_2(X^1\Sigma_g^+) + e \rightarrow \text{N} + \text{N} + e )</td>
<td>( k = 6.3 \times 10^{-6} T_e^{-1.6} \exp\left(-\frac{9.8}{T_e}\right) \text{ cm}^3\text{s}^{-1} )</td>
<td>[102]</td>
</tr>
<tr>
<td>(R11)</td>
<td>( \text{N}_2^+ + e \rightarrow \text{N} + \text{N} )</td>
<td>( k = 1.90 \times 10^{-15} T_e^{-0.3} \text{ m}^3\text{s}^{-1} )</td>
<td>[103]</td>
</tr>
</tbody>
</table>
4.4. Determination of Excitation Temperature

Optical emission from plasma is used to determine the population density of the excited states by using spectral line intensities of excited atoms. The spectral line intensity \( I_{ij} \) of transition from upper level \( i \) to lower level \( j \) is correlated with population density of atoms involved in optical emission \([79]\).

\[
I_{ij} \propto A_{ij} h \nu_{ij} N_i
\]

Where \( A_{ij} \) is the transition probability between the levels \( i \) and \( j \), \( h \) is the Planck constant, \( \nu_{ij} \) is the transition frequency \( i \rightarrow j \), and \( N_i \) is the population number density of the species in level \( i \). The excitation temperature describes the population of atomic states assuming that this follows a Boltzmann distribution.

\[
\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp \left( -\frac{\Delta E}{kT_{\text{exc}}} \right)
\]

For non-LTE plasma, electron excitation temperature cannot be considered equal to the electron temperature but in situations where the calculation of \( T_e \) is not practical or extremely complicated, one can easily calculate \( T_{\text{exc}} \) to get a rough estimate for the trend of \( T_e \) because both the temperatures show similar trends. Generally, \( T_{\text{exc}} \) is always lower than the electron temperature. The Boltzmann plot method is one of the simplest and widely used for spectroscopic measurement, especially for measuring the excitation temperature. The excitation temperature is obtained from the slope of the Boltzmann’s plot \([8, 104]\).

\[
\ln \left( \frac{I_{ij} \lambda_{ij}}{g_i A_{ij}} \right) = -\frac{E_i}{k_B T_{\text{exc}}} + C
\]

Whereas \( \lambda_{ij} \) is the wavelength, \( g_i \) is the statistical weight and \( C \) is the constant for a given atomic species. The excitation temperature is determined as a function of rf power and filling pressure by measuring the line intensity of number of argon spectral lines from the spectrum and the corresponding spectroscopic data for the lines used in Boltzmann plot given in table-2 \([105]\). The main sources of error in the calculation of excitation temperature using Boltzmann plot method come from uncertainty in the values of \( A_{ij} \), errors in the recorded emission intensities and selection of lines with small energy difference in upper energy levels. The necessary conditions
for achieving accuracy of excitation temperature using Boltzmann plot method are to use calibrated emission intensity, selecting lines with large energy difference between upper levels and using lines that correspond to a rather narrow wavelength range. The use of logarithmic relation reduces the influence of errors. For instance, an error of 20% in the factor $\frac{l_{ij}A_{ij}}{B_{ij}A_{ij}}$ of equation 3 reduces to about 5% when taking the log of this factor [106, 107]. Thus values of $ln\left(\frac{l_{ij}A_{ij}}{B_{ij}A_{ij}}\right)$ are plotted versus the values of energy of the upper level for each considered transition. The variation of $T_{exc}$ with the change of $N_2/He$ ratio is studied for various rf powers while keeping filling pressure constant. The variation of $T_{exc}$ with filling pressure is also investigated while keeping rf power constant.

4.5. Actinometry

Actinometry is a well-known OES technique that may be used for qualitative and sometimes quantitative determination of atomic densities in the plasma by addition of a small amount (1-4%) of rare gas (e.g. Ar). This technique is useful when the relative energy dependence of electron impact excitation of the trace-rare gas is comparable with that of the species of the interest. Optical emission from the trace-rare gas can be used to estimate the electron impact excitation efficiency of the reactive species when the discharge parameters are changed. This method is based on excitation and de-excitation processes that leads to the following relation [79].

$$\frac{[X]}{[Act]} = k \left( \frac{I_X}{I_{Act}} \right)$$

4.4

Where $[X]$ and $[Act]$ are the concentration of reactive and the actinometer species, $I_X$ and $I_{Act}$ are the emission intensities of the excited X and the actinometer species respectively. The factor $k$ in above relation is a constant, if the direct electron impact excitation is prevailed and the excitation cross-sections have same dependence and similar threshold while the quenching processes are negligible [15].

For this purpose argon is selected as actinometer because threshold excitation energy (13.48 eV) of Ar emission line ($\lambda = 750.39 \, nm$) matches closely with threshold excitation energy (11.99eV) of N-emission line ($\lambda = 746.83 \, nm$), therefore, excitation of both levels will take place with almost the same energy group of electrons.
Consequently, the excitation efficiency of the both species have same dependence and the ratio of emitting reactive and the actinometer species may be related with the intensity of corresponding lines as: [80]

\[
\frac{[N]}{[Ar]} = k_1 \left( \frac{I_N}{I_{Ar}} \right) \tag{4.5}
\]

In this equation, the intensities \( I_N \) and \( I_{Ar} \) are obtained from emission spectra after normalizing for the spectral response of spectrometer, optical fiber and quartz window. The emission intensity ratio \( \frac{I_N}{I_{Ar}} \) is used to monitor the relative changes in \([N]\) as the discharge parameters are changed. The flow rate and the concentration of Argon \([Ar]\) is kept fixed during the optical measurements and it’s fraction in the discharge is known. Therefore \([N]\) density can be calculated for given filling pressure and gas composition. Where, \( k \) is a constant independent of discharge parameters.

Similarly, the excitation threshold energies for radiative states \( I_{N_2}(\lambda = 337.10 \text{ nm}) \) and \( I_{Ar}(\lambda = 750.39 \text{ nm}) \) are close (11.1eV and 13.48eV) and have similar dependence of the electron impact excitation cross sections. Also the excited state \( N_2(C^3\Pi_u) \) is mainly populated by direct electron impact from the ground state \( N_2(X^1\Sigma^+_g) \) while excitation caused by metastable argon atoms can be neglected due to low densities of metastable state argon atoms in the discharge. Therefore, the emission intensity of Ar spectral line and \( N_2 \) emission can be used to determine relative \([N_2]\) particle density where Ar emission serve as actinometer for different discharge parameters [80].

\[
\frac{[N_2]}{[Ar]} = k_2 \left( \frac{I_{N_2}}{I_{Ar}} \right) \tag{4.6}
\]

Similarly, the relative density of \( N_2^+(X^1\Sigma^+_u) \) can be obtained by using emission intensities of \( I_{N_2^+}(\lambda = 391.4 \text{ nm}) \) band head and \( I_{Ar}(\lambda = 750.39 \text{ nm}) \) as follows [14]:

\[
\frac{[N_2^+]}{[Ar]} = k_3 \left( \frac{I_{N_2^+}}{I_{Ar}} \right) \tag{4.7}
\]
4.6. Measurement of Molecular Dissociation

The degree of dissociation is one of the important parameter of molecular gas plasma used for material processing applications. The dissociation is strongly influenced by the plasma parameters, such as EEDF and electron number density. The degree of dissociation of nitrogen molecule is the ratio of $[N]$ and $[N_2]$ densities and can be calculated by using actinometry method [15].

$$\frac{[N]}{[N_2]} = C_1 \left( \frac{[Ar]}{[N_2]} \right) \left( \frac{I_N}{I_{Ar}} \right)$$ \hspace{1cm} (4.8)

In this equation $I_N$ represents the N-I line intensity and $I_{Ar}$ represents the Ar-I line intensity, whereas $[Ar]$ and $[N_2]$ are the Ar and N$_2$ fractions in the plasma gas. As an alternative method, the atomic nitrogen line emission intensity at 746.831 nm and the vibrational band (0-0) of the N$_2$ second positive system 337.1 nm is used to determine the degree of dissociation and the ratio $\frac{[N]}{[N_2]}$ is given [14].

$$\frac{[N]}{[N_2]} = C_2 \left( \frac{I_N}{I_{N_2}} \right)$$ \hspace{1cm} (4.9)

Where, $C_1$ and $C_2$ are constants which depend on excitation rate coefficients, quenching rates and excitation temperature [15, 108].

4.7. Results and discussion

Figure 4-2 shows a typical emission spectrum recorded with 10 % helium, filling pressure of 0.5 mbar and rf power of 150 W. The spectral lines recognize the plasma species involved in optical emission and thus shows the kinetics of plasma excitation processes. The nitrogen first negative system ranges from the wavelength 380 nm to 500 nm, whereas in the wavelength range from 300 nm to 390 nm, the nitrogen second positive system is identified and labeled by using compiled data [108]. The nitrogen and argon atomic lines used in the actinometry and excitation temperature measurements are also identified and labeled by using NIST data [105].

For the optical emission spectroscopy of plasma, a basic requirement is that the emission lines under study should not be absorbed by the plasma itself or plasma must be optically thin for those lines. When plasmas have electron densities in the range ($\sim 10^{11}$ cm$^{-3}$) and
emission lines under study are non-resonant [109], the plasmas behave as optically thin medium for these lines.

Figure 4-3: Boltzmann's plot with 10% He, 4% Ar and 86% N₂ at filling pressure of 0.5 mbar and rf power of 150 W

<table>
<thead>
<tr>
<th>λ(nm)</th>
<th>Transitions</th>
<th>$A_{ij}(10^6 s^{-1})$</th>
<th>$g_i$</th>
<th>$E_i$ (eV)</th>
<th>$E_i$ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420.07</td>
<td>$3s^23p^5 \left( ^2P_{3/2}^o \right) 4s - 3s^23p^5 \left( ^2P_{3/2}^o \right) 5p$</td>
<td>0.97</td>
<td>7</td>
<td>14.50</td>
<td>116942.7</td>
</tr>
<tr>
<td>696.69</td>
<td>$3s^23p^5 \left( ^2P_{3/2}^o \right) 4s - 3s^23p^5 \left( ^2P_{1/2}^o \right) 4p$</td>
<td>6.39</td>
<td>3</td>
<td>13.32</td>
<td>107496.4</td>
</tr>
<tr>
<td>706.72</td>
<td>$3s^23p^5 \left( ^2P_{3/2}^o \right) 4s - 3s^23p^5 \left( ^2P_{1/2}^o \right) 4p$</td>
<td>3.80</td>
<td>5</td>
<td>13.30</td>
<td>107289.7</td>
</tr>
<tr>
<td>720.70</td>
<td>$3s^23p^5 \left( ^2P_{1/2}^o \right) 4p - 3s^23p^5 \left( ^2P_{1/2}^o \right) 6s$</td>
<td>2.48</td>
<td>3</td>
<td>15.02</td>
<td>121161.3</td>
</tr>
<tr>
<td>750.38</td>
<td>$3s^23p^5 \left( ^2P_{1/2}^o \right) 4s - 3s^23p^5 \left( ^2P_{1/2}^o \right) 4p$</td>
<td>44.5</td>
<td>1</td>
<td>13.48</td>
<td>108722.6</td>
</tr>
<tr>
<td>800.62</td>
<td>$3s^23p^5 \left( ^2P_{3/2}^o \right) 4s - 3s^23p^5 \left( ^2P_{3/2}^o \right) 4p$</td>
<td>4.90</td>
<td>5</td>
<td>13.17</td>
<td>106237.5</td>
</tr>
</tbody>
</table>
Figure 4-4: Dependence of plasma excitation temperature on (a) He percentage for rf power of 150 W and filling pressure of 0.5 mbar (b) rf power at filling pressure of 0.5 mbar and (c) filling pressure at rf power of 150 W with 10 % He in Ar-N₂ discharge.
Figure 4-5: Variation of $N_2$ (337.1 nm), $N_2^+$ (391.4 nm), He-I (501.6 nm) and Ar-I (750.39 nm) spectral bands/lines with the He percentage at filling pressure of 0.4 mbar and rf power of 150 W.

In our case both the above mentioned conditions are satisfied. Furthermore; the extreme case of self-absorption is self-reversal which appears as a dip in a line shape. Such a dip is not observed for any line under study. The self-absorption as described above in the discussion is not appearing in the Ar-He-N$_2$ discharge. The data of Ar-I spectral lines used in the calculation of excitation temperature ($T_{exc}$) are provided in Table 4-2.

Figure 4-3 presents the plot of $\ln\left(\frac{I_i\beta_i}{g_iA_i}\right)$ versus the energy of upper levels for each considered transition at 0.5 mbar filling pressure and 150 W rf power with 10% He, 4% Ar and the rest of N$_2$ gas mixture. The slope of the Boltzmann plot gives $(1.41 \pm 0.07$ eV). Figure 4-4 presents how the excitation temperature $T_{exc}$ varies with the helium percentage for different rf powers and filling pressures. The increase in $T_{exc}$ with the increase of helium percentage in the mixture may be attributed to smaller collision cross-section of helium than nitrogen, and thus decrease in electron collision frequency.
This fact in turn provides enough time for electrons to be accelerated in response of the applied rf electric field, and consequently an increase in the kinetic energy of electrons. The results also show the increase in $T_{\text{exc}}$ with rf power at fixed helium fraction. This fact can be attributed to the increase in electron energy imparted by enhanced rf electric field at higher power. The reduction of $T_{\text{exc}}$ with rise of filling pressure may be explained as follows: when the pressure in the chamber increases it causes an increase in the number of collisions between electrons and other plasma species. Consequently effective collisional transfer of energy occurs, that reduces the excitation temperature.

Figure 4-5 presents, how emission from He-I (501.6 nm), N$_2$ (337.1 nm), N-I (746.83 nm) and N$_2^+$ (391.4 nm) varies with the change in He fraction. The data is recorded at filling pressure 0.4 mbar and rf power of 150 W. The decrease in N$_2$ (337.1 nm) is expected as with the increase in He percentage, the N$_2$ percentage in the feed gas is decreasing. Similarly the He-I (501.6 nm) intensity will increase with the increase in He percentage accordingly. The increase in N-I (746.83 nm) and N$_2^+$ (391.4 nm) may be explained as under: the excitation cross-section of the helium by impact of the electrons is smaller than the excitation cross-section of nitrogen. With the increase in He percentage in the mixture, the electron collision frequency will decrease that in turn will provide the electrons more time to accelerate and gain energy. These high energy electrons may excite, ionize and at the same time create metastable states of helium. Therefore, emission intensity of N$_2^+$ (391.4 nm) is increased significantly because of its lower threshold excitation energy. The increase in excitation temperature with the increase in helium percentage may also be explained in terms of the reduced electron collision frequency.
Figure 4-6: The change in dissociation of N\textsubscript{2} with the He percentage at filling pressure of 0.4 mbar and rf power of 150 W by actinometry and the ratio of I\textsubscript{N} (746.83 nm)/I\textsubscript{N\textsubscript{2}} (337.1 nm).

Figure 4-6 shows the variation of N\textsubscript{2} dissociation degree as a function of He percentage for rf power of 150 W and 0.4 mbar pressure. The dissociation fraction is determined by employing the actinometry method (4\% Ar) and the intensity ratio method \( \left( \frac{I_{N}(746.83 \text{ nm})}{I_{N\textsubscript{2}}(337.1 \text{ nm})} \right) \) for the sake of comparison. Both the techniques give the same trend. Due to a smaller collision cross-section of helium, the increase of helium fraction results in a larger mean free path and less collision of electrons, thus the electrons accelerate and gain energy from the electric field. Since the excitation threshold energy of helium (20.61 eV) is high as compared to the nitrogen dissociation energy these electrons may account for significant dissociation of nitrogen.
Figure 4-7: Dependence of the relative densities of N-I (746.83 nm) and N2+ (391.4 nm) on the helium fraction at filling pressure of 0.4 mbar and rf-power of 150W.

Figure 4-7 shows the variations in densities of [N] and [N2+] with helium fraction in the discharge for rf-powers of 150 W and 0.4 mbar fill pressure. Initially when the helium percentage increases in the discharge, the electrons gain energy from the electric field due to a less collision cross-section of helium. Since the excitation and ionization threshold energies of helium are relatively high, the electron impact dissociation and ionization of molecular nitrogen may result in the increase of the relative densities of [N] and [N2+] respectively (R-10, R-4). A further increase in helium percentage may enhance the electron energies that can excite helium atoms efficiently, which in turn increase the relative density of [N2+] by Penning process (R-6) and charge transfer reaction (R-7). Due to large relative density of [N2+] at higher percentage of helium, the relative density of [N] is increased by dissociative recombination (R-11). The saturation of relative [N] concentration at much higher helium percentage (more than 80 %) is due to the fact that it is no longer nitrogen plasma but helium plasma doped with nitrogen and hence there is a lesser number of nitrogen molecules available to be dissociated.
4.8. Conclusion

Trace rare gas optical emission spectroscopy is carried out to investigate the excitation temperature, degree of nitrogen dissociation and relative densities of active species $[N]$ and $[N_2^+]$ in inductively coupled helium admixed nitrogen plasma using Ar as an actinometer, for different discharge parameters. The excitation temperature increases with the increase in rf power and helium fraction and decreases with the increase in fill pressure. The degree of nitrogen dissociation and the relative density of $[N]$ and $[N_2^+]$ is found to increase with helium percentage. These results suggest that helium can be a good choice for the generation of active species in nitrogen plasma.
CHAPTER 5
CHARACTERIZATION OF INDUCTIVELY COUPLED Ar-N₂ PLASMA USING LANGMUIR PROBE AND OPTICAL EMISSION SPECTROSCOPY

5.1. Introduction

Inductively coupled plasmas (ICPs) at low pressure have been widely used in material processing applications such as plasma nitriding, plasma etching, fabrication of integrated circuits and flat-panel displays, because of their high densities and spatially homogeneous profiles of reactive species including excited atoms, free radicals and ions [14]. Such plasmas are produced with high electron density ($10^{10}$-$10^{12}$ cm$^{-3}$), low surface damage and the highly uniform source of radicals, to meet the industrial/commercial requirements [39]. Moreover, inert gas admixed nitrogen plasmas have important technological applications such as polymer surface activation and modification, metallic nitriding, medical instruments sterilization and synthesis of semiconductors [40]. Especially, the addition of argon to the nitrogen plasma is useful for easy production of stable and uniform discharge. The addition of argon may also cause a change in the shape of the electron energy distribution function, electron temperature and consequently in the electron number density [25].

Many diagnostic techniques, such as Langmuir probe, optical emission spectroscopy (OES), and mass spectrometry are being used to characterize such plasmas [26, 110]. Among these techniques, Langmuir probe is used to measure plasma parameters such as electron temperature ($T_e$), electron density ($n_e$), ion density ($n_i$) and electron energy distribution function (EEDF). One of the major advantages of the Langmuir probes is the local measurements of plasma parameters that may not be possible with other diagnostic techniques. A reliable Langmuir probe system is essential to complement the optical spectroscopy measurements.

OES is one of the most widely used diagnostics for investigating neutral and ionic species in reactive plasmas owing to its non-perturbing nature [111, 112]. OES has proven to be a powerful diagnostic tool to investigate plasma parameters such as excitation temperature ($T_{exc}$), electron temperature ($T_e$), densities of active
species (\(N, N_2^+ and N_2^{++}\)), electron number density (\(n_e\)) and gas temperature. It can also be used to infer more complex plasma parameter such as EEDF and degree of dissociation [3].

Prior to the use of ICP plasma in various applications, it is necessary to determine basic plasma parameters such as \(T_{\text{exc}}^{OES}, T_e^{LP}\) and \(n_e^{LP}\). Obviously, the determination of the electron temperature and the electron density is of significant importance [3, 40]. The degree of dissociation in the nitrogen plasma is another important parameter for improving the plasma processes. Generally it is difficult to obtain high dissociation efficiency in pure nitrogen plasma due to its high bonding energy. One of the promising ways to enhance the dissociation and ionization of nitrogen is to introduce hydrogen or argon into the discharge [15]. However, insufficient literature is available for dissociation of nitrogen in high density Magnetic Pole Enhanced inductively coupled plasma (MaPE-ICP) sources.

In reactive plasma diagnostics, actinometry is one of the useful and well developed technique to determine the density of plasma species (quantitatively and qualitatively) and degree of dissociation. In this method a small amount (\(\leq 5\%\)) of rare gas (i.e. argon) is introduced as an actinometer in the discharge. Although actinometry is a straightforward technique, but the validity of this method have some constraints. It is assumed that:

- Excited states are generated by electron collisions and lost by radiative emission.
- Electron impact excitation cross-sections of the actinometer and the gas to be examined have same shape and similar threshold.
- Quenching processes are negligible.

Czerwiec et al.[15] have investigated the nitrogen dissociation in Ar/N\(_2\) plasma. It is reported that the nitrogen dissociation fraction can be enhanced by argon addition; a maximum is observed for 10 % of argon in the mixture. Nakano et al.[16] measured the dissociation degree in inductively coupled nitrogen plasma by using vacuum ultra violet (VUV) emission spectroscopy. They observed that the dissociation fraction increased from 5% to 20% with increasing the rf power from 30W to 100W, keeping pressure
constant at 0.665Pa. Itagaki et al.[20] reported dissociation degree of nitrogen ($I_N/I_{N_2}$ ~ 0.48) in Ar/N$_2$ plasmas at the input power and gas pressure of 1.5 kW and 0.27 Pa, respectively using 915 MHz electron cyclotron resonance sources.

Previously in this laboratory, Naveed et al.[113], Khan et al.[6], and Rehman et al.[114] investigated the relationship between electron temperature ($T_e$) obtained by Langmuir probe and excitation temperature ($T_{exc}$) obtained by OES in capacitively coupled nitrogen plasmas admixed with helium, argon and neon, respectively. According to these studies, $T_{exc}$ and $T_e$ have similar trend for different discharge parameters i.e. power, pressure and gas composition.

The objective of the present study is to investigate the plasma parameters ($T_{exc}^{OES}$, $T_e^{LP}$ and $n_e^{LP}$), the number density of reactive species ($N$ and $N_2$) and the degree of dissociation as a function of discharge parameters (power, pressure) and argon content (5 % - 95 %) in inductively coupled nitrogen plasma by using Langmuir probe and OES. Electron energy probability functions (EEPFs) are obtained to get better understanding of the effect of discharge parameters on the concentration of active species and the dissociation fraction.

The layout of this chapter is as follows. The description of the experimental set-up is provided in section 5-1. Langmuir probe and spectroscopic studies are described in section 5-2 and section 5-3, respectively. Results and discussion are given in section 5-4.

5.2. Experimental Setup

A schematic diagram of the Magnetic Pole Enhanced Inductively Coupled Plasma (MaPE-ICP) reactor is shown in figure 5-1. The MaPE-ICP source has been described by Meziani et al.[115]. A patented ferrite core is embedded in MaPE-ICP source, which concentrates the magnetic field of the induction coil in to the plasma chamber. Secondly, the embedded magnetic pole increases the magnetic induction thus; it concentrates the magnetic flux on the load (i.e. plasma) and reduces the losses in the back path. The strength of the core is used to support the dielectric window which serves as vacuum partition as well as the protection between coil and the plasma. Because of the ferrite
core, the window can be made significantly thin; as a result the magnetic field strength on
the load is increased [111].

**Figure 5-1: Schematic diagram of the experimental setup and diagnostics system.**
The inductive source is powered by a 13.56 MHz rf supply (PGF-RF Generator-1600 W),
which is used to excite various plasmas and thin layer processes like sputtering, etching
etc. The rf generator is operated in power regulation mode and the matchbox is set in
automatic mode so that the capacitors are automatically adjusted to reach an optimum for
zero reflected power. The chamber is evacuated by turbo molecular pump with base
pressure of 1.0×10^{-5} mbar, backed up with rotary vane pump. Hasting flow meter is used
to monitor the gases flow to the chamber. Water cooling system is installed for the
chamber, matching network and rf generator. To ensure a relatively uncontaminated
system, the inner surfaces of the chamber were cleaned by Ar discharge; Pirani and
Penning gauges are used to measure the pressure in the system. The rf power, the filling
pressure and the Ar content are varied in the range 10-100W, 0.02-0.4 mbar and 5-95% in
the nitrogen discharge, respectively. Gases are fed through feed regulators into to the
chamber at a constant flow rate of 20 sccm (standard cubic centimeter per minute). OES
is carried out by using computer controlled McPherson–2061 monochromator having a
1200 grooves/mm grating with a spectral resolution of 0.01 nm coupled to a photo-
multiplier tube (PMT-R928) and an auto-ranging Pico-ammeter (Keithley-485). The
width of the entrance slit and focal length of the monochromator were 5 μm and 1 m, respectively. An rf-compensated Langmuir probe (Smart probe, Scientific System) having a cylindrical tungsten tip with diameter of 0.38 mm and length of 10 mm is used to monitor the plasma parameter. The EEDFs are obtained by Druyvesteyn method; EEDFs are inferred from the second derivative of I-V characteristics.

5.3. Langmuir Probe Studies

5.3.1. Electron Energy Distribution Function (EEDF)

Langmuir probes are employed to measure electron energy distribution functions (EEDFs) and other plasma parameters such as \( n_e^{LP}, T_e^{LP} \) etc. Langmuir probes are currently the main contact diagnostic tool for measuring plasma parameters in weakly ionized, low-pressure plasmas in both applied and basic plasma research. The electron energy probability function \( g_p(\varepsilon) \) was acquired by differentiating the I-V curve twice in the electron retardation regime (\( V_p << V_{pl} \)) where \( V_p \) is the probe potential and \( V_{pl} \) is the plasma potential according to [26, 110]

\[
g_p(\varepsilon) = \frac{2\sqrt{2m_e}}{e^3 S_p} \frac{d^2 I}{dV^2}
\]

Whereas \( I \) and \( S_p \) are the probe current and probe tip area, \( e \) and \( m_e \) are electronic charge and mass, respectively. Electron energy distribution functions (EEDFs), which can readily be derived from measured EEPFs, are key to the characterization of rf plasmas [4].

\[
f_e(\varepsilon) = \varepsilon^{1/2} g_p(\varepsilon)
\]

Whereas \( \varepsilon \) is the electron energy and \( f_e(\varepsilon) \) is electron energy distribution function.

5.3.2. Electron Number Density and Electron Temperature

The electron number density \( n_e^{LP} \) and the effective electron temperature \( T_e^{LP} \) are found by integration of the measured EEPF, as [110]

\[
n_e^{LP} = \int_0^\infty \varepsilon^{1/2} g_p(\varepsilon) d\varepsilon
\]
\[ T_{e}^{I_L} = \frac{2}{3} \langle \epsilon \rangle = \frac{2}{3n_e} \int_{0}^{\infty} \epsilon^{3/2} g_{\rho}(\epsilon) \, d\epsilon \]

In above equation, \( \langle \epsilon \rangle \) is the average energy of electrons.

5.4. Spectroscopic Studies

Optical emission spectroscopy is carried out to investigate the rf generated Ar/N\(_2\) plasma in the pressure range of 0.02-0.4 mbar and rf power of 10-100W. In figure 5-2; the optical emission spectra show that the spectral lines and band heads originating from the atomic, molecular and ionized plasma species. These lines and bands are identified and labeled by using NIST data [105].

![Optical emission spectra of ICP plasma](image)

**Figure 5-2:** Optical emission spectra of ICP plasma for different ranges with 95% N\(_2\) and 5% Ar, recorded at a filling pressure of 0.06mbar and rf power of 20 W.

The emission intensity profiles used for the spectroscopic analysis are normalized for the spectral response curves of optical chain provided by the manufacturers. Main processes involved in the excitation and consequently de-excitation of plasma species are given in Table 5-1.
Table 5-1 Main Processes Involved in Excitation and De-Excitation of Plasma Species

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Wavelength (nm)</th>
<th>Transition probability (s(^{-1}))</th>
<th>Ref:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2(C^3\Pi_u, 0 \rightarrow B^3\Pi_g, 0))</td>
<td>337.1</td>
<td>1.34×10(^7)</td>
<td>[14, 116]</td>
</tr>
<tr>
<td>(N_2^+(B^2\Sigma^+_u, 0 \rightarrow X^2\Sigma^+_g, 0))</td>
<td>391.4</td>
<td>1.14×10(^7)</td>
<td>[14, 116]</td>
</tr>
<tr>
<td>(N(3p^4S_{3/2}^0 \rightarrow 3s^4P_{5/2}^0))</td>
<td>746.83</td>
<td>1.90×10(^7)</td>
<td>[105]</td>
</tr>
<tr>
<td>(Ar(1s_2 \rightarrow 2p_1))</td>
<td>750.40</td>
<td>44.5×10(^7)</td>
<td>[105]</td>
</tr>
</tbody>
</table>

5.4.1. Boltzmann Plot and Excitation Temperature

Most essential parameters influencing the plasma processes are the excitation temperature and electron temperature. One of the well-established diagnostics used for the determination of \(T\(_{exc}^{OES}\)\) is optical emission spectroscopy (OES) due to its nonintrusive nature [4, 117]. The excitation temperature is commonly evaluated by using the relative intensities of spectral lines. For an optically thin plasma, the spectral line intensity corresponding to a transition from an upper level \(i\) to a lower level \(k\) is given by [118].

\[
i_{ik} \propto N_i A_{ik} h \nu_{ik}
\]

Where \(A_{ik}\) and \(\nu_{ik}\) are the transition coefficient and the frequency of transition from \(i \rightarrow k\), respectively; \(N_i\) is the population density of excited state and \(h\) is the Planck’s constant.

The intensity of the different spectral lines is used with the assumption that population of the emitting levels follows the Boltzmann distribution. Instead of using two lines, it is more appropriate to plot the \(\ln\left(\frac{l_{ik} \lambda_{ik}}{A_{ik} g_i}\right)\) vis-à-vis their energy, for all the lines that are recorded. This technique averages the \(T\(_{exc}^{OES}\)\) over the available data and improves the accuracy. It is known as the Boltzmann plot method [119].

\[
\ln\left(\frac{l_{ik} \lambda_{ik}}{A_{ik} g_i}\right) = -\frac{E_i}{k_B T_{exc}^{OES}} + C
\]
Here in equation (6); \( \lambda_{lk} \) is the wavelength of spectral line and \( k_B \) is the Boltzmann constant. The excitation temperature \( T_{\text{exc}}^{\text{QES}} \) is obtained from the slope of the graph. The excitation temperature is obtained from nine Ar-I spectral lines after careful selection. The necessary conditions for achieving accuracy of excitation temperature using Boltzmann plot method are to use calibrated emission intensity, selecting lines with large energy difference between upper levels and using lines that correspond to a rather narrow wavelength range. For non-LTE plasma, excitation temperature cannot be considered equal to the electron temperature but in situations where the calculation of \( T_e \) is not practical or extremely complicated, one can easily calculate \( T_{\text{exc}}^{\text{QES}} \) to get a rough estimate for the trend of \( T_e \) because both the temperatures show similar trend [4, 8].

For the optical emission spectroscopy of plasma, a basic requirement is that the emission lines under study should not be absorbed by the plasma itself or plasma must be optically thin for those lines. When plasmas have electron densities in the range (~ 10^{11} \text{ cm}^{-3}) and emission lines under study are non-resonant [109], the plasmas behave as optically thin medium for these lines. In our case both the above mentioned conditions are satisfied.

5.4.2. Actinometry and Dissociation Fraction

In accordance with equation (5), the ratio of emission intensities of the actinometer (argon) and the examined species (nitrogen atoms) is given as [79]:

\[
\frac{I_N}{I_{Ar}} \sim \frac{[N]}{[Ar]} \int_{e_1}^{e_{\text{max}}} n_e(\varepsilon) \sigma_N(\varepsilon) d\varepsilon
\]

Whereas \( \sigma \) is the electron impact excitation cross section; \( e_1 \) and \( e_2 \) are threshold excitation energies of examined gas and actinometer. Considering the assumptions of actinometry as described in the introduction, the above equation can be written as [15]

\[
[N] = k_1 \frac{I_N}{I_{Ar}} [Ar]
\]

Whereas \( I_N \) and \( I_{Ar} \) are the emission intensities of reactive and actinometric species, and \([Ar]\) and \([N]\) are the concentrations of argon and nitrogen atom in the discharge. Whereas \( k_1 \) is a constant depends only on the properties of specific atoms [79]. For the
actinometry of Ar-N₂ discharge, the atomic lines of nitrogen at (λ = 746.83 nm) and argon at (λ = 750.39 nm) are used because they are not sensitive to two step excitation. Also, the threshold excitation energy of atomic nitrogen \( I_N(\lambda = 746.83 \text{ nm}, E > 11.99 \text{ eV}) \) matches approximately with the threshold excitation energy of the argon \( I_{Ar}(\lambda = 750.39 \text{ nm}, E > 13.48 \text{ eV}) \). Therefore, the same group of electrons will contribute for the excitation of both levels and the excitation efficiencies will have a similar dependence on the discharge parameters.

Similarly, the concentration of nitrogen molecules \([N_2]\) can be obtained by using emission intensities of \( I_{N_2}(\lambda = 337.10 \text{ nm}) \) band head and \( I_{Ar}(\lambda = 750.39 \text{ nm}) \) line as follows [120].

\[
[N_2] = k_2 \left( \frac{I_{N_2}}{I_{Ar}} \right) [Ar] \tag{5.9}
\]

The excitation threshold energies for radiative states \( I_{N_2}(\lambda = 337.10 \text{ nm}, E > 11.1\text{ eV}) \) and \( I_{Ar}(\lambda = 750.39 \text{ nm}, E > 13.48\text{ eV}) \) are close and have similar dependence of the electron impact excitation coefficient. Also the excited state \( N_2(C) \) is mainly populated by direct electron impact from the ground state \( N_2(X) \)[15].

The actinometry method is considered to be an approximate method for determining the concentration of plasma species. Since the flow rate of the actinometric gas (argon) is kept constant during the measurements and its fraction in the discharge is known, therefore, its particle density can be calculated for different fill pressure and gas composition. By using this value of argon particle density in equation 4 and equation 5, the concentrations of N and N₂ density can be estimated as a function of discharge parameters.

The dissociation fraction of N₂ molecule is defined as the ratio between the number of nitrogen atoms \([N]\) to the initial number of nitrogen molecules \([N_2]_i\)[83].

\[
D = \frac{[N]}{2[N_2]_i} \tag{5.10}
\]

The dissociation fraction by using the atomic line N \(-1 \, (\lambda = 746.83 \text{ nm}) \) to the molecular band head of nitrogen \( N_2 \, (\lambda = 337.10 \text{ nm}) \) is given by [14].
Where \( K(\lambda_{746.83}) \) and \( K(\lambda_{337.1}) \) are the spectral responses of the detection system related to the N-I atomic line and N\(_2\) (0-0) band head, respectively. \( C_1 \) is a constant, which depends upon excitation rate coefficients and the spectroscopic data [14].

5.5. Results and Discussions

**Figure 5-3 (a)** shows the emission intensities of \( I_{N_2}, I_{N_2^*}, I_{Ar} \) and \( I_N \) as a function of rf power (10-100 W) at filling pressure of 0.02 mbar with 5% N\(_2\) in Ar discharge. The increase in emission intensities of these band heads/lines with rf power suggest an increase in the population density of corresponding emitting states. The increasing trend of these excited states may be attributed to the increase in electron energy with enhanced rf electric field at higher rf powers. The EEPF is expanding toward higher energies causes an increase in high energy electrons. This increase results in an increase in excitation, ionization and the dissociation of nitrogen molecules. **Figure 5-3 (b)** shows, the emission intensities of lines/bands are decreasing with filling pressure (0.02-0.4 mbar) at fixed rf power of 100W. These results indicate that the population density of these states decrease with an increase in filling pressure. This fact may be explained as follows: When pressure in the chamber increases, it causes an increase in the number of collisions between the electrons and the other plasma species. As a result the energy transferred from the electrons to the plasma species increases, cause a decrease in the electron temperature. The EEPF shifts toward lower energies and the number of electrons, having energy above the threshold excitation energy responsible for the optical emission, are reduced.

**Figure 5-4** presents the plot of \( \ln(I\lambda/gA) \) versus the energy of upper levels for each considered transition at 0.02 mbar filling pressure and 100W rf power with 5% N\(_2\) in Ar discharge. The slope of the Boltzmann plot gives \( T_{exc}^{OES} = 1.037 \pm 0.095 \) eV. **Figure 5-5** presents the variation of electron temperature \( (T_e^{LP}) \), the electron number density \( (n_e^{LP}) \) and the excitation temperature \( (T_{exc}^{OES}) \) as a function of rf power (10-100 W), filling pressure (0.02-0.1 mbar) and Ar content. It is observed that the electron...
temperature($T_{\text{e} LP}$) has a similar decreasing trend as the excitation temperature with the applied rf power and filling pressure. In figure 5-5 (a), the decrease in electron temperature($T_{\text{e} LP}$) and excitation temperature($T_{\text{exc} ES}$) with the increase in rf power may be due to the inelastic collisions between the electrons and other plasma species. These collisions cause an increase in the ionization of plasma species. It is also evident from the increase in electron number density with the increase in rf power. Figure 5-5 (b) shows that the electron temperature ($T_{\text{e} LP}$) and the excitation temperature ($T_{\text{exc} ES}$) decrease whereas the electron number density increases with filling pressure.

![Figure 5-3 Emission intensities of N (746.83 nm), Ar-I (750.40 nm) and N$_2^+$ (B, 391.4nm), N$_2$ (C, 337.1 nm) in 5% N$_2$ and 95% Ar as function of (a) filling pressure at rf power of 100 W (b) rf power at filling pressure of 0.02mbar.](image)
Figure 5-4 The Boltzmann plot obtained from Ar-I spectral lines for filling pressure of 0.02 mbar with 5% N\textsubscript{2} in Ar discharge at rf power of 100 W.

In figure 5-5 (c), the increase in \( n_{e}^{LP} \) and the decrease in \( T_{e}^{LP} \) with Ar content is observed that may be explained as follows. As the Ar content increases, the number of energetic electrons utilizes their energy to ionize the nitrogen molecules and also create the metastable states of argon. These metastable states of argon further enhance the ionization mechanism. Thus \( n_{e}^{LP} \) increases and \( T_{e}^{LP} \) decreases with Ar content in the discharge.

Figure 5-6 (a) shows the variation of EEPFs with filling pressure at rf power of 100W and 5% N\textsubscript{2} in Ar discharge. The EEPFs are shifting towards the lower energy with the pressure supporting the decreasing trend of electron temperature and dissociation of nitrogen molecules with filling pressure. Figure 5-6 (b) and (c) demonstrate the variation of EEPFs with rf power and Ar content respectively. The number of electrons having energy in the range of 10-20 eV is observed to increase with rf power and Ar content. These electrons contribute to an increase in the dissociation of nitrogen molecules as shown in figure 5-7 (b). The relative ground state densities of N and N\textsubscript{2} are shown in figure 5-7 (a) as a function of filling pressure at rf power of 100 W and 5% Ar in nitrogen discharge. These results indicate that the density of N increases with filling pressure. The density of N\textsubscript{2} is almost two times of magnitude lower than N atomic density and nearly saturated at higher pressures. Figure 5-7 (b) presents the dependence of dissociation degree on filling pressure (0.02-0.4mbar) and Ar content (5-95%).
These results show that the dissociation fraction first increases with the filling pressure ranging from 0.02-0.06 mbar then decreases with further increase in filling pressure. This behavior is in agreement with the EEPFs measurement of Langmuir probe. The EEPFs show that high energy electrons in the tail increase for filling pressure (0.02-0.06 mbar) and then decrease. The decrease in dissociation fraction with filling pressure may be attributed to the decrease in electron energy with the increase in filling pressure. The dissociation fraction increases with argon content in the discharge. This enhancement of nitrogen dissociation as a function of argon content may be attributed to the increase in the density of Ar metastable states. These metastable states of argon interact significantly with nitrogen molecules through Penning excitation, dissociating them into two nitrogen atoms. There is also another contribution to the N-atom production: the charge exchange between nitrogen molecules and argon ions followed by a dissociative recombination [15]. The higher dissociation fraction with Ar content may also be related to the shift of EEPF towards higher energy as discussed in figure 5-6(c).
Figure 5-5 Electron number density ($n_{e\text{LP}}$), electron temperature ($T_{e\text{LP}}$) and excitation temperature ($T_{\text{exc\text{OES}}}$) as functions of (a) rf power at filling pressure of 0.02 mbar (b) filling pressure at rf power of 100 W, with 5% $N_2$ in Ar discharge, (c) Ar content

Figure 5-6 Electron energy probability functions (EEPFs) in 5% $N_2$ and 95% Ar (a) for different filling pressure at rf powers of 100W (b) for different power at filling pressure of 0.02 mbar and (c) EEPFs for different Ar content in nitrogen discharge
Figure 5-7: (a) The ground state densities of N and N\textsubscript{2} with 5\% Ar in nitrogen discharge (b) The dissociation fraction of nitrogen molecules for different Ar content; as a function of filling pressure at rf power of 100W.
5.6. Conclusion:
The plasma parameters and active species concentration have been investigated in low pressure inductively coupled plasma as a function of rf power (10-100 W), filling pressure (0.01-0.4 mbar) and argon content (5% to 95%) in nitrogen discharge. The EEPFs are measured for different Ar content and discharge parameters by Langmuir probe. The electron temperature decreases whereas the electron number density increases with the increase in rf power, filling pressure and Ar content. By using optical emission spectroscopy, the concentration of nitrogen species (N, N₂) and the dissociation fraction are estimated. It is found that active species concentration has significant dependence on the discharge parameters. The concentration of nitrogen species (N, N₂) are found to increase with filling pressure at constant rf power of 100W with 5 % Ar in nitrogen discharge. The dissociation fraction is increased with the increase of Ar content at constant rf power and filling pressure that may be attributed to the increased number of energetic electron in the discharge responsible for the dissociation as complimented by the measurement of EEPFs. The dissociation fraction first increases with filling pressure and reach to maximum value and then decrease suggesting the optimum filling pressure for dissociation. The value of optimum filling pressure move towards higher side with increase in Ar content (i.e. 0.06 mbar for 50% Ar and 0.08 mbar for 95% Ar) in the discharge suggesting higher optimum filling pressure for higher Ar content in the discharge. This study is carried out to optimize the Ar/N₂ plasma for the production of active species, which are considered to be important in material processing applications.
CHAPTER 6
ENHANCEMENT OF THE ELECTRICAL PROPERTIES OF CARBON
NANOTUBES WITH Ar/N₂ PLASMA TREATMENT

6.1. Introduction

In recent years, carbon nanotubes (CNTs) have attracted considerable attention due to their excellent field emission properties, i.e. good emission stability, long emitter lifetime and high current density [35, 121]. These are thermally stable due to high electrical conductivity in vacuum up to 2800°C and in air up to 750°C. Additionally, Carbon nanotubes have potential applications in different fields like nano electronics, medical, engineering, automotive, space industry [122].

Plasma treatment of CNTs is the current topic of research specifically with the variation of different discharge parameters that play an important role to enhance the field emission properties and the modification of microstructures [42]. In addition, plasma treatment has been applied to modify chemical, mechanical and electrical properties of CNT [43]. Yu et al.[46] treated the carbon nanotubes in rf generated hydrogen plasma at an filling pressure of 2.5 mbar, rf power of 200–300 W and process duration of 15–20 min with gas flow rate of 10 sccm. They reported that after plasma treatment, the field emission properties and surface microstructure of carbon nanotubes are changed and active sites on the surface are increased. Feng et al. [47] reported the effect of plasma treatment on microstructure and field emission properties of screen printed CNTs. The plasma treatment was carried out in the mixture of gases (H₂, N₂ and NH₃) at filling pressure of 1.5 mbar, rf power of 200–300 W and process duration of 0–40 min with gas flow rate of 10 sccm. They reported that the defect density of plasma processed samples is increased and field emission properties are improved by three orders of magnitude as compared to the untreated CNTs. It was observed that there is not any chemical bonding present between CNTs and plasma species. Nitrogen and hydrogen radicals are interacted with carbon nanotubes only physically and affect their field emission properties.
Different works are reported [42, 44, 45] for the processing of CNTs to modify the field emission properties and microstructure in the mixture plasmas. Effect of different plasma gas chemistry, working pressure and flow rate on CNTs was also observed. Hou et al.[42] reported the effect of Ar, O₂, CHF₃, and SF₆ plasma treatments on the surface morphology, microstructure, composition and electrode performance of the screen-printed CNT films in a reactive ion etching (RIE) system powered by rf source. According to their results, Ar/CHF₃/SF₆ and O₂/Ar treatments are the best choices for the improvement in the field emission and gas ionization, respectively.

However, few works [44] are reported in literature for the treatment of nanoparticles in inductively coupled plasmas (ICPs). These plasmas operating at low pressure are non-LTE, producing high density (10¹⁰-10¹² cm⁻³), low damage and highly uniform radicals.

The basic motivation behind this work is to diagnose the plasma by using Langmuir probe and optical emission spectroscopy (OES) for different rf powers (10-100W), filling pressure (0.02-0.4 mbar) and nitrogen content (5-95%) in Ar discharge. Carbon nanotubes are treated at optimum condition (rf power: 100W, filling pressure: 0.06 mbar, 5% N₂– 95% Ar) for treatment time of 0-120min. These samples are then analyzed by XRD, SEM, EDX, FTIR, Raman spectroscopy and two-probe method to explore the changes induced by plasma in crystallographic structure, surface morphology, elemental composition, structural disorder and electrical conductivity, respectively.

The layout of this chapter is as follows. The description of the experimental set-up is provided in section 6-1. Sample preparation and processing are described in section 6-2. Results and discussion are given in section 6-3 whereas conclusions are presented in section 6-4.

6.2. Experimental Setup:

A schematic diagram of the Magnetic Pole Enhanced Inductively Coupled Plasma (MaPE-ICP) reactor is shown in figure 1. The MaPE-ICP source has been described by Meziani et al.[115]. A patented ferrite core is embedded in MaPE-ICP source, which concentrates the magnetic field of the induction coil into the plasma chamber. Secondly, the embedded magnetic pole increases the magnetic induction thus; it concentrates the
magnetic flux on the load (i.e. plasma) and reduces the losses in the back path. The strength of the core is used to support the dielectric window which serves as vacuum partition as well as the protection between coil and the plasma. Because of the ferrite core, the window can be made significantly thin; as a result the magnetic field strength on the load is increased [111].

Figure 6-1 Schematic diagram of the experimental setup and diagnostics

The inductive source is powered by a 13.56 MHz rf supply (PGF-RF Generator-1600 W), which is used to excite various plasmas and thin layer processes like sputtering, etching etc. The rf generator is operated in power regulation mode and the matchbox is set in automatic mode so that the capacitors are automatically adjusted to reach an optimum for zero reflected power. The chamber is evacuated by turbo molecular pump with base pressure of $1.0 \times 10^{-5}$ mbar, backed up with rotary vane pump. Pirani and Penning gauges are used to measure the pressure in the system. Hasting flow meter is used to monitor the gases flow to the chamber. Water cooling system is installed for the chamber, matching network and rf generator. To ensure a relatively uncontaminated system, the inner surfaces of the chamber are cleaned by Ar discharge.
The discharge parameters such as rf power, the filling pressure and the Ar content are varied in the range of 10-100W, 0.02-0.4 mbar and 5-95% in the nitrogen discharge, respectively. Gases are fed through feed regulators into the chamber at a constant flow rate of 20 sccm (standard cubic centimeter per minute).

OES is carried out by using computer controlled McPherson–2061 monochromator having a 1200 grooves/mm grating with a spectral resolution of 0.01 nm coupled to a photo-multiplier tube (PMT-R928) and an auto-ranging Pico-ammeter (Keithley-485). The width of the entrance slit and focal length of the monochromator are 5 μm and 1 m, respectively. An rf-compensated Langmuir probe (Smart probe, Scientific System) having a cylindrical tungsten tip with diameter of 0.38 mm and length of 10 mm is used to monitor the plasma parameters. The EEDFs are obtained by Druyvesteyn method; EEDFs are inferred from the second derivative of I-V characteristics.

6.3. Sample Preparation and Processing

Carbon nanotubes were initially in the powder form having a mixture of single and multi-walled CNTs. These CNTs were synthesized by the catalytic decomposition of methane in the presence of Ni Catalyst. It contained approximately 60% MWCNT≈30% SWCNT and ≈10% impurities. These impurities can come from synthesis process like the catalyst or the other impurities present in the environment. There exist surface impurities in CNTs that suppress its graphitic nature. Purification of CNT powder is essential to be carried out before plasma treatment. Different methods are used for the purification. It includes heat treatment in air furnace that removes impurities from CNTs by their oxidation. Other methods are acid treatment, and ultrasonication. Fuctionalization of CNTs makes them more soluble in different solvents than the impurities, so this process can separate them from the impurity elements [34, 123]. In this work, CNTs were purified by the acid treatment. First of all CNT powder was heat treated in air furnace at 400°C for 15 minutes. If the amount of impurities is smaller, only the heat treatment is sufficient to purify CNTs. It removes the impurity elements by their oxidation. Heat treated powder was then treated with HCl acid. CNT powder was dispersed in HCl, 4000 ml HCl was used for the dispersion of 40g powder. This process of dispersion was carried out in
sonicator, for 3 hours at 60°C. HCl removed the synthetic catalyst from the CNT in the form of its chloride. Longer time HCl treatment can damage CNTs’ structure. Removal of HCl from CNT is necessary to avoid their structure damage. For this purpose, acid treated CNTs were washed four times with large amount of distilled water so that pH=7 is obtained. Approximately 200 ml distilled water was used for each washing of 1.25g powder. This process diluted the HCl present in CNTs and finally removed it almost completely. After washing, CNT powder was dried in vacuum oven at 120°C for 12 hours. In this way, the acid treatment purified the CNT powder.

It is the requirement of the processing chamber to use the sample in the pellet form, as the powder can be sucked by the vacuum pumps and can damage the pumps. Hydraulic presser was used to form the pellets of the purified CNT powder. It was very poor in hardness and broke away easily even on minute handling. Methyl cellulose powder is commonly used as binder for the formation of CNTs pellets. It was used in this experiment also as a binder, mixed with the CNT powder, and pellet of this mixture was formed by hydraulic presser. Dimensions of one pellet were 0.22 cm thickness, and approximately 1.31 cm in diameter. One pellet contained about 0.166 g of CNTs and 0.20 g of methyl cellulose powder. This pellet was good enough in hardness according to our requirements.

6.3.1 Procedure for Plasma Processing of CNTs

Pellets of CNTs were treated in argon, nitrogen mixture plasma generated in MaPE ICP set up powered by 13.56 MHz rf generator. The plasma consists of mixture of gases having 95% argon and 5% nitrogen. Flow rate of these gases was kept at 19sccm and 1sccm, respectively. Pressure inside the chamber was maintained to be 0.06mbar after filling the gases. This value of pressure was obtained by using turbo molecular pump along with rotary pump used in back up. Plasma was generated at a power of 100 W. These are the optimized operating conditions for the plasma generation. At these conditions, stable plasma generation took place and the reflection of input power was minimum. Emission intensity of the active species of nitrogen was found to be maximum at these conditions among all other possible operating conditions. These conditions were
derived on the basis of diagnostic data collected by optical emission spectrometer. The CNT pellets were treated at these conditions for different treatment times. Six different samples were treated for 20-120 min, keeping same power of 100 W, and pressure of 0.06mbar.

6.4. Results and discussion

6.4.1. Optical Emission in Ar–N₂ Mixture and Dissociation Fraction

Optical emission spectra are recorded for various rf power of 10-100 W and filling pressure of 0.02-0.4 mbar in Ar–N₂ (5–95%) discharge. The spectroscopic data of the molecular bands and the atomic lines are identified by using the data [105]. The emission intensity profiles used for the spectroscopic analysis are normalized for the spectral response of optical chain by using response curves provided by the manufacturers. 

**Figure 6-2 a and b** represents the evolution of some selected spectral line intensities as a function of the filling pressure (0.02-0.4 mbar) and rf power (10-100 W). From these results, the emission intensities of \( N_2(C), \ N - I \) and \( N_2^+(B) \) are first increased with the increase in filling pressure (from 0.02 to 0.06mbar) and then decreased with further increase in filling pressure (up to 0.4mbar). These spectral lines are linearly increasing with increase in rf power. In **figure 6-2 (a)**, the relative concentration of \( N_2^+(B) \) molecular band is decreased with filling pressure that may be explained as: the available number of energetic electrons is decreased with the increase in filling pressure result a decrease in the excitation of \( N_2^+(B) \) radiative state. However in **figure 6-2 (b)**, the increasing trend with rf power may be attributed to the increased electron energy with enhanced rf electric field. This increase cause more ionization, which in turn increases the population of various energy levels, associated with the ions. These energetic electrons cause an increase in the dissociation of \( N_2 \) molecules and the creation of radical species, which in turn cause an increase in N emission lines as shown in **figure 6-2 (b)**. However during material processing, the effect of\( N_2(C), \ N - I \) and \( N_2^+(B) \)are more important than Ar emission lines because these reactive species facilitate the material processing by transporting momentum and energy. On the other hand, Ar emissions lines are good representative of high energy electrons present in the tail of electron energy.
distribution function (EEDF). The intensity of Ar-I emission lines increases with the increase in rf power suggesting an increase in the excitation efficiency of the discharge.

The dissociation fraction is an important plasma parameter used to estimate the nitrogen molecule to be dissociated. The dissociation fraction is defined as ratio of the intensity of atomic line \( N - I \) (\( \lambda = 746.83 \text{ nm} \)) to the molecular band head of nitrogen \( N_2 \) (\( \lambda = 337.10 \text{ nm} \)) is given by [14].

\[
D = C_1 \frac{I_N}{I_{N_2}} \frac{K(\lambda_{746.83})}{K(\lambda_{337.1})}
\]

Here \( K(\lambda_{746.83}) \) and \( K(\lambda_{337.1}) \) are the spectral responses of the detection system related to the N-I atomic line and \( N_2 \) (0-0) band head, respectively. \( C_1 \) is a constant, which depends upon excitation rate coefficients and the spectroscopic data [14, 15].

Figure 6-2 (c) presents the dependence of dissociation fraction on filling pressure (0.02–0.4 mbar) at rf power of 100W with 5% \( N_2 \) in Ar discharge. These results show that the dissociation fraction first increases with the filling pressure ranging from 0.02-0.06 mbar then decreases with further increase in filling pressure. The variation in the dissociation fraction with filling pressure may be attributed to the change in the concentration of energetic electrons with filling pressure. Maximum value of dissociation fraction is obtained in the pressure range of 0.06–0.08 mbar suggesting an optimum filling pressure for dissociation and active species generation. The dissociation fraction is observed to decrease with further increase in filling pressure (0.08–0.4 mbar). The value of optimum filling pressure move towards higher side with increase in Ar content (i.e. 0.06 mbar for 75% Ar and 0.08 mbar for 95% Ar) in the discharge suggesting higher optimum filling pressure for higher Ar content in the discharge.
Figure 6-2 Dependence of spectral intensity/band head of N\textsubscript{2} (C, 337.1 nm), N\textsubscript{2}\textsuperscript{+} (B, 391.4 nm), N-I (746.83 nm) and Ar-I (750.56 nm) as function of (a) filling pressure at rf power of 100 W (b) rf power at filling pressure of 0.02 mbar with 5\% N\textsubscript{2} content in Ar discharge and (c) dissociation fraction at different nitrogen content is Ar discharge as a function of filling pressure at rf power of 100 W.
6.4.2. Electrical Probes

To measure the plasma parameters such as electron temperature and electron number density, a single Langmuir probe is used. The electron energy probability function $f_p(\varepsilon)$ is obtained by differentiating the I-V curve twice.

$$f_p(\varepsilon) = \frac{2\sqrt{2m_e}}{e^3S_p} \frac{d^2I}{dV^2} \tag{6.2}$$

Where $I$ and $S_p$ are the probe current and probe tip area, $e$ and $m_e$ are electron charge and mass, respectively; and $V$ is the probe potential referenced to the plasma potential $V_p$.

The electron number density ($n_e$) and the electron temperature ($T_e$) are found by integration of the measured EEPF $f_p(\varepsilon)$, as [4, 106].

$$n_e = \int_0^\infty \varepsilon^{1/2} f_p(\varepsilon) d\varepsilon \tag{6.3}$$

$$T_e = \frac{2}{3} < \varepsilon > = \frac{2}{3n_e} \int_0^\infty \varepsilon^{3/2} f_p(\varepsilon) d\varepsilon \tag{6.4}$$

Electron energy distribution functions (EEDFs), which can readily be derived from measured EEPFs, are key to the characterization of rf plasmas, aiding the understanding of physical behavior [124].

$$f_e(\varepsilon) = \varepsilon^{1/2} f_p(\varepsilon) \tag{6.5}$$

Whereas $\varepsilon$ is the electron energy and $f_e(\varepsilon)$ is electron energy distribution function.

A direct proportionality exists between electron temperature and difference between plasma and floating potential ($V_f$) according to

$$V_p - V_f = \frac{k_BT_e}{2e} \ln\left( \frac{m_i}{2\pi m_e} \right) \tag{6.6}$$

Where $m_i$ and $k_B$ are the ion mass and Boltzmann constant, respectively.

The floating potential $V_f$ and plasma potential $V_p$ are important parameters for plasma processing of materials determined by I–V plot of Langmuir probe.
Figure 6-3 Variation of (a) Electron temperature $T_e$ and Electron number density $n_e$ at filling pressure of 0.06 mbar, the change in the value of $V_p-V_t$ at (b) different filling pressure (c) different $N_2$ content in Ar discharge as a function of rf power.
The difference between plasma potential and floating potential $V_p - V_f$ gives the measure of energy of the sputtered particles bombarding the substrate [21]. This plasma parameter is also a direct estimate of concentration of ion number density and electron number density.

**Figure 6-3 (a)** shows the changes induced in $T_e$ and $n_e$ with variation of rf power. Results show that the electron temperature decreases and electron number density increases linearly with rf power. These results are according to the kinetic model of low-pressure nitrogen discharge [125]. The increase in $n_e$ with rf power at fixed Ar content can be attributed to the increase in electron energy imparted by enhanced rf electric field at higher power. The electron number density is increased from $7.17 \times 10^{09} \text{cm}^{-3}$ to $3.90 \times 10^{11} \text{cm}^{-3}$ and the electron temperature is decreased from 6.00 $eV$ to 2.20 $eV$.

**Figure 6-3 (b)** and (c) shows the value of $V_p - V_f$ at filling pressure (0.02-0.1 mbar) and Ar content (5-95%) in nitrogen discharge as a function of rf power, respectively. Results clearly show that the difference of $V_p - V_f$ is decreased with the increase in filling pressure and Ar content in the nitrogen discharge as a function of rf power. The drop in electron temperature and $V_p - V_f$ is due to increase in ion density with Ar content, rf power and filling pressure.

It is concluded from the results of optical emission spectroscopy and Langmuir probe that the higher rate of dissociation and active species generation is observed with a mixture of 95% Ar and 5% N$_2$ at flow rate of 20sccm operating at filling pressure of 0.06mbar and rf power of 100W. These discharge conditions are considered optimum for materials processing in rf generated MaPE-ICP. Under these conditions the carbon nanotubes are treated for different treatment time to study the changes induced in crystallographic structure, elemental composition, and surface morphology and field emission properties.
6.4.3. **SEM and EDX Analysis**

The surface morphology of untreated and plasma irradiated CNTs are studied by obtaining micrographs at a magnification of \( \times35,000, \times10,000 \) and \( \times5000 \) using a JEOL JSM-5910 scanning electron microscope (SEM). In figure 6-4 (a)-(f), SEM images are shown for magnification of \( \times10,000 \); a careful examination of these images reveals a good surface smoothness as a function of treatment time at rf power of 100 W and filling pressure of 0.06mbar. SEM images of treated samples show no obvious change in appearance and morphology as compare to those virgin samples. Plasma treatment has not destroyed their nano-tubular nature. This ensures that the intrinsic physical properties of the samples before and after irradiation are essentially identical.

Energy dispersive X-ray (EDX) spectra of the untreated and the plasma treated CNTs are carried out to determine the elemental composition as shown in figure 6-5 (a) and (b), respectively. Most abundant element is carbon in all samples; it is obvious, as the CNTs are composed of the carbon. Oxygen is the second most abundant element that may have been added to the CNT pellets from the binder methyl cellulose, or from the air. Silicon and chlorine are the environmental impurities that contaminate the samples. There is not any trace of nitrogen detected in treated samples.
Figure 6-4 Scanning electron microscopy (SEM) images of CNTs (a) untreated sample and treated sample for treatment time of (b) 20 min, (c) 40 min, (d) 80 min (e) 100 min (f) 120 min
6.4.4. Fourier Transform Infra-Red Spectroscopy

Figure 6-6 shows the Fourier transform infrared spectroscopy (FTIR) results of untreated and treated samples in Ar–N$_2$ at rf power of 100W and filling pressure of 0.06 mbar. The FTIR spectra of carbon nanotubes demonstrate the presence of different functional groups and the types of bonding present. Mainly there are three absorption peaks in the pristine as well as treated samples. These absorption peaks correspond to $\equiv C – H$ (bending), $–C = C –$ (stretching), and $–C \equiv C –$ (stretching). The stretching modes of vibration $–C = C –$ of MWCNT are observed around 1630 cm$^{-1}$. Moreover, there is a broad band at 3350 cm$^{-1}$, indicating stretching vibration of hydroxyl groups $–(OH)$. In the untreated CNTs, there is an additional peak for O–H bonding. These work are based on reported data in the literature [126-128] and [129, 130]. These oxygen and hydrogen contents may arise from the binder and the moisture content in atmosphere. There isn’t any trace of nitrogen detected in plasma treated CNTs.
Figure 6-6 FTIR results for different treatment time at rf power of 100W, filling pressure of 0.06mbar and 95% Ar in nitrogen discharge.

6.4.5. Raman Spectroscopic Analysis

Raman spectroscopy is a standard non-destructive experimental technique for probing the vibrational and structural properties of carbon rich materials. Raman spectroscopy of treated samples is performed at a power level of 100 mW with spectral range of 100-2500 cm\(^{-1}\). In Raman spectroscopic analysis of plasma treated CNTs, mainly the D-band (1275 cm\(^{-1}\)) and the G-bands (1666 cm\(^{-1}\)) are focused upon and are shown in figure 6-7. The D-band is a representative of the defects and the disorder present in the structure of carbon nanotubes. These defects include amorphous carbon, disordered graphitic carbon structures, broken sp\(^2\) and sp\(^3\) bonds on the surface of CNTs [131]. It also indicates the presence of impurities and dopants in CNTs. The G-band is characteristic of the CNTs, representing their graphitic nature and the measure of perfection in sp\(^2\) bonding network of carbon atoms in hexagonal lattice of nanotubes. Intensity of G-band is independent of the structural disorders, and its dependence on laser wavelength is also small. Generally
the ratio of intensities of D and G-bands $R = \frac{I_D}{I_G}$ is used to measure the defect density in CNTs. Value of $R$ is linearly proportional to the defects and disorders density in CNTs[132]. Moreover, the ratio is related to the size of disordered graphite clusters during the amorphization process of CNTs induced by ion bombardment during plasma treatment. Figure 6-7 (a) and (b) shows the Raman spectra of untreated and plasma irradiated CNTs for treatment time of 100 min. In these graphs, the wavelength and corresponding intensities of D and G bands are clearly shown. It is observed that the position of the D-band is shifted towards higher value and that of the G-band is shifted towards lower value of wave number, indicating the reduction of graphitic nature with plasma irradiation as a function of time.

Figure 6-7 (c) gives the value of $R$ as a function of treatment time. The maximum value of $R$ is observed at treatment time of 100 minutes, representing the creation of maximum defects. The enhancement of value of $R$ for the plasma treated CNTs can be attributed as the increased disorder and the defect density. The increase in defect density of CNTs with the plasma treatment has already been reported by different researchers. Kalbacova et al.[133] reported the plasma treatment of SWCNT films for different treatment times resulting in the increase of defect density. Similarly, Yu et al.[46] also reported the increase in $R$ value of plasma treated CNTs films as compared to the pristine CNT films. It is concluded from these results that plasma treatment of CNTs increased their defect density, active sites on surface and induced structural disorders in the CNTs, with increase in treatment time.
Figure 6-7: Raman spectra of (a) Untreated, (b) treated at t=100min and (c) Time dependence of R for pristine and treated samples at rf power of 100W, filling pressure of 0.06mbar with 5% N₂ in Ar discharge
6.4.6. XRD Analysis

X-ray diffraction (XRD) spectra are acquired by using (JEOL JDX-3532, CuK$_\alpha$ radiation, 1.54 Å) operated at a voltage of 40 kV and current of 30 mA in the range 10°-60° (2θ) with a step size of 0.01 and a time per step of 1s. The X-ray diffraction analysis (XRD) provides identification of crystalline phases present in the samples along with structural changes induced during the plasma irradiation.

![XRD Analysis](image)

Figure 6-8 X-ray diffraction patterns of (a) treated and untreated samples (b) showing relative change in 2-theta of the (100) plane with treatment time at rf power of 100 W and filling pressure of 0.06 mbar with 5% N$_2$ in Ar discharge.
The acquired XRD spectra of treated (20-120 min) and untreated CNTs are shown in figure 6-8 (a). In untreated CNTs, there are mainly three peaks appearing, correspond to different phases. The peaks corresponding to (a) $2\theta \approx 26.80^\circ$(002), (b) $2\theta \approx 42.18^\circ$(100) and (c) $2\theta \sim 48.42^\circ$(201) are also present in the spectrum of treated CNTs samples as shown in table 6-1.

A graphitic carbon crystal phase corresponding to the plane (002) is observed at $2\theta \approx 26.80^\circ$ that is in good agreement with literature having inter planar spacing $d \leq 3.7 \ \text{Å}$ [134-138]. It is the main characteristic peak of CNTs (JCPDS-ICDD 411487). It exhibits the basis of graphitic nature of CNTs [139-141]. In our results, intensity of this peak is smaller as compared to other peaks appearing in pattern. It indicates that there are some surface impurities in the CNTs. These impurities suppress their graphitic nature, resulting in weaker (002) peak. With the plasma irradiation these peaks are blunt showing that the graphitic nature is disturbed with treatment time and disordered is induced in the CNTs. The second peak with miller indices (100) corresponding to the graphitic nature of carbon atoms appears at $2\theta \approx 42.18^\circ$ with inter planar spacing $d = 2.28 \text{Å}$. It is a sharp peak, indicating the good crystalline and graphitic structure of CNTs. Well broad and resolvable peaks for (100) phase but found to decrease with higher treatment time. This indicates the crystalline structure is disturbed with treatment time. There is another sharp peak of impurities appearing in the XRD pattern of pristine CNTs at $2\theta \sim 48.05^\circ$ correspond to oxygen–hydrogen bonding also confirmed by FTIR results. These impurity peaks may arise from the methyl cellulose used as binder during pellet formation. The 100 and 201 reflections, which are very strong as compared to 002, are found to be greatly weakened after plasma irradiation; especially 100. This may imply that the crystallinity can be decreased by plasma treatment.

All the phases appearing in treated samples are same as that of pristine CNTs. There isn’t any new phase appearing in treated samples, implying that after the plasma treatment elemental composition of CNTs remains the same. Plasma generated nitrogen ions do not interact with the carbon atoms of CNTs or with the oxygen and hydrogen contents of methyl cellulose.
It is observed from figure 6-8 (b) that with the increase in treatment time, the characteristic phase peaks of (100) plan is broad and weekend, showed downward shift up to $2\theta = 41.77$ (graphite, $2\theta = 42.3^\circ$). The broadening indicates that the long range order in CNT, is lower than that of graphite, in addition, the $2\theta$ downward shift in CNT relates to an increase in the $sp^2$ layers spacing. These planes are interconnected through weak attractive Vander Waals forces. Plasma treatment distorted these weak bonds and causes to reduce the mutual interaction of the planes. This can also lead to the change in diameter of CNTs.

Table 6-1 Summary of X-ray diffraction analysis parameters of untreated and treated sample

<table>
<thead>
<tr>
<th>Treatment time (minutes)</th>
<th>C (002)</th>
<th>2$\theta$</th>
<th>d</th>
<th>C (100)</th>
<th>2$\theta$</th>
<th>d</th>
<th>H-O (201)</th>
<th>2$\theta$</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2$\theta$</td>
<td>d</td>
<td></td>
<td>2$\theta$</td>
<td>d</td>
<td></td>
<td>2$\theta$</td>
<td>d</td>
</tr>
<tr>
<td>0</td>
<td>26.80</td>
<td>3.70</td>
<td>42.18</td>
<td>2.28</td>
<td>48.05</td>
<td>2.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>26.45</td>
<td>3.83</td>
<td>42.05</td>
<td>2.29</td>
<td>48.16</td>
<td>2.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>26.42</td>
<td>3.75</td>
<td>41.98</td>
<td>2.29</td>
<td>48.22</td>
<td>1.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>26.41</td>
<td>3.8</td>
<td>41.80</td>
<td>2.31</td>
<td>48.27</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>26.51</td>
<td>3.81</td>
<td>41.77</td>
<td>2.31</td>
<td>48.41</td>
<td>1.98</td>
<td></td>
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</tr>
</tbody>
</table>

Finally, it is concluded on the basis of XRD results that the plasma treatment distorted the graphitic crystalline nature of CNTs, structural disorders are induced and defects are created on CNTs surface. Some carbon bonds are broken away and interaction strength between different planes of carbon atoms is becoming weak, degree of crystallinity of CNTs is reduced, and defect density is increased as compared to the pristine CNTs.

6.4.7. Electrical Conductivity of CNTs

Electrical conductivity of carbon nanotubes is one of the most promising applications for industry [35, 142]. The electrical conductivity of plasma irradiated carbon nanotubes is investigated as function of temperature. The variation in resistance is measured by using
two probe method at different set of fixed applied voltage (10V, 20V, 50V). Measurements are made at four different positions on surface of each sample and the mean values are reported here. **Figure 6-9 (a)** shows that the electrical conductivity of CNTs is improved with the increase in the time duration of Ar–N₂ plasma. This increase in the electrical conductivity of CNTs is mainly arisen due to the change in the crystalline structure and disorder induced due to plasma irradiation. In untreated CNTs, electrons are emitted from the tips of tubes only. While in the treated CNTs, surface microstructure is reconstructed, and active sites for electron emission on the surface are increased. In such a case the electrons are generated from every available site of the surface.

Moreover, a decrease in the resistance is observed for all the plasma irritated and pristine samples with the increase in temperature as shown in **figure 6-9 (b)**. This dependence suggests the semiconducting behavior of CNTs which is due to joule heating (thermal effect) [142, 143]. A good agreements is obtained with the results of Ebbesen *et al.* [144] as a function of temperature. They reported the electrical conductivity in terms of resistance as function of temperature for different size of CNTs pellets. They reported that the electrical resistance is linearly increases with the decrease in temperature determined by two-probe and four-probe. The difference could also stem from the intermediate temperature range used by Ebbesen *et al.* (4-300K) to our results at comparatively higher temperature range. The submission of this work, is to report the enhancement of electrical conductivity with effect of Ar–N₂ discharge at low power measured by two-probe. In conclusion, the electrical conductivity of CNTs is significantly increased with the increase in treatment time, which in turn, is intimately correlated with the change in optical emission spectral characteristics of the plasma.
Figure 6-9 (a) Electrical conductivity of treated and pristine CNT’s (b) Resistance of untreated sample as function of temperature.

6.5. Conclusion

The plasma parameters have been investigated by OES and Langmuir probe in low pressure inductively coupled as function of discharge parameter such as rf power of 10-100 W, filling pressure of (0.02-0.04) mbar and different Ar contents (5-95 %) in N₂ discharge. Optical emission spectroscopy is used to estimate the nitrogen active species (N, N₂, and N₂⁺) and degree of dissociation of nitrogen molecule as a function of
discharge parameters. The nitrogen active species are estimated by using OES. Electron temperature, plasma potential, floating potential and electron number density are measured by using Langmuir probe. These results show that plasma composition with a mixture of 95% Ar and 5% N₂ at flow rate of 20sccm operating at filling pressure of 0.06mbar and rf power of 100W are best suited for material processing. This condition is best for the production of active species and processing of materials due to higher emission intensity of ions, higher dissociation fraction and stable plasma discharge conditions.

CNTs are then treated under the optimum conditions for different times (20-120min) in MaPE-ICP powered by 13.56MHz rf generator. Plasma treated CNTs are characterized by SEM, EDX, FTIR, XRD, Raman spectroscopy and two probe method. FTIR results shows that no nitrogen bond is present with the carbon and it is also confirmed by EDX showing that no nitrogen content are present on the surface of CNTs. Results of these characterizations revealed that there is not any trace of nitrogen detected in treated CNTs. But these nitrogen molecules transfer their excitation and vibrational energy into the substrate to cause structural disorder on the surface. It is observed from the XRD and Raman spectroscopy results that plasma treatment changed the microstructure of CNTs. Structural disorders are induced in bonding network of carbon and defect density is increased. It is predicted that active sites available on the CNTs surface are increased that cause to increase the electrical conductivity of the materials.

On the basis of these results, it is concluded that Ar-N₂ plasma treatment is an effective way to modify the microstructure, induced structural disorder and to increases electrical conductivity of CNTs. These plasmas may also lead to a transition from a crystalline phase to an amorphous structure of carbon nanotubes.
CHAPTER 7
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1. Introduction

This chapter summarizes the study of non-LTE He-Ar-N$_2$ and Ar-N$_2$ mixture plasmas. Optical emission spectroscopy (OES) and Langmuir probe are the two main diagnostics that have been used to investigate the plasma parameters. Effect of helium mixing on plasma parameters such as excitation temperature ($T_{exc}$), dissociation fraction and concentration of active species in ground electronic state keeping argon as trace gas has been observed. These plasma parameters are also studied in N$_2$ plasma with effect of argon as mixture gas and also as trace gas. Other plasma parameters such as EEPF, electron temperature, electron number density, plasma potential and floating potential obtained by Langmuir probe are also included in the thesis. Effect of Ar-N$_2$ plasma on the microstructural and other physical properties of CNTs will be concluded in this chapter.

7.2. Conclusions

In first experiment, trace rare gas optical emission spectroscopy is carried out to investigate the excitation temperature, degree of nitrogen dissociation and relative densities of active species [$N$] and [$N_2^+$] in helium admixed nitrogen plasma using Ar as an actinometer. The inductively coupled plasma is generated by rf power of 13.56MHz for different discharge parameters such as rf power of 50-150W, filling pressure of 0.2-0.5 mbar and He concentration (10-90%) in N$_2$ discharge The aim of this study is to determine experimentally the excitation temperature, concentration of active species in their ground electronic state and dissociation fraction of nitrogen molecule in He-N2-Ar plasma as a function of gas composition, filling pressure and rf power. To observe the effect of He on excitation temperature in nitrogen discharge, He concentration is varied from 10% to 90% in nitrogen discharge while Ar is kept as trace gas (4%). The excitation temperature is calculated by number of argon spectral lines using Boltzmann plot method. It is observed that the excitation temperature increases with the increase in rf power and helium fraction and decreases with the increase in fill pressure. The effect of He is also observed on the dissociation fraction and the relative density of active species...
([N],[N_2^+]) in their ground state. The degree of nitrogen dissociation and the relative density of [N] and [N_2^+] is found to increase with helium percentage. The degree of dissociation of nitrogen molecule is calculated by two methods: the actinometry method and line ratio method. The relative values of dissociation fraction obtained by these two methods are quite different but their trend is similar. These results suggest that helium can be a good choice for the generation of active species in nitrogen plasma.

In the second experiment, the plasma parameters and active species concentration have been investigated in low pressure inductively coupled plasma as a function of rf power (10-100 W), filling pressure (0.01-0.4 mbar) and argon content (5% to 95%) in nitrogen discharge. The electron temperature, electron number density, plasma potential, floating potential and EEPFs are measured using Langmuir probe. The electron temperature decreases whereas the electron number density increases with the increase in rf power, filling pressure and Ar content. By using optical emission spectroscopy, the excitation temperature, the emission intensity of nitrogen active species (N, N_2, and N_2^+), the concentration of nitrogen species in their ground electronic states ([N], [N_2]) and the dissociation fraction are estimated. The excitation temperature is obtained by Boltzmann plot using a cloud of argon spectral line. The excitation temperature is found to decrease with filling pressure and rf power. The concentration of active species (N, N_2) is obtained using actinometry method with Ar as trace gas (5%) in nitrogen discharge. The concentration of nitrogen species are found to increase with filling pressure and rf power. The dissociation fraction by using the atomic line N I (λ = 746.83 nm) to the molecular band head of nitrogen N_2 (λ = 337.10 nm) is given by for different discharge parameters. The dissociation fraction increases with the increase of Ar content at constant rf power and filling pressure that may be attributed to the increased number of energetic electrons in the discharge responsible for the dissociation as complimented by the measurement of EEPFs. The dissociation fraction first increases with filling pressure and reach to maximum value and then decrease suggesting the optimum filling pressure for dissociation. The value of optimum filling pressure move towards higher side with increase in Ar content (i.e. 0.06 mbar for 50% Ar and 0.08 mbar for 95% Ar) in the discharge suggesting higher optimum filling pressure for higher Ar content in the
discharge. It is found that active species concentration and excitation temperature have significant dependence on the discharge parameters. This study is carried out to optimize the Ar/N₂ plasma for the production of active species, which are considered to be important in material processing applications.

According to these results the plasma composition with a mixture of 95% Ar and 5% N₂ at flow rate of 20sccm operating at filling pressure of 0.06mbar and rf power of 100W are best suited for material processing. This condition is best for the production of active species and processing of materials due to higher emission intensity of ions, higher dissociation fraction and stable plasma discharge conditions.

In the third experiment, CNTs are treated under the optimum conditions for different times (20-120min) in MaPE-ICP powered by 13.56MHz rf generator. Plasma treated CNTs are characterized by SEM, EDX, FTIR, XRD, Raman spectroscopy and two probe method. FTIR results shows that no nitrogen bond is present between the carbon and the nitrogen molecules and it is also confirmed by EDX showing that no nitrogen content is present on the surface of CNTs. Results of these characterizations revealed that there is not any trace of nitrogen detected in treated CNTs. But these nitrogen molecules transfer their excitation and vibrational energy into the substrate to cause structural disorder on the surface. It is observed from the XRD and Raman spectroscopy results that plasma treatment changed the microstructure of CNTs. Structural disorders are induced in bonding network of carbon and defect density is increased. It is predicted that active sites available on the CNTs surface are increased that cause to increase the electrical conductivity of the materials. On the basis of these results, it is concluded that Ar-N₂ plasma treatment is an effective way to modify the microstructure, induce structural disorder and to increases electrical conductivity of CNTs. These plasmas may also lead to a transition from a crystalline phase to an amorphous structure of carbon nanotubes. It is also deduced from our results that, to reduce damages on the nanotubes structure, appropriate plasma parameters have to be used, i.e., low plasma power and short time treatments.
7.3. **Suggestion for Future Work**

The kinetics of the discharge and investigation of various plasma parameters in Inductively Coupled Ar-N\textsubscript{2} and Ar-He-N\textsubscript{2} plasma need to be further analyzed. The experimental data may be simulated to study the plasma chemistry. The properties of plasma processed CNTs (dielectric behavior, surface activation etc.) should be studied in detail. Nanotubes alignment is particularly important to enable both fundamental studies and applications, such as Flat Display Panels (FDPs). The plasma-based growth of highly oriented, multi-walled carbon nanotubes should be studied. The density functional calculations need to be studied theoretically to find most stable absorbed configuration.

Far from closing the thesis about diagnostics of plasmas and plasma processing of carbon nanotubes in the laboratory, this thesis is expected to be the starting point of new projects and collaborations. It offers new perspectives for the future in both fundamental and practical research on plasma diagnostics and plasma processing of carbon nanotubes. Also it can be suggested to use different gases other than argon and nitrogen during plasma processing of nanoparticles/carbon nanotubes. It may also be a start to the study of metal decorated nanotubes, to increase collaboration between theoreticians and experimentalists and to work on the elaboration of industrial applications.
References


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