

ÜMMÜGÜL ERÖZBEK - GÜNGÖR

METU 2014

**SURFACE MODIFICATION OF UNSIZED PAN-BASED
CARBON FIBER BY USING HIGH FREQUENCY SINGLE AND DUAL
RF DISCHARGE SYSTEM**

ÜMMÜGÜL ERÖZBEK-GÜNGÖR

FEBRUARY 2014

SURFACE MODIFICATION OF UNSIZED PAN-BASED CARBON FIBER BY
USING HIGH FREQUENCY SINGLE AND DUAL RF DISCHARGE SYSTEM

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ÜMMÜGÜL ERÖZBEK-GÜNGÖR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
IN
PHYSICS

FEBRUARY 2014

Approval of the thesis:

**SURFACE MODIFICATION OF UNSIZED PAN-BASED CARBON FIBER
BY USING HIGH FREQUENCY SINGLE AND DUAL RF DISCHARGE
SYSTEM**

submitted by **ÜMMÜGÜL ERÖZBEK-GÜNGÖR** in partial fulfillment of the requirements for the degree of **Doctor of Philosophy in Physics Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen _____
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Mehmet Tevfik Zeyrek _____
Head of Department, **Physics**

Prof. Dr. Sinan Kadri Bilikmen _____
Supervisor, **Physics Dept., METU**

Assoc. Prof. Dr. Demiral Akbar _____
Co-Supervisor, **Adv. Tech. Res. Center, Hacettepe University**

Examining Committee Members:

Prof. Dr. İbrahim Günel _____
Physics Dept., METU

Prof. Dr. Sinan Kadri Bilikmen _____
Physics Dept., METU

Assoc. Prof. Dr. Barış Bayram _____
Elec. Electr. Engineering Dept., METU

Assoc. Prof. Dr. Serhat Çakır _____
Physics Dept., METU

Assist. Prof. Dr. Kemal Efe Eseller _____
Elec. Electr. Engineering Dept., Atılım University

Date: February 2014

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last Name: Ümmügül ERÖZBEK-GÜNGÖR

Signature :

ABSTRACT

SURFACE MODIFICATION OF UNSIZED PAN - BASED CARBON FIBER BY USING HIGH FREQUENCY SINGLE AND DUAL RF DISCHARGE SYSTEM

ERÖZBEK-GÜNGÖR, Ümmügül

Ph.D., Department of Physics

Supervisor : Prof. Dr. Sinan K. BİLİKMEN

Co-Supervisor : Assoc. Prof. Dr. Demiral AKBAR

February 2014, 118 pages

The aim of this thesis is to examine the effects of HF-RF nitrogen plasma treatment on unsized PAN-based carbon fiber surfaces. The fibers were treated under different plasma processing conditions; exposure times, RF powers and gas pressures in a homemade RF-PECVD reactor having two modes; single “40.68 MHz” and dual “40.68 /2.1 MHz”. Then, Raman and FT-IR spectroscopies were used to analyze the structure and functional groups of the fibers, respectively. Also, tensile strain of the samples was tested with micromechanical analyzer. In addition, the plasma parameters were diagnosed by using single and double Langmuir probes.

In this thesis, the first-order Raman-band peaks “*D and G*” of the fibers were investigated to be aware of changes in order/disorder structure, crystallinity and strain. In single RF mode, at low pressures, the degree of disordered structure increases with HF-RF power and process time. However, at high pressures, 84.51 % - very high order structure “*crystallinity*” is observed. In dual RF mode, structural ordering effects are explicitly observed at all pressures, powers and treatment times. Moreover, plasma diagnostic results revealed that single RF mode has two transition

points. The first transition “ α - γ ” was seen at 0.3 Torr whereas the other one “ γ - α ” was observed at 0.3 Torr-150 Watt. And, according to strain analysis, the fibers were generally more strengthened after γ -mode plasma treatments while they were more weakened with α -mode plasma treatments. Lastly, FT-IR spectroscopy results showed that the chemical structure of the treated carbon fibers was changed due to plasma treatment conditions.

Keywords: PAN-based Carbon Fiber Nitrogen RF-CCP Treatment, Raman Spectroscopy, FT-IR Spectroscopy, Strain Measurement, Plasma Diagnostic

ÖZ

EPOKSİ İLE KAPLANMAMIŞ PAN-TABANLI KARBON ELYAF YÜZEYLERİN YÜKSEK FREKANSLI TEK VE ÇİFT RF BOŞALTMA SİSTEMİ İLE MODİFİKASYONU

ERÖZBEK-GÜNGÖR, Ümmügül

Doktora, Fizik Bölümü

Tez Yöneticisi : Prof. Dr. Sinan K. BİLİKMEN

Ortak Tez Yöneticisi : Doç. Dr. Demiral AKBAR

Şubat 2014, 118 sayfa

Bu tezin amacı, yüksek frekanslı radyo dalgası ile üretilen azot plazmasının, epoksi ile kaplanmamış PAN-tabanlı karbon elyaf yüzeylere etkilerini incelemektir. Elyaf, tek “40.68 MHz” ve çift “40.68 / 2.1 MHz” olmak üzere iki moda sahip olan, ev yapımı bir RF-PECVD reaktör içinde, farklı plazma koşullarında “*maruz kalma süresi, RF güçleri ve gaz basınçları*” işlendi. Daha sonra, Raman ve FT-IR spektrometreleri, sırasıyla elyafın yapılarını ve içindeki fonksiyonel grupları analiz etmek için kullanıldı. Ayrıca, örneklerin çekme gerilimleri ise mikromekanik analizörü ile test edildi. Ek olarak, plazma parametreleri, tek ve çift Langmuir sonda tekniği kullanılarak saptandı.

Bu tezde, elyafın birinci dereceden Raman-bant zirveleri, düzen/düzensizlik yapıları, kristallilik ve gerginliklerdeki değişimleri fark etmek için incelendi. Tek RF modunda, düşük basınçlarda, düzensizlik yapısının derecesi, HF-RF güç ve işleme zamanı ile artar. Fakat yüksek basınçlarda, 84.51 % derecesinde çok yüksek

düzenlilik yapısı “*kristallilik*” gözlenir. Çift RF modunda, yapısal düzenlilik etkileri her basınç, güç ve işleme zamanında açıkça görülür. Ayrıca, Raman zirve konumları, her RF mod işlemlerinden sonra kaydı. Buna ek olarak, plazma tanı sonuçları, tek RF modunun iki tane geçiş noktasına sahip olduğunu açığa çıkardı. İlk geçiş “ $\alpha\text{-}\gamma$ ”, 0.3 Torr’da görülürken, diğeri ise 0.3 Torr-150 Watt’da gözlemlendi. Ve, gerilme analizlerine göre, elyaflar, genellikle γ -mod plazma işlemlerinden sonra daha güçlenirken; α -mod plazma işlemleri ile daha zayıfladı. Son olarak, FT-IR sonuçları, işlenen fiberlerin kimyasal yapılarının plazma koşullarından dolayı değiştiğini göstermektedir.

Anahtar Kelimeler: PAN-tabanlı Karbon Elyaf Radyo Frekanslı Kapasitif Etkileşmesiyle Azot Plazma İşlemi, Raman Spektrometresi, FT-IR Spektrometre, Gerilme Ölçümü, Plazma Tanısı

...To My Darling and My Sweet Baby

ACKNOWLEDGEMENTS

I would like to thank my supervisor Prof. Dr. Sinan K. BİLİKMEN and co-supervisor Assoc. Dr. Demiral AKBAR for their guidance and supports throughout the research.

I would also like to thank Prof. Dr. Erdal BAYRAMLI because of providing carbon fiber samples.

Also, I appreciate to UNAM in Bilkent University for usage of their experimental devices; confocal Raman spectroscopy and Instron micromechanical tester. And, I would like to thank Mr. Hüseyin Avni VURAL for his assistance during my Raman studies and Mrs. Gökçe ÇELİK for her close attention and assistance during Instron mechanical studies.

My special thank go to my lovely husband; Özgür GÜNGÖR, for his confidence, supports, pains, endless love and patience.

TABLE OF CONTENTS

ABSTRACT	v
ÖZ	vii
ACKNOWLEDGEMENTS	x
TABLE OF CONTENTS	xi
LIST OF FIGURES	xiii
LIST OF TABLES	xvii
LIST OF ABBREVIATIONS	xviii
CHAPTERS	1
1. INTRODUCTION	1
2. BACKGROUND	5
2.1 Plasma	5
2.1.1 Direct Current (DC) Glow Discharges.....	6
2.1.2 Radio-Frequency (RF) Discharges.....	10
2.1.2.1 Capacitively Coupled RF Plasma (RF-CCP)	11
2.1.2.1.1 Electron Heating Modes of RF-CCP.....	13
2.2 Langmuir Probe Theory	16
2.3 Carbon Fiber	30
2.3.1 PAN-Based Carbon Fiber	33
2.4 Some Analysis Techniques of Carbon Fiber	37
2.4.1 Raman Spectroscopy	37
2.4.1.1 Raman Bands of Carbon Fiber	42
2.4.2 Fourier Transform Infrared (FT-IR) Spectroscopy	45

3. THE EXPERIMENTAL SET-UP	49
3.1 Single and Dual RF-CCP Discharge System	49
3.2 Plasma Diagnostics	55
4. RESULTS AND DISCUSSION.....	75
5. CONCLUSION	103
REFERENCES.....	105
CURRICULUM VITAE	114

LIST OF FIGURES

FIGURES

Figure 1. The experimental set-up of DC plasma generation [13].....	7
Figure 2. VCC of the DC low pressure electrical discharge [13]	8
Figure 3. Schema of (a) single and (b) dual RF-CCP	12
Figure 4. Photos of 40.68 MHz RF-CCPs that are generated under different operational conditions (a) 0.2 Torr - 50 Watt and (b) 0.5 Torr - 50 Watt.....	16
Figure 5. A typical plasma current-probe voltage characteristic graph of a Langmuir cylindrical probe.....	18
Figure 6. Schematic diagram of an RF-compensated single Langmuir probe [26] ...	19
Figure 7. Schematic diagram of an identical double Langmuir DC probe [90].....	27
Figure 8. A CVC sample obtained with Langmuir double probe	28
Figure 9. Schematic of Lattice structure of a single graphite crystal [34]	31
Figure 10. Schematic of PAN-based carbon fiber lied along the fiber axis [37]	32
Figure 11. Structure of a turbostratic carbon fiber [38]	34
Figure 12. Flow chart of a typical PAN-based carbon fiber production process with showing mechanical properties of the fibers in each steps [41].....	35
Figure 13. Molecular orbital distortion after being exposed to electric field [45]	38
Figure 14. Diagrams showing (a) frequency and (b) energy levels of Rayleigh “ <i>elastic</i> ” and Raman “ <i>inelastic</i> ” scatterings [48].....	39
Figure 15. Schematic diagram showing the working mechanism of a simple Fourier Transform Infrared Spectroscopy [66].....	46
Figure 16. Schematic diagrams of (a) single and (b) dual modes of capacitively coupled high frequency RF-PECVD reactors.	49
Figure 17. Picture of our RF-PECVD reactor	50
Figure 18. Picture of the SEREN R01 model RF power supply [70]	52

Figure 19. Pictures of SEREN AT-Series matching network with MC2 controller [72]	52
Figure 20. Basic configuration of matching network system [71]	53
Figure 21. Picture showing the inside of SEREN AT-6 matching network system ..	54
Figure 22. The experimental diagrams showing HF single RF-CCP diagnostic of a) single and b) double Impedans Langmuir probe systems.	55
Figure 23. Photos of Impedans Langmuir (a) double probe and (b) single probe	56
Figure 24. Dimensions of Impedans Langmuir double probe [28]	57
Figure 25. Impedans ALP System TM controller	58
Figure 26. Impedans ALP software program	59
Figure 27. Plasma process setting parameters for single probe RF plasma diagnostic	60
Figure 28. Configure parameter panel for single probe RF plasma diagnostic.....	61
Figure 29. An example of CVC curve of the discharge obtained by Impedans Langmuir single probe system	62
Figure 30. The CVC curve, first and second derivatives of the CVC of the discharge obtained by Impedans Langmuir single probe system	62
Figure 31. Electron energy distribution function versus energy graph of the discharge obtained by Impedans Langmuir single probe system	63
Figure 32. An example of CVC curve of RF discharge obtained by Impedans Langmuir double probe system	64
Figure 33. Pictures of PAN-based carbon fibers manufactured by AKSACA TM [73]	65
Figure 34. Production processes of AKSACA TM PAN-based carbon fibers and its precursor.....	66
Figure 35. Picture of WITec Alpha300 S [75]	67
Figure 36. Diagram of WITec confocal Raman microscopy [76].....	68
Figure 37. Raman spectrum of carbon fiber taken by WITec software	69

Figure 38. An example of Lorentzian multiple-peak fitted Raman spectra of a treated carbon fiber with its parameter results. Treatment conditions: single RF-N ₂ discharge, 1 Torr, 200 Watt, 90 min	71
Figure 39. Photo of FT-IR spectroscopy system.....	72
Figure 40. Photos of Instron micromechanical analyzer.....	73
Figure 41. Schematic of cardboard designed for a single carbon filament tensile strain testing	73
Figure 42. Force-extension graph and analysis results of untreated “as-received” carbon filament that are obtained by the use of Instron testing machine	74
Figure 43. Electron current density square “ Je^2 ” as a function of the gas pressure in the HF single RF mode	76
Figure 44. Electron current density square “ Je^2 ” as a function of the HF-RF power in the single RF mode at $p = 0.3$ Torr	76
Figure 45. Nitrogen gas pressure dependence of a) density and temperature of electron and b) ion density in the bulk plasma at $P = 150$ Watt	78
Figure 46. HF-RF power dependence of a) density and temperature of electron and b) ion density in the bulk plasma at $p = 0.3$ Torr	80
Figure 47. (a) Pressure and low HF-RF power dependence of ion density in a single RF plasma that measured by double probe and (b) pressure and high HF-RF power dependence of ion density in single RF plasma that measured by a double probe	81
Figure 48. (a) Pressure and low HF-RF power dependence of energy of electrons in a single RF plasma that measured by a double probe and (b) pressure and high HF-RF power dependence of energy of electrons in a single RF plasma that measured by a double probe.....	82
Figure 49. Effects of applied N ₂ pressure and HF-RF power on the order/disorder structure of the carbon fibers treated under different treatment times; (a) 30 min, (b) 60 min and (c) 90 min	83
Figure 50. Effects of HF-RF power and treatment time on the order/disorder structure of the carbon fibers treated under different applied N ₂ pressures; (a) 0.3 Torr, (b) 0.5 Torr, (c) 0.75 Torr and (d) 1 Torr.....	84

Figure 51. Effects of applied N ₂ pressure and treatment time on the order/disorder structure of the carbon fibers treated under different HF-RF powers; (a) 50 Watt, (b) 100 Watt, (c) 150 Watt and (d) 200 Watt.....	86
Figure 52. Effects of applied N ₂ pressure and LF-RF power on the disordered/ordered structure of the carbon fibers treated under different treatment times; (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min	88
Figure 53. Effects of LF-RF power and treatment time on the disordered/ordered structure of the carbon fibers treated under different applied N ₂ pressures; (a) 0.1 Torr, (b) 0.3 Torr, (c) 0.5 Torr, (d) 0.75 Torr and (e) 0.9 Torr	90
Figure 54. Effects of applied N ₂ pressure and treatment time on disordered/ordered structure of the carbon fibers treated under different LF-RF powers; (a) 50 Watt, (b) 100 Watt, (c) 150 Watt and (d) 200 Watt.....	91
Figure 55. A chart showing tensile strain value of the samples listed in the Table 5	96
Figure 56. The relation between peak locations of the a) D and b) G bands and tensile strain of the carbon fiber filaments listed in the Table 5	98
Figure 57. FT-IR spectrum of untreated unsized PAN-based carbon fiber	101

LIST OF TABLES

TABLES

Table 1. Experimental parameters of RF plasma treatment process.....	51
Table 2. Mechanical properties of A - 42 model 12K PAN-based carbon fibers that used in the experiments [74]	65
Table 3. RF plasma treatment processing conditions of HS unsized PAN-based carbon fibers.....	93
Table 4. Lorentz-fitted parameters of D and G Raman bands of untreated (as-received) and treated fibers listed in the Table 3.	94
Table 5. Treatment conditions of the samples, which tensile strain were tested	96
Table 6. FT-IR results of untreated and some treated carbon fibers.....	100

LIST OF ABBREVIATIONS

AC	: Alternating current
AFM	: Atomic force microscopy
AN	: Acrylonitrile
CCD	: Charge-coupled device
CCP	: Capacitively coupled plasma
CVC	: Current-voltage characteristic
DC	: Direct current
D-RF	: Dual radio frequency
ECR	: Electron cyclotron resonance
EEDF	: Electron energy distribution function
FT-IR	: Fourier-transform infrared
HF	: High frequency
HS	: High strength
IC	: Inductively coupled
IPS	: Industrial power systems

IR : Infrared

ISO : International organization for standardization

LF : Low frequency

LTE : Local thermal equilibrium

PAN : Polyacrylonitrile

PECVD : Plasma enhanced chemical vapor deposition

RF : Radio frequency

SEM : Scanning electron microscopy

S-RF : Single radio frequency

SW : Surface wave

TM : Trademark

UHTS : Ultra-high throughput spectroscopy

VCC : Voltage-current characteristic

XPS : X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION

In the last couple of decades, the radio-frequency “RF” plasmas are taking an indispensable role in industrial areas for materials processing [1]. The most popular applications in semiconductor manufacturing are etching “*removing material from the surface*”, surface modification “*existence of changes on the surface*”, cleaning “*removing all possible undesired residues*”, ashing “*removing organic fragments from inorganic surfaces*”, and surface hardening “*hardening the surface layer, without affecting the bulk properties of the material*”. Among these applications, plasma surface modification is commonly used in carbon fiber technologies [2]. In fact; there are four surface modification techniques that are mechanical, combustion, chemical and plasma. It is impossible to use mechanical and combustion techniques in carbon fiber treatment process because of having diameter of a few micrometers. Moreover, popularity of the chemical treatment is gradually getting lost due to environmental pollution problems. On the other hand, in addition to environmental and economic benefits, protection of bulk mechanical properties of the carbon fiber is also possible with the use of plasma treatment [3]. Therefore; the most suitable surface modification technique used in the carbon fiber technology is “*plasma treatment*”.

Plasma treatment is a process that structure and surface of materials are modified after being exposed to an electric discharge. The surface of the materials is mostly bombarded with ions in the discharge. Hence, ion density and also ion energy are two important parameters in materials processing. The discharge can be generated by using a DC or RF generator. Because of supplying more dense and energetic

particles, the RF discharge is commonly preferred for plasma treatment of carbon fibers. Moreover, nowadays, popularity of dual RF capacitively coupled plasma is increasing in materials processing. The main reason of this is controlling ion flux and ion bombardment energy independently [4]. In dual RF-CCP design, one electrode is connected to the HF-RF source that is responsible for controlling power deposited into the bulk plasma and the other one is connected to the LF-RF source which is responsible for controlling energy transfer to the ions [5]. Furthermore, crystalline structure and properties of the carbon fibers can be improved with the use of plasma treatment according to sectorial needs. Two well-known sectors that use carbon fibers are: high technology “*aerospace, nuclear and general engineering*” and transportation “*automobile bodies, bearings, gears, cams and fan blades*”. Mechanical property improvement is desired by high technology sector [6]. In fact, there is a very close relationship between crystalline structure “*graphitization-ordering, crystallinity and in-plane crystallite size (L_a)*” and mechanical property “*tensile strain, fiber modulus and stress*” of the carbon fibers. To have high qualified carbon fibers, ordering structure thereby L_a should be controlled [7]. In a plasma treatment process, this can be possible with the knowledge of convenient experimental conditions “*pressure, power and time*” that is strongly related to the change in crystalline structure and properties of the fibers. Additionally, appropriate treatment conditions can be determined by using plasma diagnostic techniques. Among many techniques, Langmuir probe is commonly used for this purpose because of being the most simplest and the cheapest one. It is basically composed of a conducting tungsten wire tip that is inserted in the generated plasma between the electrodes. When a variable voltage is applied to the probe, it collects plasma current data and the behavior of this current with respect to the applied voltages is known as current-voltage characteristic of the plasma. All plasma parameters are calculated from to this curve. To get better experimental calculations, it is important to eliminate or minimize the RF noises signals from the CCP reactor by using compensation circuits.

After the treatment process, structural changes of carbon fibers are usually analyzed by using Raman and FT-IR spectroscopies and property analysis is mostly done with a mechanical tester. Raman spectroscopy is mainly used for ordering/disordering analysis in crystalline structure and for calculating the crystallite size of carbon fibers by interpreting spectrum of inelastic scattered lights coming from the samples. In the carbon fiber spectrums, two Raman peaks “*D-diamond and G-graphite*” are observed and crystallite size of the fibers is calculated by intensity ratio of these peaks. Also, there exists a relation between peak shift of these bands and tensile strain of the fibers that can be tested with a mechanical tester. On the other hand, analysis of chemical functional groups in the treated fibers is made by using FT-IR spectroscopy according to transmitted or absorbed lights from the samples.

When going through all scientific journals, there exist only few studies about single LF “*13.56 MHz*” plasma treatment on carbon fibers surfaces. In addition, there is no study concerning deeper investigation of the effect of plasma treatment conditions on crystalline structure and properties of carbon fibers. The previous studies were exclusively done by changing one experimental parameter or not to observe crystalline structure and changes in carbon fiber’s properties. For example, one of the study is about the effect of 13.56 MHz RF inductively coupled “*high density*” discharge on crystalline structure and properties of carbon fibers at constant pressure “*p = 0.3 Torr*” and power “*P = 14.4 Watt*” under different treatment time “*t = 10, 20 min for argon discharge and t = 2, 5, 10 min for oxygen discharge*” [8]. The other one is related to be modified surface of carbon fibers treated by using 13.56 MHz RF oxygen and ammonia capacitively coupled plasma “*CCP*” under constant pressure “*p = 0.374 Torr for oxygen discharge and p = 0.18 Torr for ammonia discharge*” and power “*P=50 Watt*” and the variable parameter in this study was only treatment time “*t = 1, 3, 5, 10, 20 min*” [9].

There are three main objectives of this thesis. The first objective is comparing the effect of single HF “*40.68 MHz*” RF-CCP on carbon fibers structure and property with that of single LF “*13.56 MHz*” RF-CCP. The second one is to learn what would

happen to the structure of carbon fibers if they are treated with a dual “40.68/2.1 MHz” HF RF-CCP. The last one is to understand the physical mechanism of plasma treatment processes. For this purpose, a homemade RF-PECVD reactor was used to modify the surfaces of unsized high strength PAN-based carbon fibers. After the treatment process, structural changes were analyzed by WITec Confocal Raman Microscopy, mechanical changes were tested with Instron Mechanical Analyzer and chemical functional group analysis was done by using Bruker FT-IR spectroscopy. In addition, plasma parameters were measured by use of a single and a double Langmuir probes.

CHAPTER 2

BACKGROUND

2.1 Plasma

Plasma, the fourth state of matter, is a quasi-neutral ionized gas. With increasing temperature of a gas medium, particles gain more energy and start to move more freely in random directions. At some definite high temperature, insulation breaks down and the medium becomes conductive and so plasma is generated. The generated plasma consists of positive “*ion*” and negative “*electron*” charges and also neutral species.

The plasmas used in experimental studies are mainly called “*high temperature (fusion) plasmas*” and “*low temperature (soft) plasmas*” or “*gas discharges*” [10]. Between these two plasmas, gas discharges have many applications in microelectronic field and material surface processing such as etching, deposition, surface modification and surface treatment.

The gas discharges can be also defined as “*local thermal equilibrium (LTE) plasmas*” or “*non-thermal equilibrium (non-LTE or cold) plasmas*”. When temperatures of all particles in local mediums are the same, plasma “*arc plasma, plasma torches, inductively coupled RF discharges*” is called as “*LTE*”. If the temperatures of all species are different, then the plasma “*glow, corona, capacitively coupled RF discharges, atmospheric pressure plasma jet and so on*” will be called as “*non-LTE plasma*”. In general, scientists prefer to use non-thermal equilibrium plasmas for applications in which heat is unnecessary. In this type of plasmas,

electrons have higher temperature than heavy particles “*ions, atoms and metastable particles*” [11]. The reason of this is that electrons can move easily by the means of their small masses. In fact, this difference in temperatures is resulted in unsatisfied energy coupling between electrons and heavy species [10]. Among heavy particles; on the other hand, interactions are strong. As a result of this, bombarding energy of the heavy particles is much higher than that of electrons. By the way, only the heavy particles are responsible for bombarding surfaces of substrates.

There are many RF plasma generating schemes: capacitively coupled “*CC*”, inductively coupled “*IC*”, helicon, microwaves, electron cyclotron resonance “*ECR*” and surface wave “*SW*” [12]. Among these schemes, “*capacitively coupled*” and “*inductively coupled*” are two well-known RF plasma systems used for decades in industrial fields that are electronics, aerospace, automotive and biomedical. And, the capacitively coupled one is commonly used in microelectronic industry and material technology for surface modification processes.

Experimentally, there are two basic plasma sources called “*direct current (DC)*” and “*Radio - frequency (RF)*”.

2.1.1 Direct Current (DC) Glow Discharges

Direct current is a current that flows in one direction with a constant value. Low temperature “*gas*” discharges can be generated and sustained by a DC source. In this type of experimental set-up, there exist two conductive electrodes called cathode (-) and anode (+) that are immersed into a low-pressure neutral gas in a chamber and these two electrodes are connected to a DC plasma source as shown in Figure 1 [13].

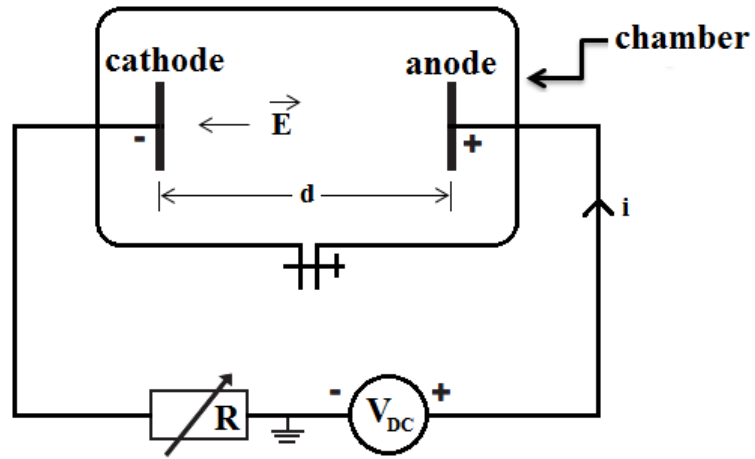


Figure 1. The experimental set-up of DC plasma generation [13]

To understand the physical mechanism of DC discharge, firstly, we should examine its voltage-current characteristic “VCC” curve profile as shown in Figure 2. This curve profile can be slightly changed according to the value of resistance that is located in the circuit in the Figure 1 [14].

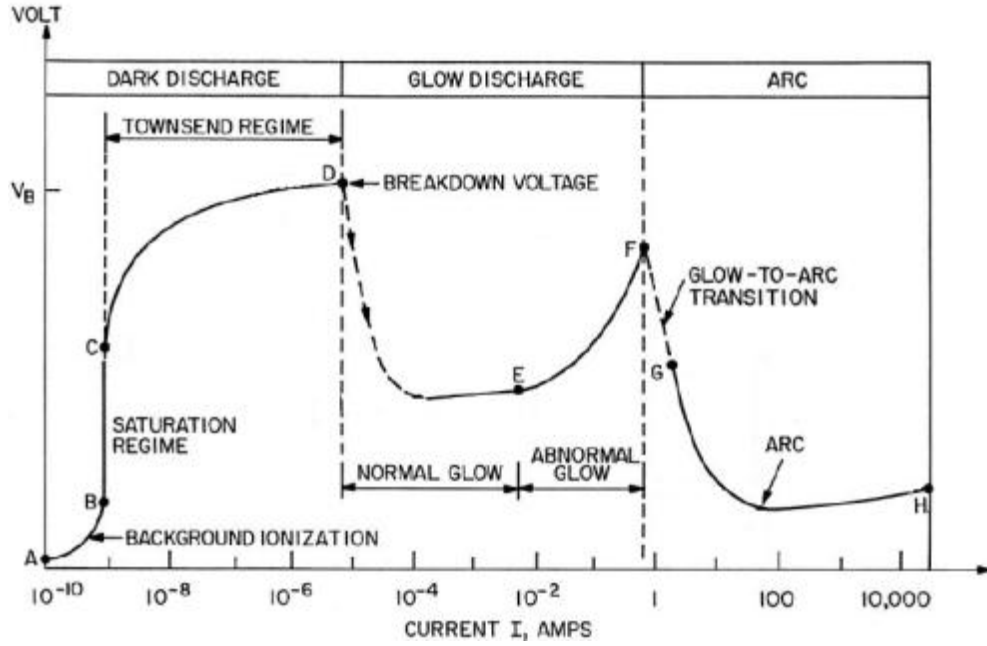


Figure 2. VCC of the DC low pressure electrical discharge [13]

As shown in the Figure 2, the curve is divided into seven main parts; A-B, B-C, C-D, D-E, E-F, F-G and G-H [13].

In A-B “Background Ionization” Region:

In fact, there exist some free electrons and ions that emitted by cathode electrode as a result of omnipresent cosmic and radioactive radiation interaction with the feed gas [10, 16]. However, these particles do not sustain the plasma. As soon as applying potential difference between the electrodes, the electrons are accelerated by an external electric field towards the anode that is resulted in a weak electric current [13].

In B-C “Saturation Regime” Region:

As the electric field strength is increased, more electrons can move toward to the anode electrode and then the electric current increases. When all electrons that are

emitted from the cathode electrode are attracted by the anode, the value of current increases more and then becomes almost constant [13].

In C-D “Townsend Regime” Region:

The strength of the generated E-field increases more by increasing applied voltage. As a result of this, the electrons gain sufficient kinetic energy to ionize neutral atoms or molecules by electron impact. Therefore, they pull away electrons from the molecules by leaving positive ions there. The number of negative ions and the positive ions increases between the electrodes. The positive ions have large mass and they move slowly; on the other hand, electrons with small mass move faster and reach to anode in a short typical time. This motion in the gap can be seen as an avalanche from the further. Hence, this phenomenon is known as “*Avalanche*”. Moreover, an exponential increase in the electric current is seen in this region. If the voltage is higher than the critical breakdown voltage “ V_B ”, the discharge is generated in the gap [13].

In D-E “Normal Glow” Region:

By increasing voltage over the V_B , a cathode fall region that has higher electric field strength is created near the cathode electrode due to positive space charges. This high electric field increases electron multiplication that causes a voltage drop by increasing the current. As a result of a further increase in current, the generated discharge expands over the surface of the electrodes. Then, voltage drop stops and it becomes almost constant [13].

In E-F “Abnormal Glow” Region:

After the electrodes are completely covered by the discharge, high increase in current is resulted in a sharp increase in voltage [13].

In F-G “Glow to Arc Transition” Region:

This region is observed in VCC as shown in the Figure 2 because of low internal resistance of the DC power supply.

In G-H “Arc” Region:

With higher electric current, the discharge becomes brighter that is called as “Arc” and the voltage drops again [14].

2.1.2 Radio-Frequency (RF) Discharges

Radio frequency is a time-varying alternating current “AC” that changes its direction and its value periodically and the plasmas generated by AC are called “*RF discharges*” or “*RF plasmas*”. In RF discharge generation process, there are many operation conditions, however, the most important and significant parameters are the power and the gas [15]. For low-pressure systems, it is better to use high frequency to obtain more efficient RF discharge [10]. Because, when we use high frequency voltage, particles gain more energy to increase productivity of new electrons and ions. In addition, high frequency means low period of time. Therefore, sign of the AC voltage and also electrodes change more rapidly. When the sign of the electrode becomes negative, created ions accelerate toward this electrode with high energy and this motion continuous during every period of time. To have more efficient collision with the electrode, it is convenient to decrease distance between the electrodes. By this way, more ions with high energy can strike to negative electrode in a short time.

There are some advantages of using RF source to generate plasma as compared to the DC source. The first advantage is obtaining an additional electric field. We have only a static electric field accelerating the particles when we use a DC source. With RF source, on the other hand, we have a static electric field and an induced electric field that is generated by magnetic field. By this external electric field, particles move faster and discharge takes place more easily. The second advantage is; Generated RF

electrical current flows along the conductor surface whereas DC current moves along the middle of the electrodes [10]. This means that particles in RF plasma can easily interact with the electrodes or with the samples located on the electrodes. Hence, RF source is more preferred technique in material processing applications. The last advantage is that both electrodes act as cathode or anode in sequence when a RF source is used in plasma production. This change in polarity prevents charging of the electrodes because of accumulation. Therefore, we can say that this is an essential property for material processing applications. The reason is that we have to place an insulating piece of material on one of the electrodes to analyze the effects of plasma on it. However, to sustain DC discharge plasma, we have to use two conductive electrodes. Because insulating medium in this plasma does not allow charges to move freely. As a result, both positive and negative charges accumulate on this region to cause disappearance of the discharge [10].

2.1.2.1 Capacitively Coupled RF Plasma (RF-CCP)

In the simplest experimental design of capacitively coupled plasmas “CCPs”, there are two parallel metal plate electrodes separated by a small distance in a reactor chamber filled with an inert gas “*O₂, N₂, Argon or their mixture*”.

When one applies RF voltage between the electrodes, an oscillating electric field is generated. In addition, the gaseous atoms are immediately ionized and create new electrons in the region. The generated electrons are accelerated by the means of RF electric field. During this movement, the electrons collide with gas atoms elastically and inelastically that cause new electron and ion generations. When the electric field become stronger, much more new electrons that look like an “*electron avalanche*” are generated and the region becomes conductive. Some of the electrons and ions escape from the plasma and move toward the solid body “*chamber wall or electrode*”. The electrons are faster than the ions because of their light masses. Then, they can reach the solid body “*chamber wall*” earlier. As soon as arriving, they start

to pull the ions toward solid body whereas they push the other electrons toward the bulk plasma. By this way, the bulk plasma becomes approximately neutral “*quasi - neutral*” and the region close to the solid body having more ions called “*dark space* (sheath)” [16, 17].

It is possible to generate capacitively coupled plasma by using two different experimental configurations that are “*single RF plasma*” and “*dual (double) RF plasma*” as shown in Figure 3.

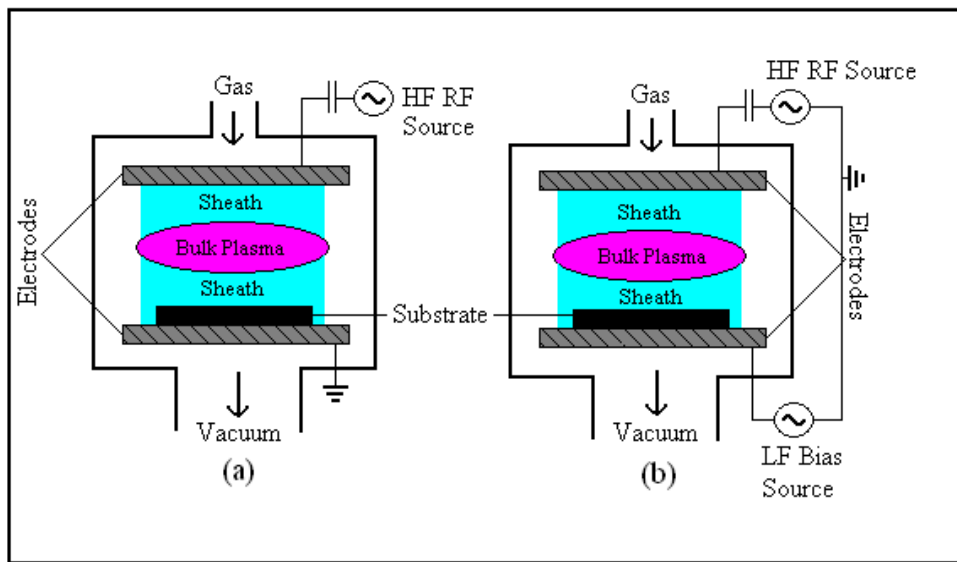


Figure 3. Schema of (a) single and (b) dual RF-CCP

The main parts of the experimental set-ups are the same for both plasma-generating systems. The only difference in configurations is that both electrodes are connected to the RF source. In the single RF capacitively coupled systems, one electrode is connected to the RF source and the other one is connected to the ground. On the other hand, in dual RF systems, both electrodes are connected to the RF sources and also both are grounded. One electrode is connected to the low frequency “*in our case 2.1 MHz*” RF source as a bias and the other is connected to the high frequency

“40.68 MHz” RF source. High frequency controls plasma density and low frequency controls ion motion and sheath drop [18].

2.1.2.1.1 Electron Heating Modes of RF-CCP

For plasma material processing applications, understanding of weakly ionized low-pressure discharge mechanism especially electron heating “*burning*” modes and their transition between them in RF-CCP is becoming very essential [19] due to supplying higher growth and etch rate, less micro loading effect and better uniformity of a-Si:H film deposition [20]. The two well-known burning modes are α -mode “*collisionless or Stochasting*” and γ - mode “*collisional or Ohmic*”. The reason of Stochasting electron heating is momentum transfer from high voltage moving sheaths to the electrons in the plasma while the reason behind collisional electron heating is electron-neutral collisions [21]. If EEDF of the generated plasma is Maxwellian, collisionless and collisional heating time-averaged power per unit area in RF discharges can be calculated according to following formulas [1];

$$\bar{S}_{ohmic} = \frac{1}{2} J^2 \frac{m_e \vartheta_m d}{e^2 n_e} \approx 1.73 \frac{m_e n_s}{2e n_o} \epsilon_o \omega^2 \vartheta_m T_e^{\frac{1}{2}} V^{\frac{1}{2}} d \quad \text{when } \lambda_i \geq \left(\frac{T_i}{T_e} \right) d \quad (1)$$

$$\bar{S}_{stoc} = \frac{1}{2} J^2 \frac{m_e \bar{\vartheta}_e d}{e^2 n_e} \approx 0.45 \left(\frac{m_e}{e} \right)^{\frac{1}{2}} \epsilon_o \omega^2 T_e^{\frac{1}{2}} V \quad \text{when } \omega s_m \leq \bar{\vartheta}_e \quad (2)$$

where;

J = the real part of the RF conduction current density “ $J \sim J_e$ electron conduction current”

m_e = electron mass

e = electron charge

n_e = electron density

ϵ_0 = permittivity constant of free space

ω = RF frequency

T_e = effective electron temperature

T_i = ion temperature

λ_i = ion mean free path

V = fundamental RF voltage across a single sheath

ϑ_m = collision frequency of electron with neutral particles that is proportional to gas pressure

$\overline{v_e}$ = average speed of electron that is equal to $\left(\frac{8kT_e}{\pi m_e}\right)^{\frac{1}{2}}$

d = the bulk plasma thickness that is equal to $l - 2s_m$ where l is distance between the electrodes and s_m is the sheath thickness.

As seen from the Eqs. 1 and 2, electron Ohmic heating density is directly proportional to gas pressure because of ϑ_m while there is no relation between gas pressure and electron Stochastic heating phenomena. Therefore, α - γ transition is seen with increasing the gas pressure in RF discharge. Also, from the Eqs. 1 and 2, it can be inferred that RF voltage dependence of Stochastic heating power density is significantly higher than that of Ohmic heating power density. Because of that reason, another transition from γ - mode to α - mode “ γ - α transition” is seen with increasing RF voltage “ V_{RF} ” or RF power “ P_{RF} ” [21].

In addition, both electron heating modes have their own specific discharge characteristics that are the important criteria to be preferred to use in different kind of processing applications. For example, as compared to the α - mode, the electron multiplication phenomena that increases plasma density significantly is observed with the existence of higher electric field strength in smaller electrode sheath region

in the γ - mode. Therefore, the more energetic discharge in the γ - mode is more proper to use in etching applications while α - mode is more convenient for sputtering applications because of having high discharge stability and uniformity in excited species production. Moreover, there is a strong relationship between mode characteristics and plasma processing conditions. For instance, at moderate gas pressures, electron temperature " T_e " in γ - mode bulk discharges is as high as the temperature in α -mode bulk discharges. On the other hand, at low pressures, T_e in γ - mode bulk discharges is very low as compared to that one in α -mode discharge as a result of secondary electron emission process. Additionally, in the γ - mode, the density of plasma is higher than that in the α -mode because of high electron multiplication in the sheath region [22]. Therefore, the α - γ mode transition can be determined by analyzing T_e or density profiles of the bulk discharge from the inverse relation between electron temperature and the plasma density [23]. Furthermore, it is possible to detect the transition point by just looking to the bulk discharge that turns to be more brightened and an increase in the number of produced excited neutral particles [22]. From Figure 4, we can determine how the color of the glow discharges plasma change by changing the gas pressure.

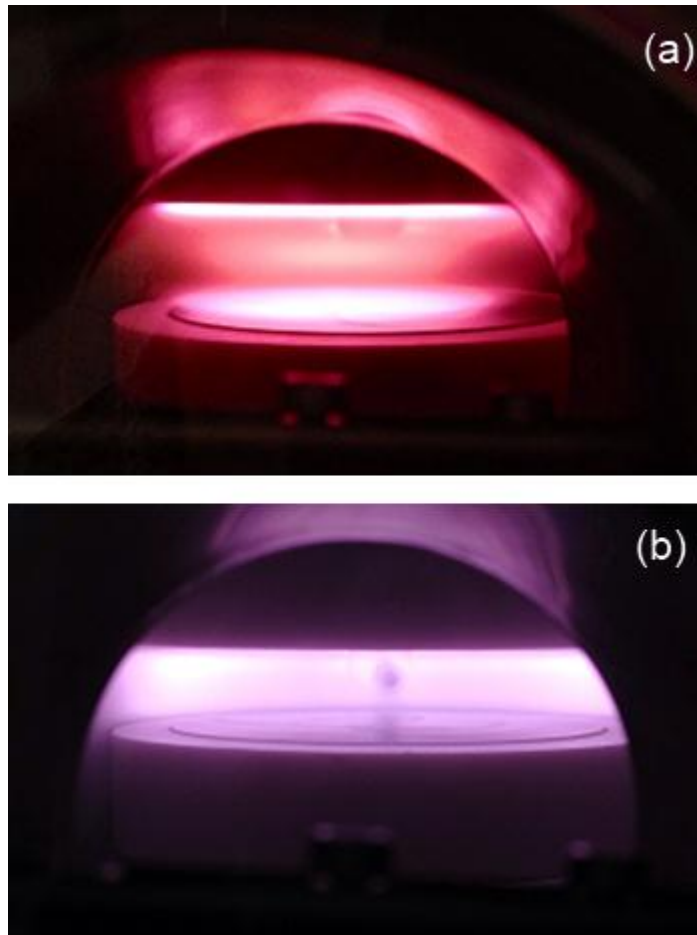


Figure 4. Photos of 40.68 MHz RF-CCPs that are generated under different operational conditions (a) 0.2 Torr - 50 Watt and (b) 0.5 Torr - 50 Watt

2.2 Langmuir Probe Theory

Among many plasma diagnostic techniques, the Langmuir cold probe is the simplest, least expensive and the easiest technique to handle [24]. Basically, it is composed of a metal conductor to measure the electron temperature or energy, electron density, ion density, plasma potential, floating potential and electron energy distribution function. A short piece of the conductor “*especially tungsten*” tip is exposed to the plasma; the other part remaining is coated with insulation to minimize plasma

distortion. Although the Langmuir probe has a different geometrical shape such as; spherical, cylindrical, planar, or elliptical, the cylindrical probe is the most prevalent [25].

In a simple design, when a conducting tip is inserted into the plasma reactor, it behaves like another electrode. By applying variable bias voltage to the probe that is referenced with respect to either an electrode, grounded metal wall, or another probe or probes, drained plasma currents are generated. The relationship between this current and the variable probe voltage “*plasma current-probe voltage characteristic (CVC) graph*” shown in Figure 5 is used to calculate parameters in the generated plasma. There are two kind of Langmuir probe, the first one is the single probe and the second one is the double probe.

Langmuir RF Single Probe Theory

From Figure 5, for the single Langmuir probe, current-voltage characteristic of any plasma is divided into three main regions that are called as “*ion saturation, electron retardation and electron saturation*”.

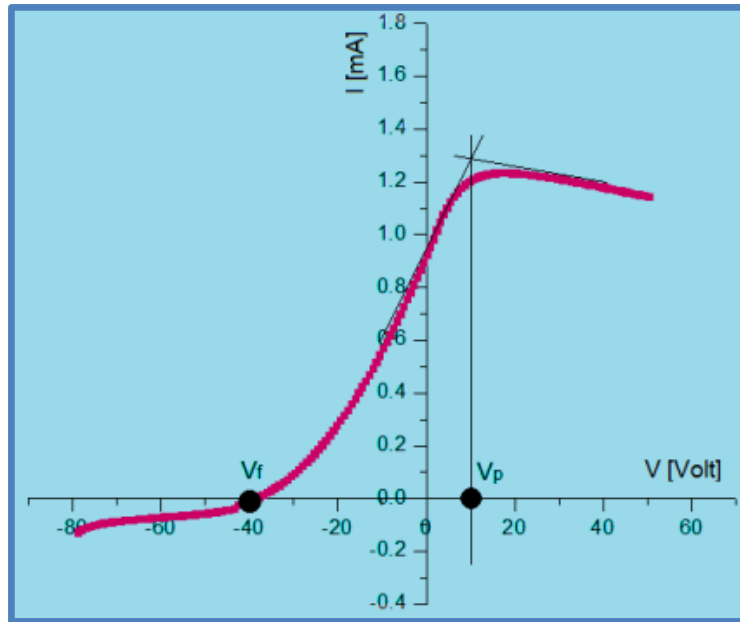


Figure 5. A typical plasma current-probe voltage characteristic graph of a Langmuir cylindrical probe

Ion saturation region: It is the region located at the left hand side of floating potential “ V_f ” that is the potential where plasma current is zero “*Electron current = Ion current*”. When probe voltage becomes more negative than the floating potential, electrons are repelled whereas ions are attracted. Therefore, in this region, positive ions mostly generate plasma current.

Electron retardation “transition” region: When the probe voltage becomes more positive relative to floating “zero current” voltage until it equals to plasma “space” voltage, the probe collects both particles; positive ions and electrons. However, the electron current is more dominant than the ion current in this region. The reason is that the electrons move faster than the ions because of having lighter mass.

Electron saturation region: The region that is located at the right hand side of plasma potential is called as “*electron saturation region*”. When potential applied to the probe becomes more positive relative to the plasma, the probe starts to collect extra

electrons from the plasma while it repels positive ions. Therefore, very thin constant area sheath “ion” region exists around the probe surface. And, with increasing probe voltage, the electron current having thermal motion goes through the constant sheath region. As a result of this, the electron current is saturated and so the plasma current becomes almost constant.

As shown in the Figure 5, the plasma characteristics in the ion and the electron saturation regions are distinguishably asymmetric. Since, masses of electrons and ions and so value of their current are different from each other significantly.

In RF discharges, one of the major complications of Langmuir probes measurement is the distortion of CVC of the probe due to RF fluctuations in plasma potential [26]. According to passive filter method, an RF compensation circuit that includes inductors “RF chokes - $L1$ and $L2$ ” and capacitors are connected to the probe as shown in Figure 6 by an RF band stop filters to minimize these fluctuations [27].

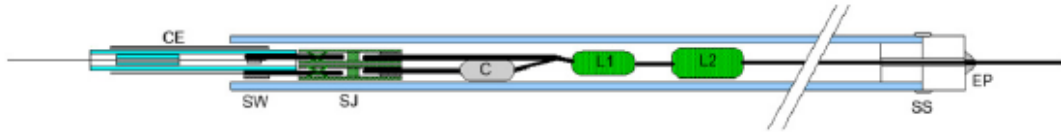


Figure 6. Schematic diagram of an RF-compensated single Langmuir probe [26]

In fact, these chokes that have self-resonant frequencies at the plasma driving frequency are placed to increase the probe-to-ground impedance to minimize the RF voltage drop across the probe sheath. In addition to chokes, it is better to use a compensation electrode in the Langmuir single RF probe to reduce impedance of the probe sheath. By this way, probe impedance can be larger than the probe sheaths impedance. However, cooling of the chokes and sputtering of the compensation electrode in the plasma are two important problems of this probe design. These problems are achieved by using Impedans ALP System™ Langmuir probe design. In this design, the chokes are moved away from the probe tip into the re-entrant ceramic

tube to be protected from high temperatures and the probe shaft with a ceramic coated stainless steel tube behaves like a compensation electrode by taking away the need of exposed metal surface in contact with the plasma. Thickness of the probe shaft and the ceramic coating is only 10's of microns for maximizing the plasma capacitance that is in the range of 100's of pF. For a broadband RF compensation, impedance of the RF filter is high relative to the sheath capacitance across the frequency range [28].

For measurements of the Langmuir single RF probe that are done at low discharge pressures, the “*Lafromboise Orbital Motion Theory*” is preferred. Since it is supposed that the sheath region around the probe is collisionless because of large ion mean free path. According to this theory, the ion current collected by the cylindrical probe is impressed by the energy and trajectory of the ions that enters the sheath region. During this motion, some of the ions turn back to the plasma region without collected by the probe after entering the sheath region and orbiting around the probe. It is important to take into account this effect when calculating ion density to get more accurate result [28].

By using Lafromboise theory and considering sheath expansion, the ion current collected by the probe can be found as [29];

$$I_i = I_0 a (-X)^b \quad (3)$$

where;

I_0 = ion flux at the sheath edge

a and b = the parameters that are relating to the probe radius “ r_p ”

X = dimensionless probe potential and it can be expressed as [28];

$$X = \frac{(V - V_p)}{kT_e} \quad (4)$$

where;

V = probe potential

V_p = plasma potential

kT_e = electron temperature in eV unit

Additionally, the coefficients “ a and b ” of a cylindrical probe is obtained by the studies of Narasimhan and Steinbruechel [32];

$$a_{cyl} = 1.18 - 0.00080 \left(\frac{r_p}{\lambda_D}\right)^{135} \quad (5)$$

$$b_{cyl} = 0.0684 + \left(0.722 + \frac{0.928r_p}{\lambda_D}\right)^{-0.729} \quad (6)$$

where;

λ_D = Debye length

These parameters are sometimes identified with the following different formulas because of hemispherical sheath generation around the end face of the probe tip under special plasma conditions. New expressions for hemispherical end sheath are given by [32];

$$a_{sph} = 1.98 + 4.49 \left(\frac{r_p}{\lambda_D}\right)^{1.31} \quad (7)$$

$$b_{sph} = 2.95 + 3.61 \left(\frac{r_p}{\lambda_D}\right)^{-0.0394} \quad (8)$$

Then, the total current collected by the cylindrical probe becomes sum of these two currents that are I_i (cyl) and I_i (sph). Also, these currents are related to each other with the following formula [28];

$$\frac{I_i(sph)}{I_i(cyl)} = \left(\frac{r_p}{L_p}\right) \left(\frac{a_{sph}}{a_{cyl}}\right) (-X)^{\Delta b} \quad (9)$$

where;

$\Delta b = b_{sph} - b_{cyl}$

L_p = length of the probe tip

For the measurements done at higher pressures, the “*Allen-Boyd-Reynolds (ABR) Theory*” is used. This theory states that collisions of the ions with neutral gas particles in the sheath region is very important and so it is assumed that the sheath region is “*collisional*”. Because of this reason, the orbital motion conservation law is not satisfied and the trajectory of the ions is almost radial. Therefore, all the ions that enter the sheath region are collected by the probe. To define correct ion current value, it is essential to know the value of ion-neutral collisions’ number in the sheath region that can be found as [28];

$$X_i = \frac{s}{\lambda_i} \quad (10)$$

where;

s = sheath width = r_s (sheath radii) - r_p (probe radii) that is defined as;

$$s = \lambda_D \sqrt{(0.59 + 1.86r_p/\lambda_D)(-X + 3.5) - 4} \quad (11)$$

λ_i = ion mean free path can be expressed as [1];

$$\lambda_i = \frac{k_B T_g}{p \sigma_{i-n}} \quad (12)$$

where;

k_B = Boltzman’s constant = 1.381×10^{-23} J. K⁻¹

T_g = neutral gas temperature

p = neutral gas pressure

σ_{i-n} = cross section of the ion-neutral momentum transfer

Then, the total current for collisional sheath at high pressures can be calculated according to the following formula that is a revision of the Eqs. 3 and 9 [28].

$$I_i = [I_o a(-X)^b + I_{i(sph)}] \gamma_1 \gamma_2 \quad (13)$$

where;

$$\left[\begin{array}{l} \gamma_1 = X_i \left\{ \frac{I_{i(ABR)}}{I_{i(LAF)}} - 1 \right\} \\ \gamma_2 = \frac{3 - 2e^{-X_i}}{1 + 2X_i} \end{array} \right] \quad \text{if } X_i < 1 \quad (14)$$

$$\left[\begin{array}{l} \gamma_1 = \left(\frac{I_{i(ABR)}}{I_{i(LAF)}} \right) \\ \gamma_2 = \frac{3 - e^{-X_i}}{2(1 + X_i)} \end{array} \right] \quad \text{if } X_i > 1 \quad (15)$$

where;

$I_{i(LAF)}$ = ion current collected by the probe at low pressure regime

$I_{i(ABR)}$ = ion current collected by the probe at high pressure regime that is equal to [33];

$$I_{i(ABR)} = a \left(\frac{-X}{b} \right)^c \quad (16)$$

where the a, b and c coefficients are represented as;

$$\left[\begin{array}{l} a = (r_p + 0.6)^{0.05} + 0.04 \\ b = 0.09 \left(e^{\left(\frac{-\lambda_D}{r_p} \right)} + 0.08 \right) \\ c = \left(\frac{r_p}{\lambda_D} + 3.1 \right)^{-0.6} \end{array} \right] \quad (17)$$

This high pressure model supplies the ALP System™ users more accurate results up to the pressure 10 Torr [28].

In fact, all the RF discharge parameters are calculated according to CVC graph obtained by Impedans ALP single probe system for each measurements under

different discharge processing conditions. And, the calculated parameters are; plasma potential “ V_p ”, floating potential “ V_f ”, electron temperature “ kT_e ”, electron flux “ J_e ”, electron density “ N_e ”, ion flux “ J_p ”, ion density “ N_i ”, electron energy distribution function “ $EEDF$ ” $g_e(\varepsilon)$ and its parameters “ N_e , average energy ($\bar{\varepsilon}$) and kT_e (relative to $\bar{\varepsilon}$)” [28].

V_f : It is the potential when $I(V_f) = 0$ shown in the Figure 5.

V_p : The plasma potential is calculated according to the following formula in the principle of intersection point of the slope of line tangent to the electron saturation region “ $V_{\max}$ to V_{sat} and the slope of line tangent to the transition region curve “ V_f to V_{sat} ” as shown in the Figure 5 [28].

$$V_p = \frac{-b + \ln[I(V_{\max})] - \frac{V_{\max}}{kT_e}}{a - \frac{1}{kT_e}} \quad (18)$$

kT_e : It is calculated from the slope of electron retardation region bounded between V_f and V_p . And, the formula giving the electron temperature is [28];

$$\frac{1}{kT_e} = \frac{I(V_p)}{\int_{V_f}^{V_p} I_e(V) dv} \quad (19)$$

N_e : Electron density in the bulk RF plasma is defined as [28];

$$N_e = \frac{I(V_p)}{A_p} \sqrt{\frac{2\pi m_e}{e^2 kT_e}} \quad (20)$$

where;

$I(V_p)$ = probe current when the probe potential equals to the plasma potential

A_p = probe tip area

m_e = electron mass = 9.11×10^{-31} kg [1]

e = electron charge = -1.6×10^{-19} C [1]

N_i : The formula that gives the positive ion density in the bulk RF plasma is [28];

$$N_i = \frac{I_0}{A_p} \sqrt{\frac{2\pi m_i}{e^2 k T_e}} \quad (21)$$

where;

m_i = mass of dominant ion

I_0 = after solving the Eqs. 9 and 13 with together, the ion current at the sheath edge can be found as [28];

$$I_0 = \frac{I(-80V)}{a_{cyl}(-X)^{b_{cyl}} \left[1 + \frac{r_p a_{sph}}{\lambda_D a_{cyl}} (-X)^{\Delta b} \right] \gamma_1 \gamma_2} \quad (22)$$

where;

$I(-80 \text{ V})$ = current collected by the probe at the default voltage (-80 V)

J_e : As soon as the probe voltage equals to the plasma voltage and there does not exist any sheath region around the probe, the electron flux to the probe is calculated as [28];

$$J_e = \frac{I(V_p)}{A_p} \quad (23)$$

J_p : The ion flux to the sheath edge of the single probe is calculated in terms of I_0 given in the Eq. 19 [28];

$$J_p = \frac{I_0}{A_p} \quad (24)$$

$EEDF$: It is calculated from the single point-second derivative of the CVC curve to get more reliable results after subtraction of the ion current.

$N_e (EEDF)$: By using the Druyvesteyn equation of EEDF, the electron density is calculated as [28];

$$N_e = \int_0^{\varepsilon_{max}} n(\varepsilon) d\varepsilon \quad \text{when } n(\varepsilon) = \frac{2I''}{eA_p} \left(\frac{2m_e \varepsilon}{e} \right)^{\frac{1}{2}} \quad (25)$$

where;

I'' = second derivative of the CVC

ε = energy given by (Vp-V)

$\langle \varepsilon \rangle$ = average electron obtained by the EEDF is represented as [28];

$$\langle \varepsilon \rangle = \int_0^{\varepsilon_{max}} \varepsilon f(\varepsilon) d\varepsilon \quad (26)$$

kT_e : The electron temperature that obtained by a Maxwellian EEDF is defined as [28];

$$kT_e = \frac{2}{3} \langle \varepsilon \rangle \quad (27)$$

If the EEDF of the system is non-Maxwellian; then, the electron temperature in the Eq. 18 will be effective electron temperature “ kT_{eff} ” [28].

Langmuir RF Double Probe Theory

Double probe plasma diagnostic method is mostly preferred instead of the single probe method when a reference point in the system does not exist. In fact, the main reason of using double probe system that belongs to Johnson and Malter is measurement of the parameters of decaying plasma. Because the plasma potential is time varying in decaying plasma and so, it is hard to obtain constant probe-plasma potential [29].

Basically, a double probe system consists of two floating probes which are biased with respect to each other but they are insulated from the ground and current flowing between them is recorded like seen in Figure 7. For accurate RF plasma diagnostics,

it is better to use two RF band stop filters that are connected to the probes and these filters should be identical with their circuit components when they are used in the double Langmuir RF probe with symmetric probe tips [30].

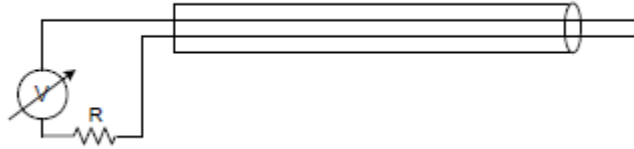


Figure 7. Schematic diagram of an identical double Langmuir DC probe [30]

In our IMPEDANS Brand Langmuir double RF probe system, the identical RF filters are combined into the re-entrant $\frac{1}{2}$ inch ceramic tube and also the probe tips are identical “*lengths and diameters are the same*”. Therefore, symmetric CVCs are obtained after all measurements. And, analysis of CVC of double Langmuir probe is different from that of the single Langmuir probe. As shown in Figure 8, there are two curves: pink and yellow colors. The yellow one is the corrected curve after sheath expansion that causes a linear increase in the probe current in the ion saturation region.

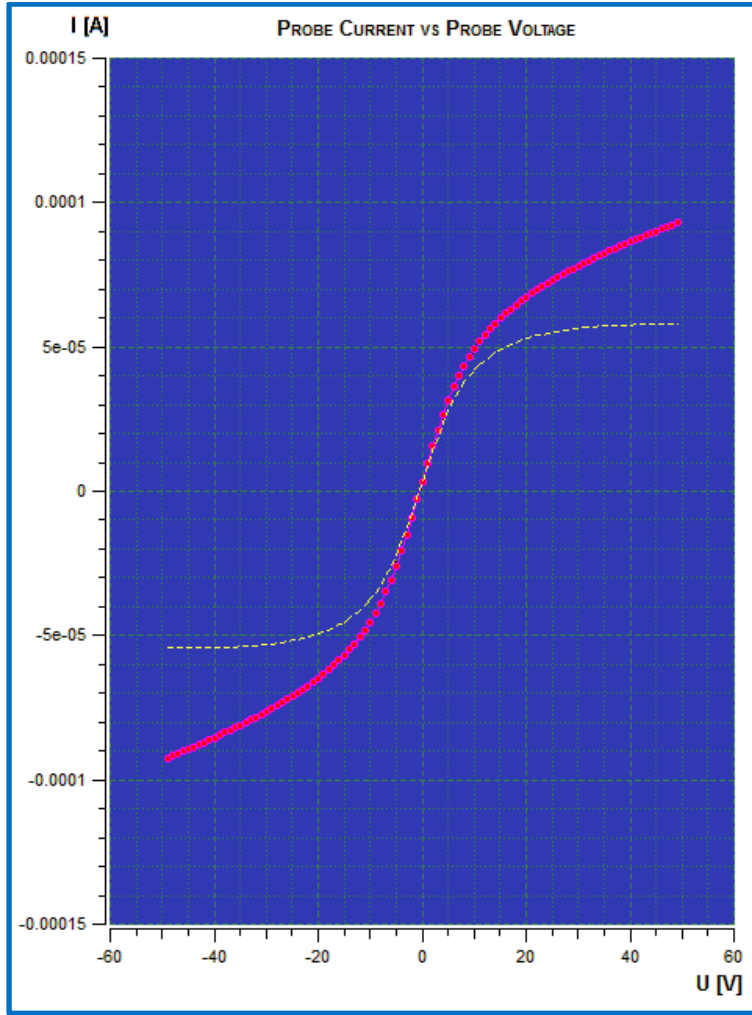


Figure 8. A CVC sample obtained with Langmuir double probe

As seen from the Figure 8, when the voltage across the probes “ U ” that is defined as the voltage difference of individual probes “ $U_1 - U_2$ ” is equal to zero, the current flowing between the probes becomes also zero. In general, both probe voltages are negative because the electrons have lighter mass. And, if $U < 0$ “ U_1 is more negative than the U_2 ”, the current will flow from the probe 2 towards to the probe 1. Therefore, negative saturated ion current is obtained. On the other hand, when the applied bias voltage becomes positive “ $U > 0$ ”, the current flows toward the probe 2 and the saturated ion current is positive. The saturated currents shown in the Figure 8

are symmetric because of identical probes. If the probes had different tip dimensions, the saturated current profiles became different from each other [33].

The RF plasma parameters calculated from the yellow corrected curve are: temperature of the electron located at the tail of the EEDF “ kT_e ”, ion flux to the probe “ J_p ”, ion density “ N_i ” and the plasma Debye length “ L_d ”

kT_e : Electron temperature of the electrons is calculated according to the following equation [28];

$$\frac{eV}{kT_e} = 2 \tanh^{-1} \left(\frac{I_{corrected}}{I_{isat}} \right) \quad (28)$$

where;

$I_{corrected}$ = current collected by the double probe

I_{isat} = ion saturation current calculated from negative region of the CVC graph of double probe seen in the Figure 8

N_i : For Maxwellian electron energy distribution function, the ion density formula is defined as [28];

$$N_i = \frac{I_{isat}}{A_p e \sqrt{\frac{kT_e}{2\pi m_i}}} \quad (29)$$

where;

m_i = ion mass

L_d : plasma Debye length is defined as [28];

$$L_d = \sqrt{\frac{\epsilon_0 kT_e}{e N_i}} \quad (30)$$

2.3 Carbon Fiber

Carbon fiber is an artificial material including at least 92 % carbon by weight. Remarkable properties of these fibers are having excellent tensile strength, excellent creep resistance, and low density, good thermal and electrical conductivities [34]. The fibers can be produced by using some polymeric precursor materials; for example, cellulose, rayon, polyvinylchloride, pitch, and polyacrylonitrile “PAN”.

In 1880, two scientists, T. Edison in the United States and J. W. Swan in England, used the first carbon fibers that made of cellulose precursor for light - bulb filaments [35, 37]. Then, experimental needs have let scientists to use new carbon fibers. Lately, PAN-based and Mesophase pitch-based carbon fibers have become more popular. PAN-based fibers are used for high strength applications whereas Pitch-based are preferred for high modulus “*stiffness*” applications. Tensile strength of PAN-based fiber is “5” times greater than the one of steel. Likewise, modulus of Pitch-based fibers is “4” times greater than the one of steel [11].

A typical carbon fiber structure consists of some hexagonal - shaped in other words honeycomb carbon atom layers as shown in Figure 9.

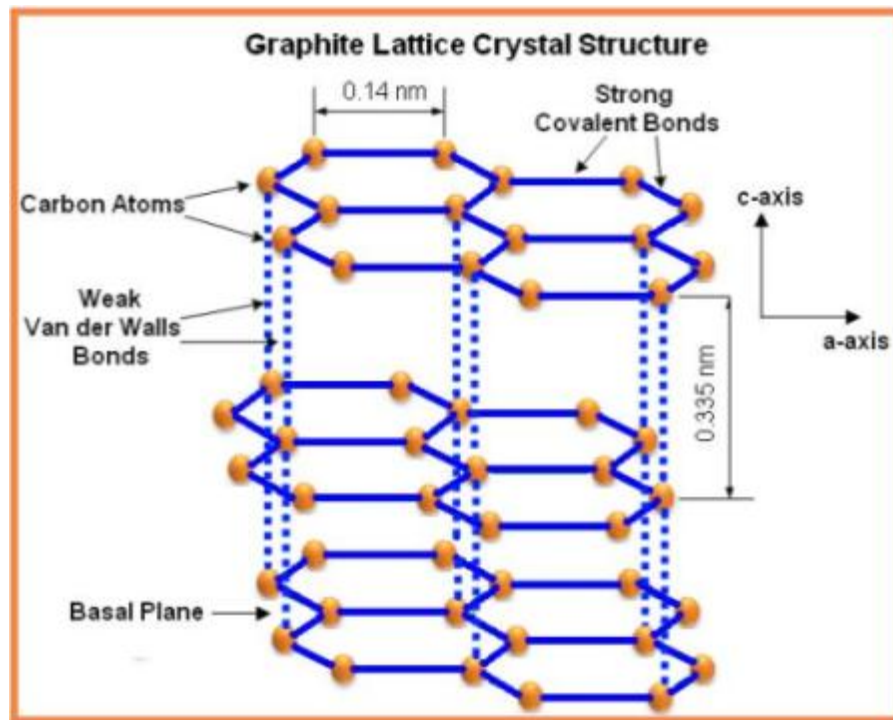


Figure 9. Schematic of Lattice structure of a single graphite crystal [36]

The placement of the layers can be different from one fiber to another due to used precursor type and production process. These different structures are called as turbostratic and graphitic or hybrid. PAN-based fibers have turbostratic crystalline structure whereas pitch-based fibers have well stacked graphitic structure. As seen in the Figure 9, the graphitic structure has a regular shape with parallel carbon layer planes. All carbon atoms in a plane are bounded with sp^2 strong covalent bounding and these planes act very weak intermolecular “*Van der Waals*” force to each other. Also, the distance between two layers in a single crystal, d -interlaying spacing “ d_{002} ”, is about 0.335 nm. In contrast, turbostratic structure has an irregular shape. The parallel layer planes in this structure are randomly folded, tilted or split and all the atoms in a layer are bounded with sp^3 bounding. This bounding type causes a small increase in the distance between two planes and it becomes 0.344 nm [34].

In a single crystal, number of the carbon layers i.e. crystallite height or the c-axis crystallite size is represented as “ L_c ” and crystallite width or in-plane crystallite size is symbolized by “ L_a ” as seen in Figure 10. Typically, in a carbon fiber L_a is $\sim 2 - 6$ nm and L_c is $\sim 1 - 10$ nm as a result of measurements with X-ray diffraction [37, 38].



Figure 10. Schematic of PAN-based carbon fiber lied along the fiber axis [39]

In fact, higher crystallite size is related to more graphitic structure, high modulus, better thermal and electrical conductivity in the fiber direction and smaller crystallite size “*turbostratic*” is related to the higher tensile strength [40] that was proved by researcher, Endo [41]. Higher treatment temperature resulted in a larger and better aligned graphitic crystal structure to improve modulus while removing flaws resulted in high tensile strength [34].

In general, carbon fiber production process is mainly composed of three parts: oxidization, carbonization and heat treatment “*graphitization*”. Firstly, in

oxidization, precursor fibers are stabilized at around 200 - 400 °C in air. Secondly, in carbonization, the stabilized fibers are treated by around 1,000 °C in an inert atmosphere to get rid of non-carbon elements such as nitrogen, hydrogen and oxygen. Finally, carbon fibers are treated at higher temperature around 3,000 °C to increase quality of carbon properties and their constituents. This temperature is changeable according to the goal of manufacture. For example, this temperature can be 1,500 °C to obtain high strength “> 4 GPa” fibers like PAN-based and treatment at 2,000 °C increases modulus of the fibers like pitch-based. In addition, like crystallinity, crystalline distribution, amount of defects, molecular orientation, carbon content factors have an important role on the form of mechanical properties. For instance, modulus of the fibers increases with high crystallinity and well alignment of carbon crystal in the fiber direction. Additionally, amount of defects and the crystalline distribution cause a change in the value of carbon fiber strength [34].

There are many industrial applications of carbon fibers such as; portable power, rechargeable batteries and fuel cell electrodes, sporting goods, marine, infrastructure, pressurized vessels, woven fabrics, energy production “*windmill blades*”, fiber reinforced plastics, concrete and asphalt reinforcements, soil erosion barriers, composite materials for automotive, aerospace “*aircraft and space systems*”, military, light weight cylinders, medical and so on.

2.3.1 PAN-Based Carbon Fiber

It is a type of turbostratic carbon fibers shown in Figure 11 that manufactured by polyacrylonitrile “*PAN*” precursor. In 1959, Shindo of Osaka Industrial Institute of Japan produced the first PAN-based carbon fiber in the world and the first commercialization was in 1971 [43].

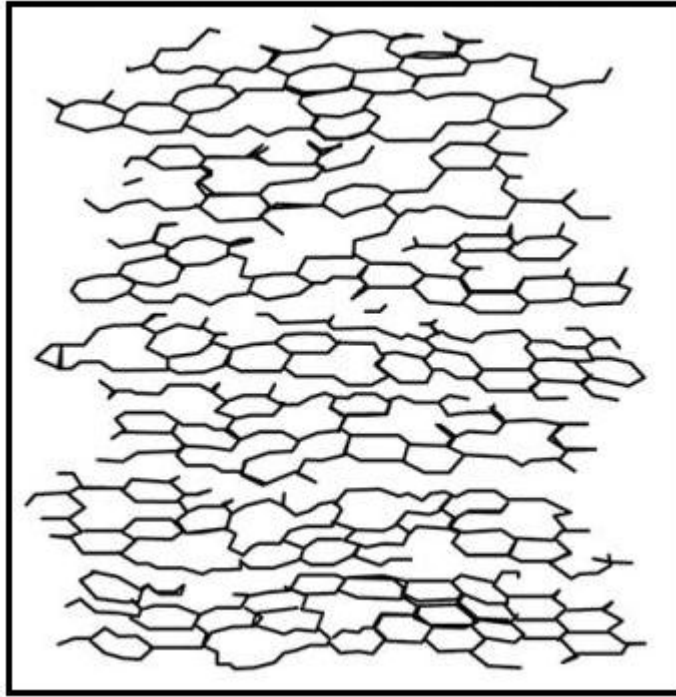


Figure 11. Structure of a turbostratic carbon fiber [40]

From Figure 12, a typical PAN-based carbon fiber production process is composed of five main steps: polymerization of PAN “*production of precursor*”, spinning of fibers “*production of precursor*”, thermal stabilization, carbonization and graphitization.

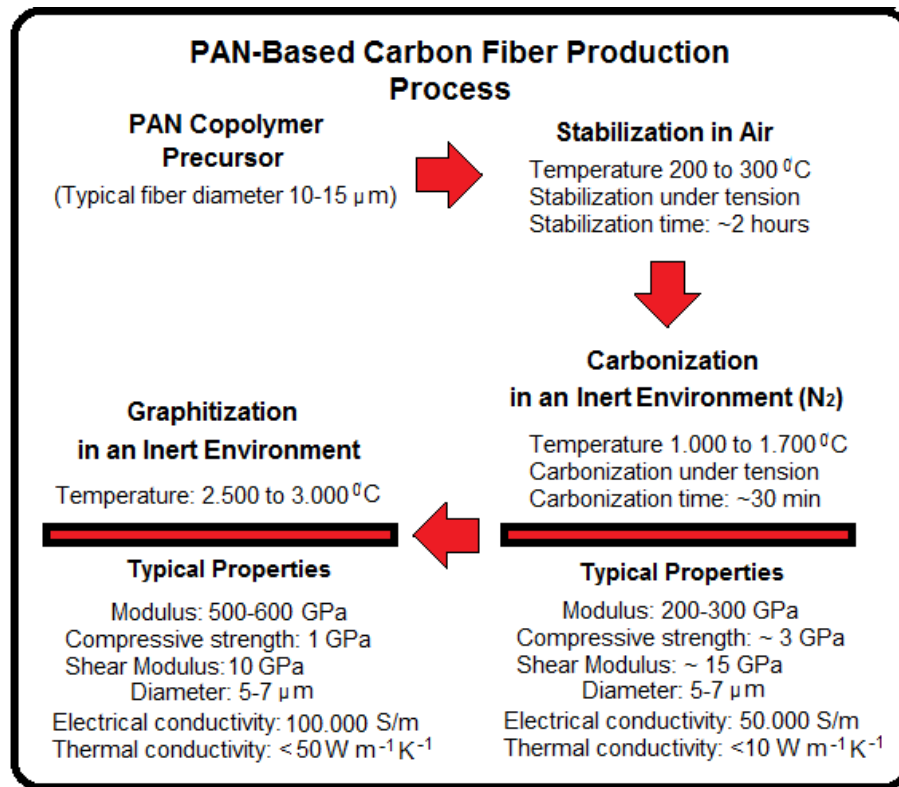


Figure 12. Flow chart of a typical PAN-based carbon fiber production process with showing mechanical properties of the fibers in each steps [43]

In the first step, polymerization, acrylonitrile “AN” is polymerized by using a “comonomer”; such as, acrylic acid, methacrylic acid and methacrylate. Because the number of polar nitrile groups in the PAN - Homopolymer is high and that causes disappearing of the alignment of molecular chains during spinning procedure. Using comonomer, it is resulted in better chain alignment by preventing nitrile-nitrile interactions and has better mechanical properties of carbon fibers [43].

In the second step, spinning, the bulk PAN polymer can be spun by different techniques: wet, melt, dry, gel and dry - jet wet spinning. Among them, wet spinning is the well - known. In this technique, a highly polar solvent; for instance, dimethyl acetamide, dimethyl formamide, sodium thiocyanate or their mixtures is used to

obtain a bulk PAN polymer solution of 10 - 30 % by weight [45]. This solution is then filtered and is extruded in a coagulation bath applying stress to get better alignment [34, 43]. To ignore defects both inside of the fibers and on the fiber surfaces, temperature of the bath and concentration of the non-solvent in the bath should be low. Also, duration of the bath should be as short as possible ~ 10 seconds. Bathing can be several times with different temperatures and compositions to have better properties. After bathing, the fibers are washed and stretched in steam. By this way, the fibers get rid of the solvent ending up with high molecular orientation and precursor fiber is ready to use in carbon fiber production.

In the third step, thermal stabilization also called oxidization, the precursor fiber is exposed to stress between 200 °C and 300 °C in an oxidizing atmosphere resulted in high density [43]. The main purpose of this process is cyclization of the linear PAN precursor that leading ladder polymer structure [34, 43]. Bounding structure of the precursor changes throughout stabilization process. There are many proposals about new polymer structure. In general, Hydrogen atoms displace their positions and new oxygen atoms connected to the structure. Duration of this process depends on type of the used copolymer composition [34].

The main goal of the fourth process, carbonization, is increasing carbon material content as high as possible “*above 90 %*” by removing non-carbon elements. The stabilized precursor fibers are carbonized in an inert nitrogen gas atmosphere in the 1,000 °C to 1,700 °C range. High process temperature is resulted in high strength ~1500 °C but greater temperature causes high modulus and low tensile strength. Moreover, duration of this step depends on the fiber diameter, composition, and morphology [34].

In the last step, graphitization, carbonized fiber is heated to higher temperatures between 2,000 °C and 3,000 °C to have more ordered structure, high crystalline orientation in the fiber direction, higher modulus, and low d-spacing. In addition,

local defects cause low tensile strength. In this step, Argon gas is used instead of N₂ to ignore nitrides formation [34].

Polyacrylonitrile (CH₂=CHCN)_n based carbons include 68 % non-graphitizing “disordered” carbons and carbon yield of this precursor is 50 – 55 %. This property supplies high modulus fibers “> 300 GPa”. Although carbon yield of the pitch-based fibers “85 %” is high with very high modulus “> 500 GPa”, PAN-based is the most preferred precursor. Because, pitch-based fibers have graphitizing carbon structure that leads to lack of compression and transverse features [48].

2.4 Some Analysis Techniques of Carbon Fiber

2.4.1 Raman Spectroscopy

Raman or vibrational molecular spectroscopy is one of the structural data analyzing techniques that are discovered in 1928 by Sir Chandrasekhra Venkata Raman [45]. It is basically related to the light – surface “material” interactions. This technique examines vibrational, rotational and other low-frequency modes of interaction between the molecules in samples under the electromagnetic radiation.

In fact, the physics of Raman scattering is explained by two theories; classical and quantum mechanical.

Classical Theory:

Real part of oscillating electric field of the laser or light is equal to;

$$\vec{E} = E_0 \cos \omega t = E_0 \cos 2\pi \nu_i t \quad (31)$$

where;

E₀ = vibrational electric field amplitude

ν_i = frequency of laser beam or light

And, as it can be seen from Figure 13, when the beam focused onto the sample, the electric field strength polarizes the electron distribution “cloud” of molecules in the sample that creates an induced dipole moment “ P ”.

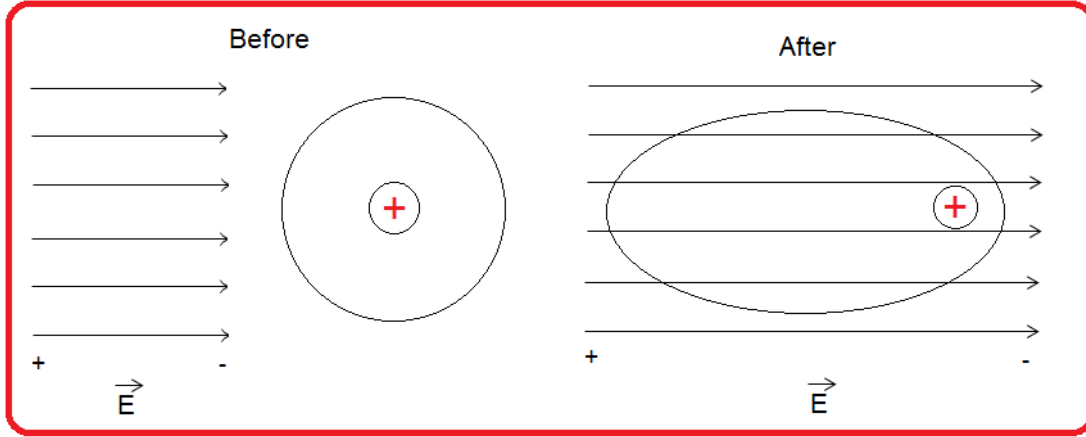


Figure 13. Molecular orbital distortion after being exposed to electric field [47]

For weak electric field strength, induced electric dipole moment is given as;

$$\vec{P} = \vec{\alpha}\vec{E} = \alpha E_0 \cos 2\pi \nu_i t \quad (32)$$

where;

α = a tensor quantity which is called as polarizability of the molecule in the sample.

Then, the polarized electrons in the molecules due to incoming electromagnetic beam emit scattered lights having the same and different frequencies with that of molecular vibrations. The elastical scattering is called “*Rayleigh scattering*” while the inelastic one is called “*Raman scattering*”. In Rayleigh scattering, the frequency of incident photons is equal to the frequency of scattered photons that means energy of these photons can be seen in Figure 14. As a result of this scattering, we have no

spectroscopic information about the material. On the contrary, in Raman scattering, the frequency of incident and the scattered photons are different from each other and energies are different either as shown in Figure 14-b. If the frequency of scattered photon is lower than the incident one, this scattering is defined as “*Stokes scattering (vibrational excitation)*” vice versa is called as “*Anti-Stokes scattering (vibrational de-excitation)*” [48].

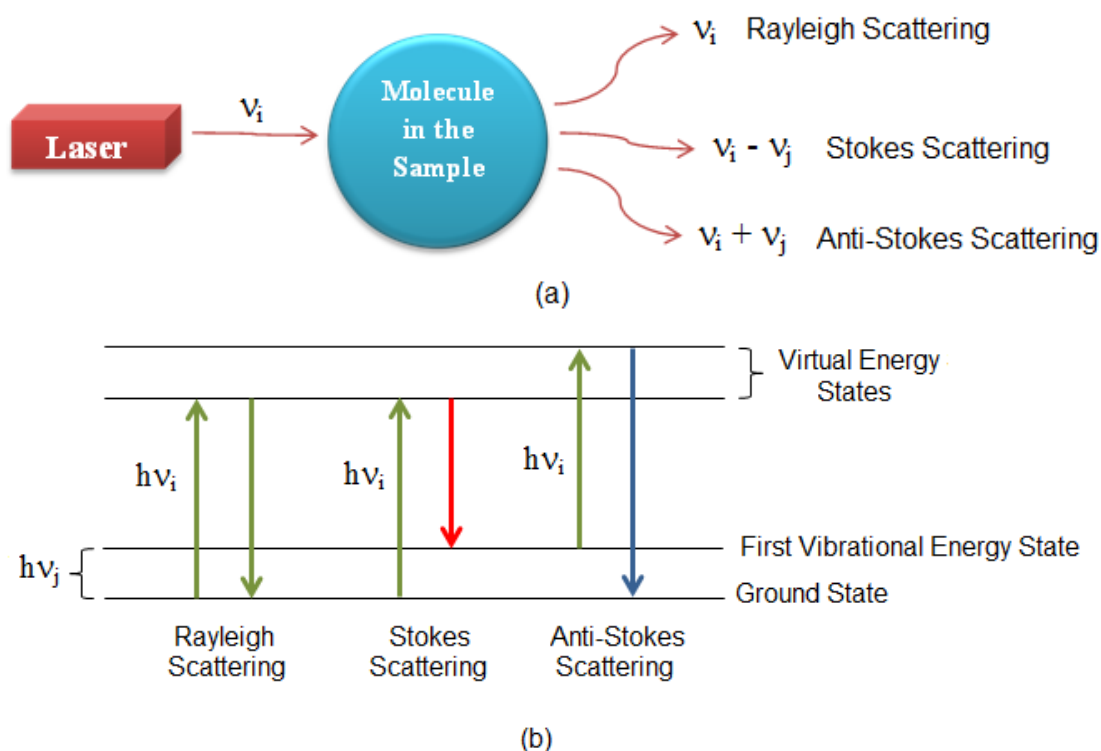


Figure 14. Diagrams showing (a) frequency and (b) energy levels of Rayleigh “*elastic*” and Raman “*inelastic*” scatterings [50]

Moreover, we know that molecular vibrations mainly consist of normal modes, Q_j . The number of normal modes in a molecule can be calculated as follows;

Knowing that each atom can have a movement in x, y or z dimensions, and then N-atom molecules have $3N$ degrees of freedom. However, it is necessary to think there

exists six degrees of freedom in $3N$ that belong to translational and rotational motions. Then, the remaining degrees of freedom for vibrational motion “*normal modes*” become $3N - 6$. Moreover, for a linear molecule it is equal to $3N - 5$ because one rotational degree of freedom is the molecular axis [45] .

Additionally, there exists a relation between dipole moment and molecular vibrations “*normal modes*” in terms of polarizability that can be formulated according to Taylor series [50];

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q_j} \right)_0 Q_j + \dots \quad (33)$$

where;

α_0 = the polarizability at the equilibrium position

$(\partial \alpha / \partial Q_j)_0$ = the rate of change of α with respect to the change in Q_j that evaluated at the equilibrium position.

Q_j = normal modes of vibrations and it can be found from following formula [50];

$$Q_j = Q_j^0 \cos 2\pi \nu_j t \quad (34)$$

where;

Q_j^0 = vibrational amplitude

ν_j = frequency of j^{th} normal mode

Then, the induced electric dipole moment can be revised as [50];

$$\begin{aligned}
P &= \alpha E_0 \cos 2\pi \nu_i t + \left(\frac{\partial \alpha}{\partial Q_j} \right)_0 Q_j^0 E_0 \cos 2\pi \nu_i t \cos 2\pi \nu_j t \\
&= \underbrace{\alpha E_0 \cos 2\pi \nu_i t}_{\text{Rayleigh Scattering}} + \frac{1}{2} \left(\frac{\partial \alpha}{\partial Q_j} \right)_0 Q_j^0 E_0 \left\{ \underbrace{\cos 2\pi (\nu_i - \nu_j) t}_{\text{Stokes Scattering}} + \underbrace{\cos 2\pi (\nu_i + \nu_j) t}_{\text{Anti-Stokes Scattering}} \right\} \quad (35)
\end{aligned}$$

By analyzing the Eq. 35, it is possible to get some physical meaningful explanations. The first one is that there is a linear relation between the laser intensity and intensities of polarization and scattering. The second one is that polarizability can be changed only with the vibrations. The third one is that the sign of the Raman shift can be negative “*Stokes*” or positive “*Anti-Stokes*”. The last one is that Raman intensity is strongly related to the quantity, $\frac{\partial \alpha}{\partial Q_j}$, whose value depends on molecular type and also modes in molecules [50].

In addition, the radiation intensity in terms of oscillating induced electric dipole moment is given as [50];

$$I = \frac{\nu_i^4}{12\pi\epsilon_0 c^3} |\vec{P}|^2 \quad (36)$$

By putting the Eq. 35 into the Eq. 36, we will get the following ratio [51];

$$\frac{I(\text{Stokes})}{I(\text{Anti-Stokes})} = \left[\frac{\nu_i - \nu_j}{\nu_i + \nu_j} \right]^4 \quad (37)$$

This classical formula is not supported by experimental results. For this reason, the classical theory for Raman spectroscopy fails and so the scientists need another theory “*Quantum Mechanical*” for meaningful physical explanation of Raman spectroscopy [51].

Quantum Mechanical Theory:

For quantum mechanical explanation, time-dependent Schrödinger equation of photon in molecules is solved by using the perturbation theory. Then, the radiation intensity equation becomes [51];

$$I_k^{nm} = \frac{4e^4}{16\pi^2\epsilon_0^2c^4} (\nu_i \pm \nu_j)^4 |\langle n|m_k|m \rangle|^2 \quad (38)$$

where;

$$\langle n|m_k|m \rangle = \frac{\pi}{h} \sum_j \sum_r \left\{ \frac{\langle n|\hat{P}_k|r \rangle \langle r|\hat{P}_k\hat{E}_j^0|m \rangle}{\nu_{rm}-\nu_i} + \frac{\langle n|\hat{P}_k\hat{E}_j^0|r \rangle \langle r|\hat{P}_k|m \rangle}{\nu_{nr}-\nu_i} \right\} \quad (39)$$

And, according to Boltzmann distribution, the intensity ratio in the Eq. 37 turns out to be [51];

$$\frac{I(\text{Stokes})}{I(\text{Anti-Stokes})} = \left[\frac{\nu_i - \nu_j}{\nu_i + \nu_j} \right]^4 e^{hc\tilde{\nu}_j/kT} \quad (40)$$

2.4.1.1 Raman Bands of Carbon Fiber

According to literature, there are some Raman bands revealed in carbon fiber structure depending on the level of graphitization, laser power, and laser excitation wavelength and precursor type. In the first order region, two well-known Raman bands; D “disordered” and G “graphitic or ordered” are mostly appeared in the range of 1200 - 1700 cm^{-1} Raman band shift. Exact peak position of the D-band is $\sim 1330 \text{ cm}^{-1}$ whereas position of the G-band is $\sim 1585 \text{ cm}^{-1}$. These locations can be changed with respect to the fiber type. Reason behind the existence of the G peak is the bond stretching of all pairs of sp^2 atoms in both rings and chains “symmetric E_{2G} vibration mode” while the D peak appears as a result of the breathing modes of sp^2 atoms in rings “symmetric A_{1G} vibration mode” [52].

The Raman lines are strongly related to some structural properties. For example, width of G-band line is concerned with the quantity of disorder [53-55], shift in peak location as a result of applied strain [56] and integrated intensity ratio of the peaks is essential to reveal the amount of disorder carbon structure [57, 58] and crystallinity of carbon fibers [8, 38, 55, 56].

In-plane crystallite size “ L_a ” of carbon fibers related to crystallinity property can be calculated as follow [8, 52, 61];

$$L_a = C(\lambda) \frac{I_G}{I_D} \quad (41)$$

where;

L_a = in-plane crystallite size in “nm” unit

$C(\lambda) = \frac{560}{E^4} = 2.4 \times 10^{-10} \lambda^4$ is pre-factor depending on excitation wavelength “ λ ” [59]

I_D = integrated intensity of Lorentzian fitted D-band

I_G = integrated intensity of Lorentzian fitted G-band

As inferred from the Eq. 41, when carbon fibers become more disordered, in-plane crystallite size of them decreases whereas it increases with being more-ordered.

The other structural property that is related to the Raman band of carbon fiber is “*strain*”. Strain of a substance is generated when the distance between molecules in a substance decreased “*compression*” or when the distance between molecules in a substance increased “*stretching*”. In other words, frequency of crystal phonons is shifted with strain resulted in locational changes. And, there is a close relationship between the rate of this frequency change and the Grüneisen parameters. Also, all these relationships are explicitly seen in the following formula [55, 64, 66];

$$\frac{\Delta\omega}{\omega_o} \approx -\gamma (\varepsilon_{xx} + \varepsilon_{yy}) \quad (42)$$

where;

γ = Grüneisen parameter

ε_{xx} = uniaxial strain “%”

$\varepsilon_{yy} = -\nu \varepsilon_{xx}$ is relative strain in the perpendicular direction according to the Poisson's ratio of PAN-based carbon fiber “ $\nu \cong 0.3$ ” [60]

ω_0 = Raman band peak position in “ cm^{-1} ” unit

$\Delta\omega$ = Raman band shift of ω_0 in “ cm^{-1} ” unit

For PAN-based carbon fiber, there are two Raman bands; D and G. Therefore, it is important to investigate the strain relation with these bands separately. Then, for D-band, the Eq. 42 becomes;

$$\frac{\Delta\omega_D}{\varepsilon} \approx -\omega_D^0 \gamma_D (1 - \nu) \quad (43)$$

where ω_D^0 is D-band peak position at minimum strain value and γ_D is the Grüneisen parameter of the D-band.

And, for G-band, it is;

$$\frac{\Delta\omega_G}{\varepsilon} \approx -\omega_G^0 \gamma_G (1 - \nu) \quad (44)$$

where ω_G^0 is G-band peak position at minimum strain value and γ_G is Grüneisen parameter of the G-band.

In fact, the formula in the Eq. 42 is derived after many previous experimental studies. And, as seen from the Eq. 42, shift location of carbon fiber bands “*D and G*” is an evidence of changes in uniaxial strain of the carbon fibers. The scientists proved that Raman band peaks shift to the left “*lower frequency*” with an accretion of tensile strain “*increase in length of the fiber*” resulted in broader band peaks width [55, 58] and the peaks shift to the right “*higher frequency*” with a wave of

compressive strain “*decrease or compression in length of the fiber*” [67]. The reason of these changes is due to bond anharmonicity “*alteration of molecular lattice structure and vibrations because of displacement between two atoms as a result of an external force*”, decrease in bond modulus, vibrational frequencies generated by a result of an increase in stress and fiber modulus [69, 70].

2.4.2 Fourier Transform Infrared (FT-IR) Spectroscopy

Fourier transform infrared “*FT-IR*” spectroscopy is one of the nondestructive, high speed and high sensitive analyzing technique [70]. In carbon fiber technology, it is mostly used for detecting the existence of chemical functional groups such as; C=C, C=N, C-H and so on [71].

Basically, FT-IR spectrometer is composed of five main parts: a radiation source, interferometer “*generally-Michelson*”, sample, detector and computer as shown in Figure 15.

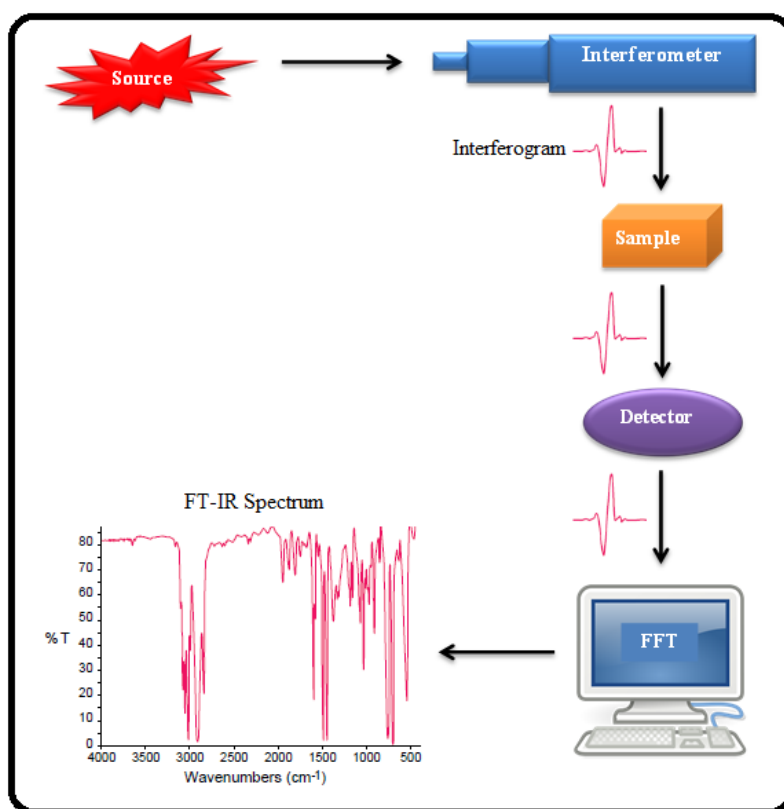


Figure 15. Schematic diagram showing the working mechanism of a simple Fourier Transform Infrared Spectroscopy [68]

As shown in the Figure 15, first of all, continuous radiated beam from a broadband IR source “generally; *Nernst glower, Globar or Nichrome coil*” is sent to the interferometer that consists of a moving mirror, a fixed mirror and a beam splitter. As soon as entering the interferometer, the beam is directed onto the beam splitter that splits the beam into two halves. And, one of the halves is transmitted to the fixed mirror whereas the other one is reflected to the moving mirror. Then, these splitted beams are recombined onto the beam splitter again after reflected from the mirrors. By this way, an interfering pattern is generated because of optical path difference. This pattern is called as “*Interferogram*”. After transmitted or reflected from the sample, the Interferogram signal comes to the detector. And, the detector signal is

recorded in a short time interval throughout the mirror scan. In addition, this operation is controlled by a He-Ne laser beam that is directed on another detector. Lastly, the Interferogram that has information about the selected IR region “*Near-IR* (13,000 – 4,000 cm^{-1}), *Mid-IR* (4,000 – 200 cm^{-1}) or *Far-IR* (200 – 10 cm^{-1})” is sent to the computer having Fourier transform program. And, this program converts the Interferogram signal to the final IR spectrum. As seen in the Figure 15, x-axis of the spectrum is wavenumber “ $\bar{\nu}$ - cm^{-1} ” or sometimes wavelength “ λ - μm ” whereas y-axis is percent transmittance or sometimes absorption intensity. Generally, percentage transmittance is preferred because it supplies better contrast between intensities of strong and weak bands. For a more accurate analysis and assigning percentage transmittance, a background spectrum without sample must be taken [70].

Lastly, it is necessary to mention that physical mechanism of this spectroscopy technique. The FT-IR spectroscopy analyzes vibrational motion of molecules like the Raman spectroscopy. However, their analyzing techniques and working light region are different from each other. The Raman analysis is done according to scattered lights whereas the FT-IR analysis is done according to light absorption. And, for Raman analysis, ultra violet “*UV*”- visible “*VIS*” and near-infrared “*N-IR*” lights are used whereas mid infrared “*M-IR*” lights are generally used for FT-IR analysis [50].

CHAPTER 3

THE EXPERIMENTAL SET-UP

3.1 Single and Dual RF-CCP Discharge System

The experimental set-up shown in Figure 16 (a-b) is basically composed of a stainless steel cylindrical chamber, two-isolated identical aluminum electrodes, automatic matching networks, turbo and rotary pumps, a high band pass filter and RF generators.

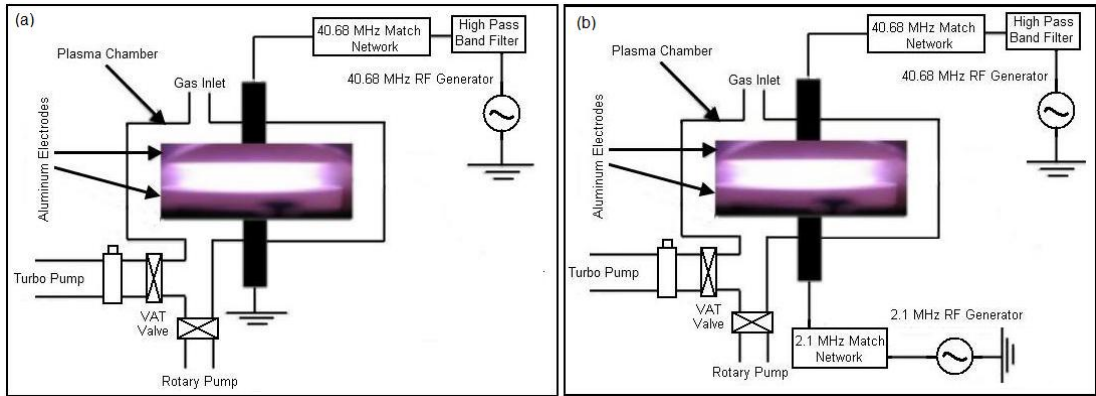


Figure 16. Schematic diagrams of (a) single and (b) dual modes of capacitively coupled high frequency RF-PECVD reactors.

As seen from Figure 17, it is a homemade huge RF-PECVD system and it is “*the first*” in TURKEY. Dimension of the plasma processing chamber is “ $500 \times 400 \text{ mm}^2$ ” and diameter of the electrodes is “ 200 mm ”. These two identical electrodes with a “ 40 mm ” distance were assembled into the plasma chamber like a parallel plate

capacitor “*RF diode*”. And, high purity “99.995 %” nitrogen “*electro-positive*” gas was used as an activation gas.

Two RF sources were used: High frequency is “40.68 MHz” with 600 Watt and low frequency is “2.1 MHz” with 600 Watt.



Figure 17. Picture of our RF-PECVD reactor

In the experiment, firstly, carbon fiber samples were placed onto a non-conducting glass substrate with 1 cm thickness as a sample holder on the lower electrode connected to the ground and LF-RF power supply. Secondly, the plasma chamber was vacuumed around $p = 10^{-2}$ Torr. After filling the chamber with nitrogen gas, RF plasma discharge was generated by using S-RF or D-RF modes. Then, surface of the

156 carbon fibers were treated under different processing time, gas pressure and exposure time as shown in Table 1.

Table 1. Experimental parameters of RF plasma treatment process

RF Type	Pressure (Torr)	Power (Watt)	Time (Minute)
S-RF	0.3	50	30
			60
			90
	0.5	100	30
			60
			90
	0.75	150	30
			60
			90
	1	200	30
			60
			90
D-RF	0.1	50-50	15
			30
			45
			60
	0.3	50-100	15
			30
			45
			60
	0.5	50-150	15
			30
			45
			60
	0.75	50-200	15
			30
			45
			60
	0.9		15
			30
			45
			60

Trademark of our high band pass filter, RF power supplies and their automatic matching systems is “*SEREN IPS*” as seen in Figure 18 and Figure 19.



Figure 18. Picture of the SEREN R01 model RF power supply [72]

There are two RF generators “*HF and LF*” in the experiment. Models “*SEREN R601*” thereby directions and output powers of the both equipment are the same, 600 Watt. Only output frequency of the systems is different. Frequency of HF is “*40.68 MHz*” while frequency of LF is “*2.1 MHz*”. As soon as setting desired powers, load and reflected powers are directly shown on the front panels.

Model of the automatic matching networks connected to the generators is “*SEREN MC2*” as seen in Figure 19 and typical configuration of the system connection is explicitly shown in Figure 20 [73].



Figure 19. Pictures of SEREN AT-Series matching network system [74]

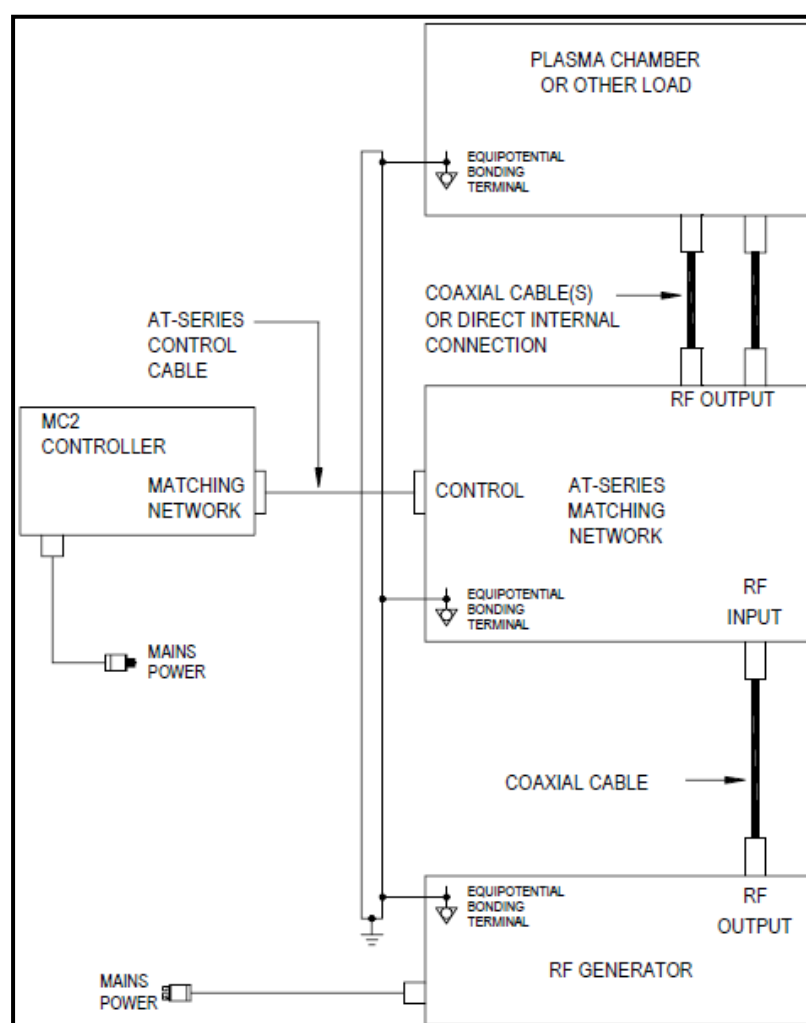


Figure 20. Basic configuration of matching network system [73]

From the Figure 20, the MC2 controller that is shown in the Figure 19 is connected to the AT “Automatic” series network system with a control cable and this network system is connected to the RF generator and to the plasma chamber with coaxial cables. In our experimental set-up, a high pass filter is also connected between the RF generator and the AT-series network system. The reasons of using matching network system between the RF generator and the plasma chamber are transferring maximum RF power to the load “RF chamber” and having less reflected power to protect devices. In our matching network, these conditions are supplied by using an

L-type circuit topology in the device. As seen from Figure 21, our circuit is composed of a variable load capacitor, a variable tune capacitor and a fixed inductor. The capacitors are controlled by a servo-motor [73].

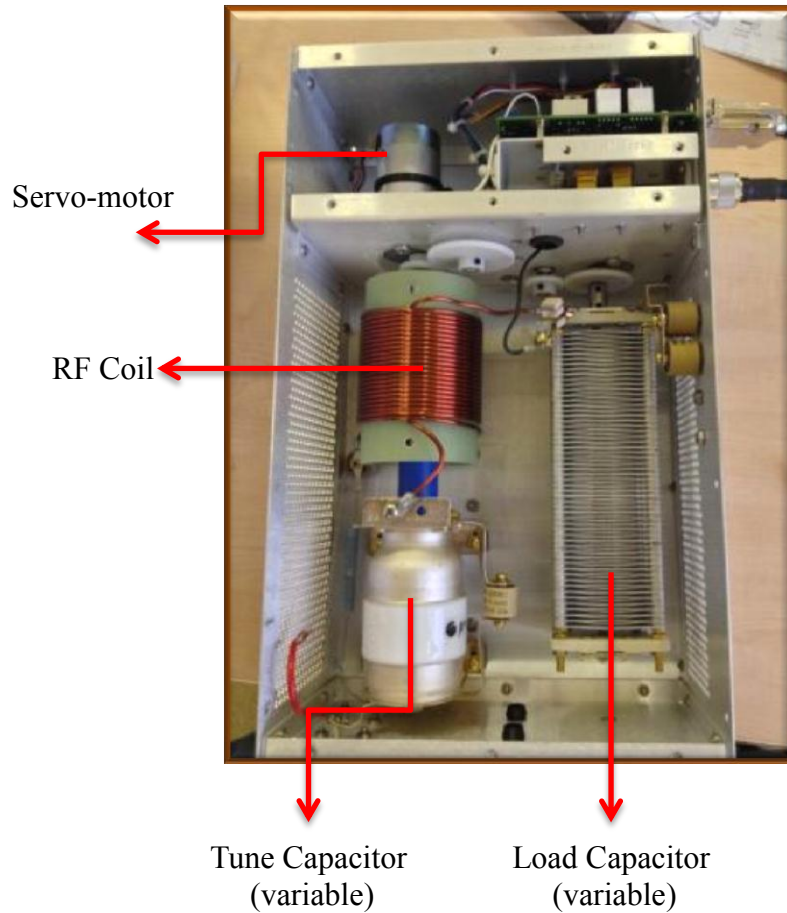


Figure 21. Picture showing the inside of SEREN AT-6 matching network system

There are two modes of the matching network system which are; automatic and manual. In automatic mode; as soon as generating an error signal with an internal phase and magnitude sensor, servo-motors are driven to control capacitors for getting appropriate plasma impedance [73]. In manual mode; the users can control the rotation of servo-motors by pressing Min/Max buttons on the right side in front panel

of the MC2 controller and they can tune the system manually by changing the position of variable capacitors to get appropriate plasma impedans [73].

3.2 Plasma Diagnostics

In addition to design shown in the Figure 16-a, for plasma diagnostics, some extra equipment were connected to the system that are Langmuir probes, their probe controlling system and a software program as shown in Figure 22 (a-b).

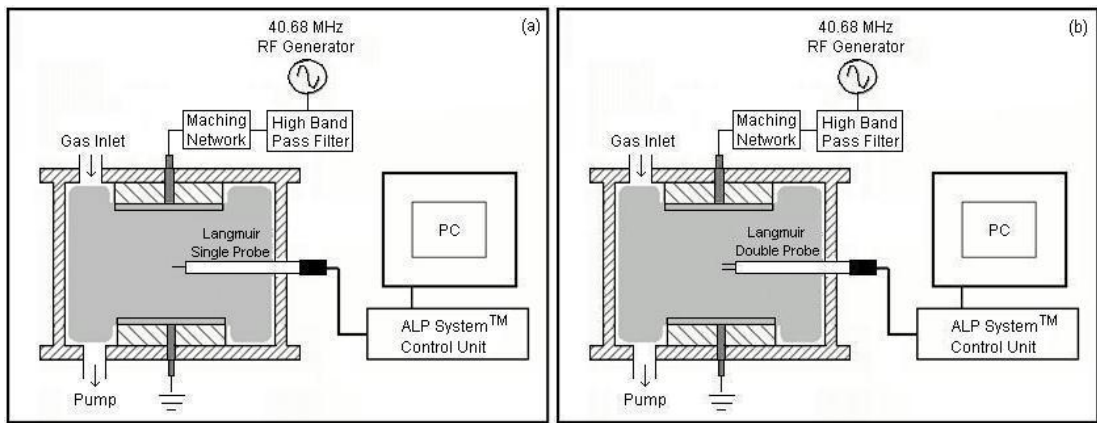


Figure 22. The experimental diagrams showing HF single RF-CCP diagnostic of a) single and b) double Impedans Langmuir probe systems.

For diagnostic measurements; a single and a double ALP “Automatic Langmuir Probe” System™ Langmuir probes “Impedans Ltd.” that controlled by ALP System™ control unit were placed between the electrodes in the plasma reactor separately as shown in the Figure 22 (a-b). The distance of the probes to the upper and the lower electrodes were 1.5 and 2.5 cm, respectively. Therefore, all diagnostic measurements were done in bulk plasma that is generated very close to the upper sheath region. In addition, the probes are DC and RF compensated. And, the tungsten probe tips were different in dimensions as a result of experimental challenges. Tip length of the single probe is “5 mm” while tip length of the double probe is “10 mm”.

Again, 99.995 % purity nitrogen gas was used as an activation gas for diagnostic analysis. The range of RF power was $P = 50 - 200$ Watt and the nitrogen gas pressure range was $p \approx 0.1 - 1$ Torr.

Langmuir Probe

Plasma diagnostic system is basically composed of three parts; probe, controller unit and computer. In this study, Impedans automatic Langmuir cylindrical single and double probes as seen in Figure 23 were used for characterization of HF single RF plasma.

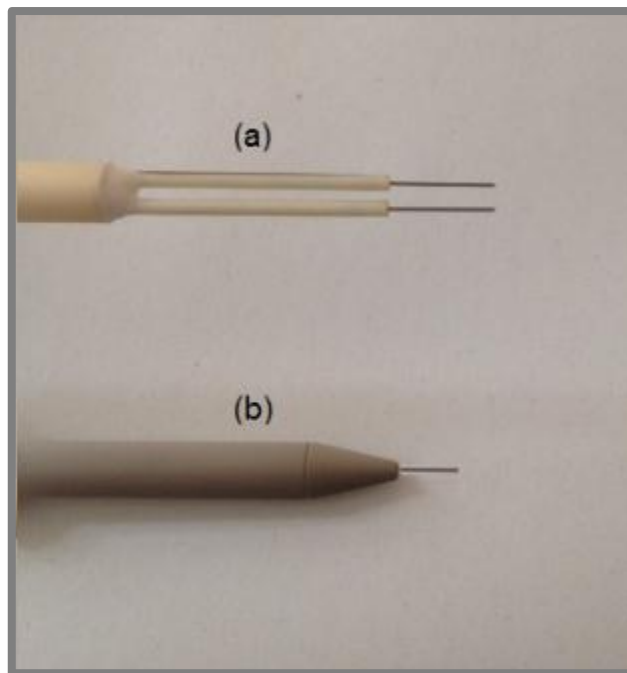


Figure 23. Photos of Impedans Langmuir (a) double probe and (b) single probe

Basically, both probe structures are the same. As seen from Figure 24, the tungsten probe tips “*standard dimensions: 0.4 mm in diameter and 10 mm long*” mounted in a push-fit cradle and the probe shaft are coated with ceramic to minimize plasma

distortion. And, there exist an integrated re-entrant $\frac{1}{2}$ inch ceramic tube in which RF filters are, a QC to KF hybrid adapter “*vacuum to 8 - 10 Torr*” and a termination enclosure [28].

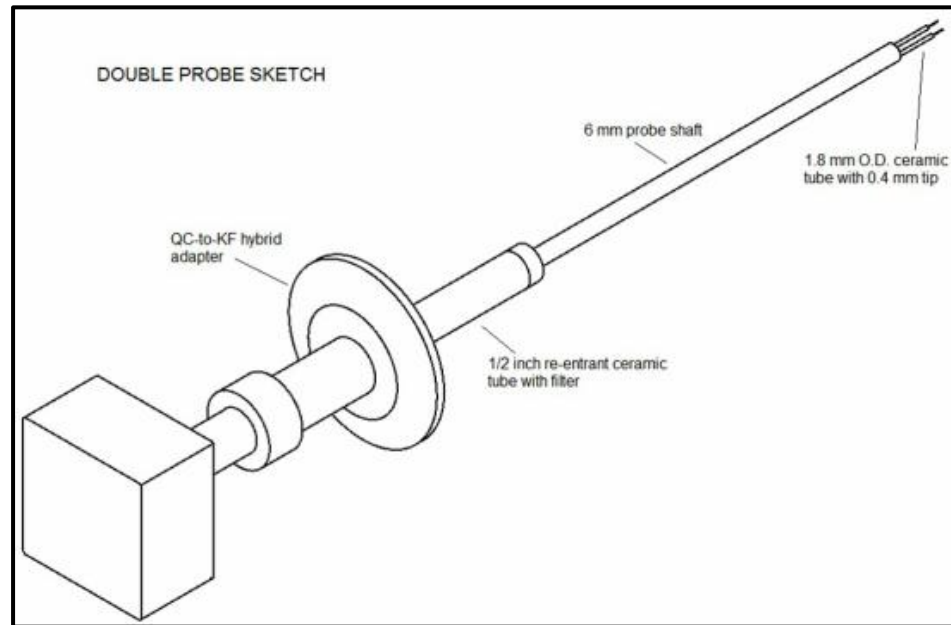


Figure 24. Dimensions of Impedans Langmuir double probe [28]

System Controller

Impedans ALP System™ controller shown in Figure 25 supplies a connection between probes and software program. The probes are connected to rear panel of the controller with BNC cables and the controller is connected to the PC with an USB cable.



Figure 25. Impedans ALP System™ controller

Main mission of this cotroller is performing the data acquisition, control and initial analysis of the Langmuir probe before passing the data to the ALP System™ software for analysis, display and data management with the use of electronics in it [28].

Software Program

Impedans ALP software program supplies the user real time plasma analysis with single and double probes separately. As soon as running the program, the screen is seen like shown in Figure 26. From this screen, the user can select the convenient section for the probe connected to the plasma reactor.

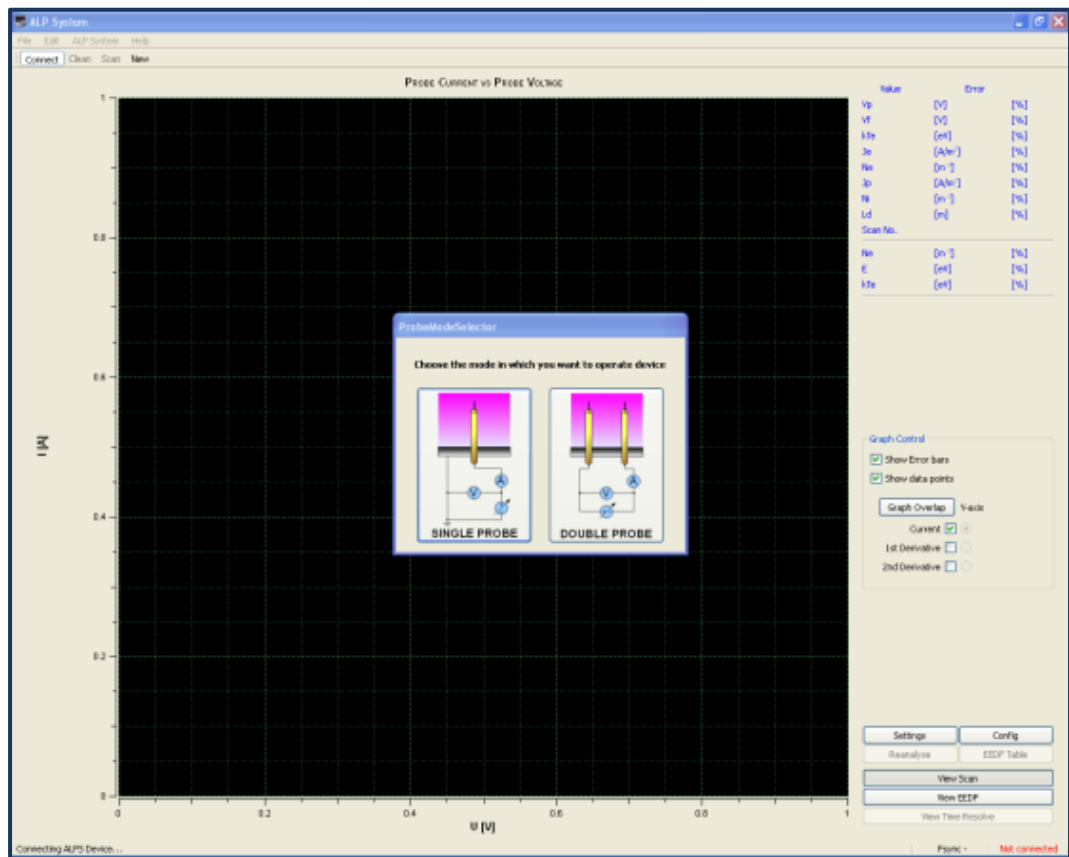


Figure 26. Impedans ALP software program

If the user is connected to the single probe section, he will come across a new screen seen like in the Figure 26. Before taking each data under different process conditions, the first step is controlling the values of process setting shown in Figure 27 by clicking on “Settings” button. From the Figure 27, there exists only one variable parameter for measurements and so value of the others must remain the same.

Parameter	Value	Unit
Probe radius	0.00025	[m]
Holder radius	0.002	[m]
Probe length	0.01	[m]
Probe resistance	0	[Ohm]
Ion Mass	28.08	[amu]
Gas temperature	300	[K]
Gas pressure	0.108	[Torr]
Vp Method	Use Intersecting Slopes	
DC Compensation	☒	
Collision cross-section		
Ion-Neutral	8.8e-19	[m²]
Electron-Neutral	4.14e-20	[m²]

Figure 27. Plasma process setting parameters for single probe RF plasma diagnostic

The second step is to apply appropriate bias voltage to the probe from “*Config*” button shown in the Figure 26. After clicking on this button, a panel shown in Figure 28 will appear on the main screen. From the voltages part of the panel, the users can apply appropriate bias voltage to the probe to get more correct results with less error.

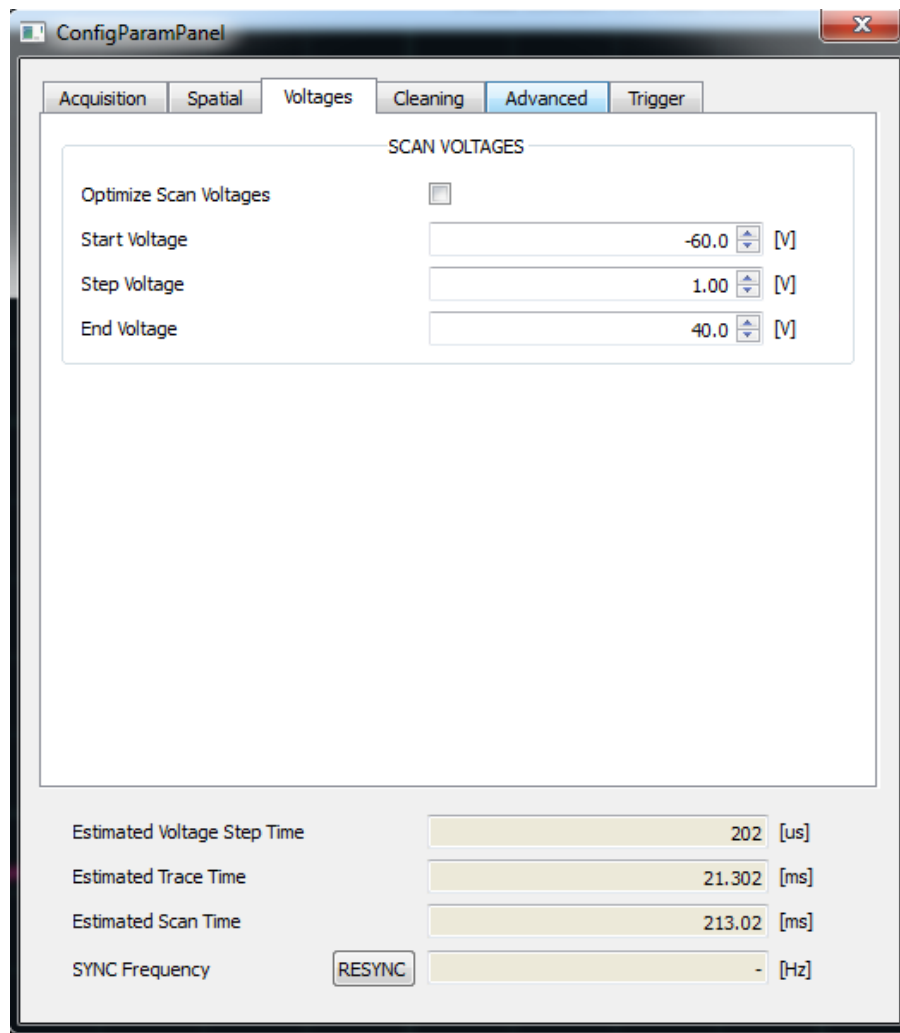


Figure 28. Configure parameter panel for single probe RF plasma diagnostic

The third step is to click on the “Scan” button that is located at the upper left hand corner of the screen in the Figure 26 to get CVC curve of the RF discharge as shown in Figure 29.

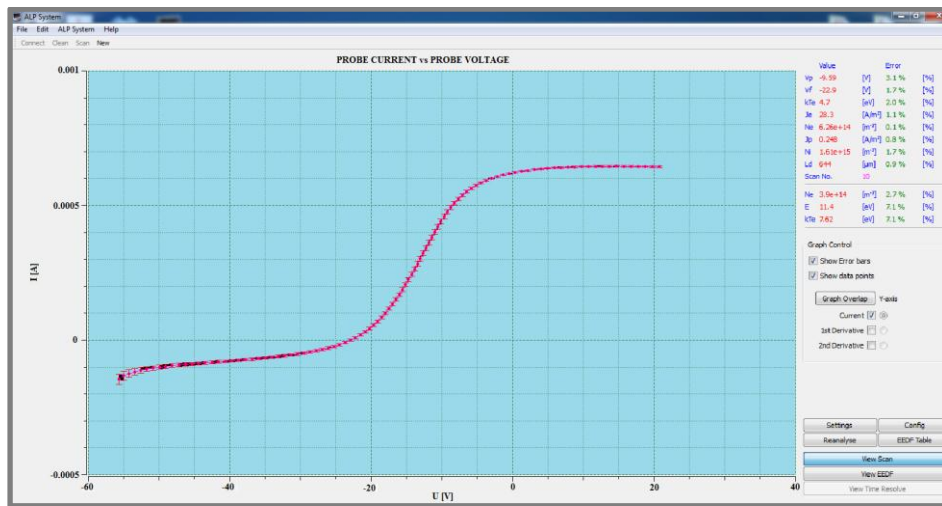


Figure 29. An example of CVC curve of the discharge obtained by Impedans Langmuir single probe system

Moreover, the first and second derivative of this curve can be seen together on the same screen like seen in Figure 30 as soon as checking the respective box seen on right side of the screen in the Figure 26.

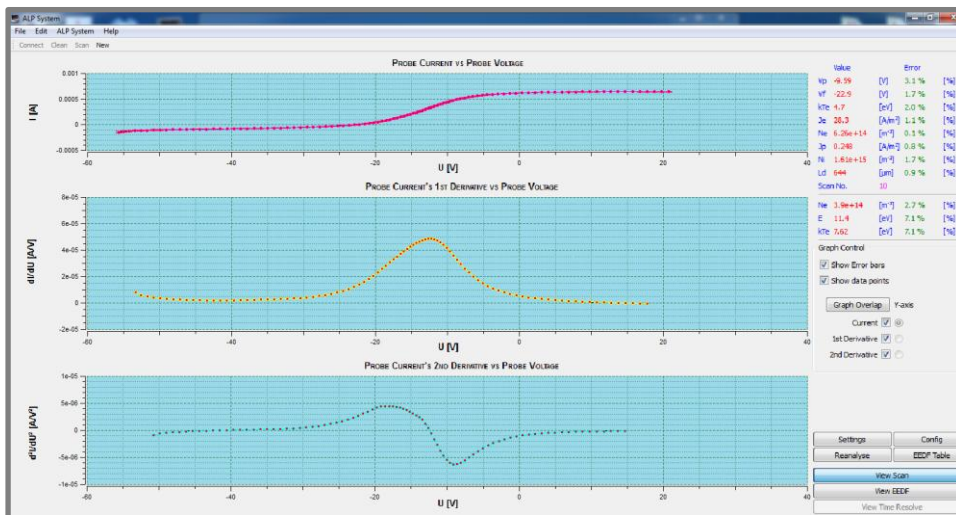


Figure 30. The CVC curve, first and second derivatives of the CVC of the discharge obtained by Impedans Langmuir single probe system

Furthermore, the single probe plasma diagnostic supplies the users a deeper analysis including EEDF profile with its calculated parameters seen in Figure 31.

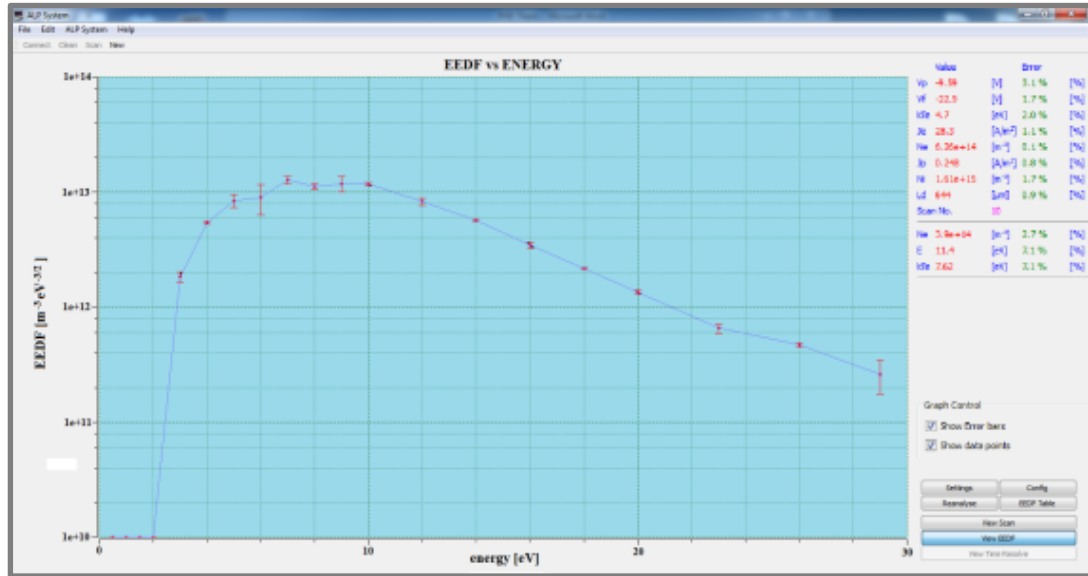


Figure 31. Electron energy distribution function versus energy graph of the discharge obtained by Impedans Langmuir single probe system

If the user wants to do RF discharge diagnostic experiments by using double probe, the same software program would be used only by clicking on the “*Double Probe*” button seen in the Figure 26 after changing the single probe system that is connected to the chamber with the double probe system. After that, it is so important to check the values of parameters shown in Figure 27 to protect the probe tip dimensions during cleaning operation. Again like in the single probe, the unique variable parameter for each measurement in this part is gas pressure after entering the correct values once. And then, CVC curve of the discharge appears on the screen like seen in Figure 32.

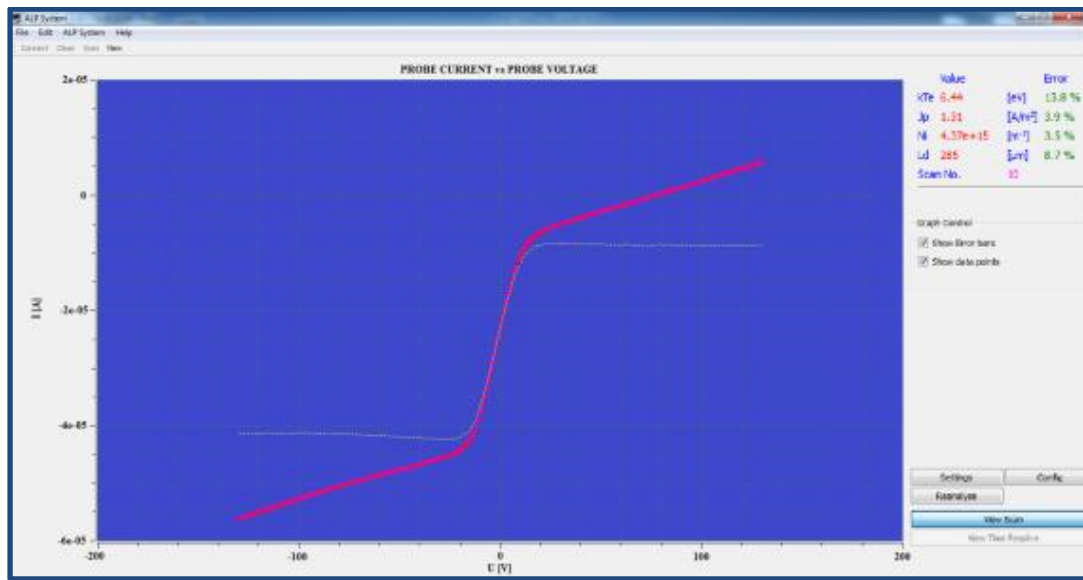


Figure 32. An example of CVC curve of RF discharge obtained by Impedans Langmuir double probe system

As seen from the Figure 32, the curve and the calculated results are different from those of a single probe. As mentioned in the section “*Double probe theory*”, there are two curves and the yellow one is the corrected one that is essential curve for calculations. Additionally, learning about the first and second derivatives of the curve and also EEDF of the discharge are not possible with this type of probe system.

PAN-based Carbon Fiber

We bought our carbon fibers from AKSA Company in Yalova / TURKEY in 2010 shown in Figure 33.



Figure 33. Pictures of PAN-based carbon fibers manufactured by AKSACA™ [75]

They were A-42 model 12K “12000 filaments in each fiber” unsized “no coatings on the surface of fibers” PAN-based carbon fibers which have higher tensile strength in the range of 600 Ksi / 4200 MPa and standard modulus 34 Msi / 240 GPa as seen in Table 2.

Table 2. Mechanical properties of A - 42 model 12K PAN-based carbon fibers that used in the experiments [76]

	English		Metric		Test Method
Tensile Strength	610	Ksi	4200	MPa	ISO 10618
Tensile Modulus	34.8	Msi	240	GPa	ISO 10618
Strain	1.8	%	1.8	%	ISO 10618
Density	0.064	lbs/in ³	1.76	g/cm ³	ISO 10119
Yield	1.862	ft/ lbs	800	g/1000m	ISO 1889

Manufacturing process of the carbon fibers in AKSA Company is mentioned in Figure 34.

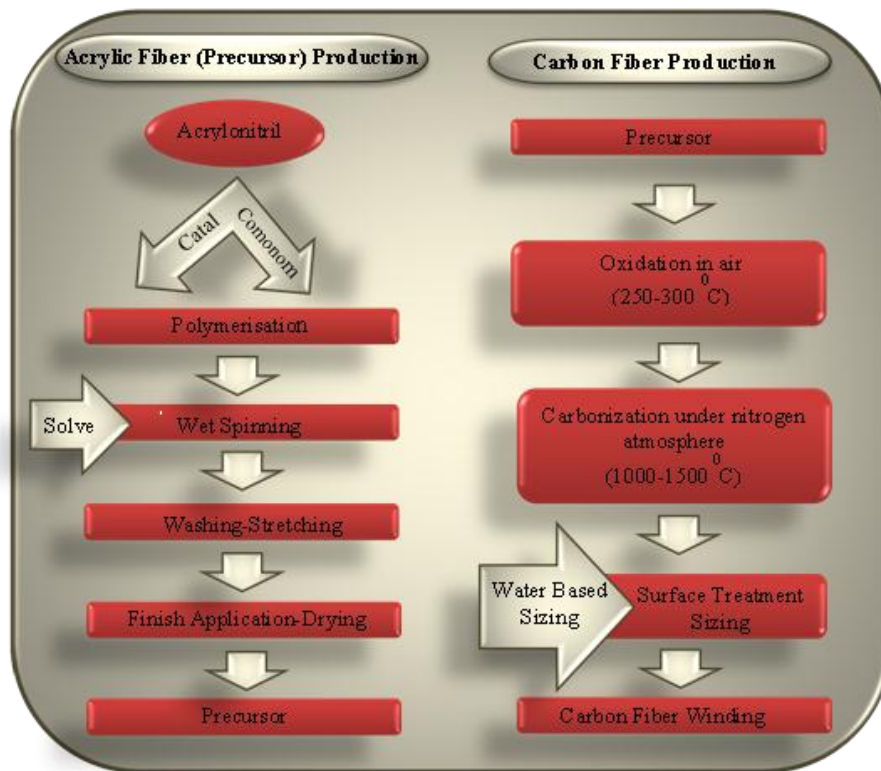


Figure 34. Production processes of AKSACA™ PAN-based carbon fibers and its precursor

Raman Spectroscopy

The WITec Scanning Near-field Optical Microscope “*alpha300 S*” seen in Figure 35 is the general name of used instrument to get Raman spectrum of the carbon fibers. This instrument supplies researcher three different operating modes: SNOM “*alpha300 S*”, Atomic force microscopy “*alpha300 A*” and confocal Raman microscopy “*alpha300 R*”. It is easy to use these three different modes separately only by rotating objective turret of the instrument.



Figure 35. Picture of WITec Alpha300 S [77]

We used confocal Raman microscopy mode shown in Figure 36 to analyze the surface structure of the fibers. This mode integrates an ultrahigh-throughput confocal microscope with an extremely sensitive spectroscopy system for unrivaled resolution and chemical sensitivity. It supplies nondestructive Raman imaging with optical resolution down to “ 200 nm ” laterally, “ 500 nm ” vertically and spectral resolution down to “ 0.02 wavenumbers ”. For a single spectrum, the acquisition time is significantly less than “ 100 ms ”. This is important to collect images with tens of thousands of spectra in a few minutes. This system also minimizes unwanted background signals, enhances contrast, and provides depth information [78].

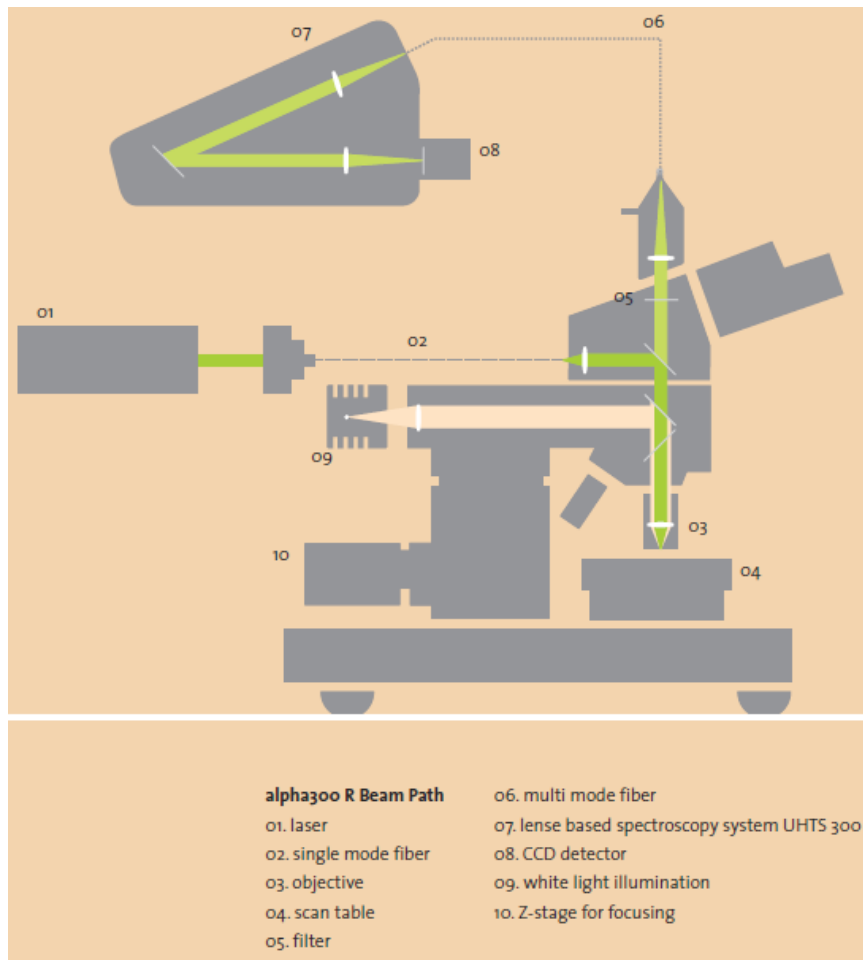


Figure 36. Diagram of WITec confocal Raman microscopy [78]

Confocal Raman microscopy setup is mainly composed of two parts: Operating system and ultra-high “up to 70 %” throughput WITec UHTS 300 spectroscopy system [78]. As you see from Fig. 13, first of all, a 532 nm He-Ne laser with a power ~ 100 mW is focused onto the carbon fiber sample by objectives. Focusing process is easy with different objectives “ $\times 100$, $\times 50$, and $\times 20$ ”, white light illumination and all axis control stages with “4 nm” lateral and “0.5 nm” vertical positioning accuracy. This laser light excites the surface by inducing vibrations of the chemical bonds within the sample. Then, spectrometer collects scattered lights from the surface with chemical information after filtering photons that have the same wavelength with the

that of excitation laser and send them to the CCD camera detector connected to a powerful computer and WITec special software system. Lastly, obtained Raman spectrum is seen on the screen of the computer as shown in Figure 37.

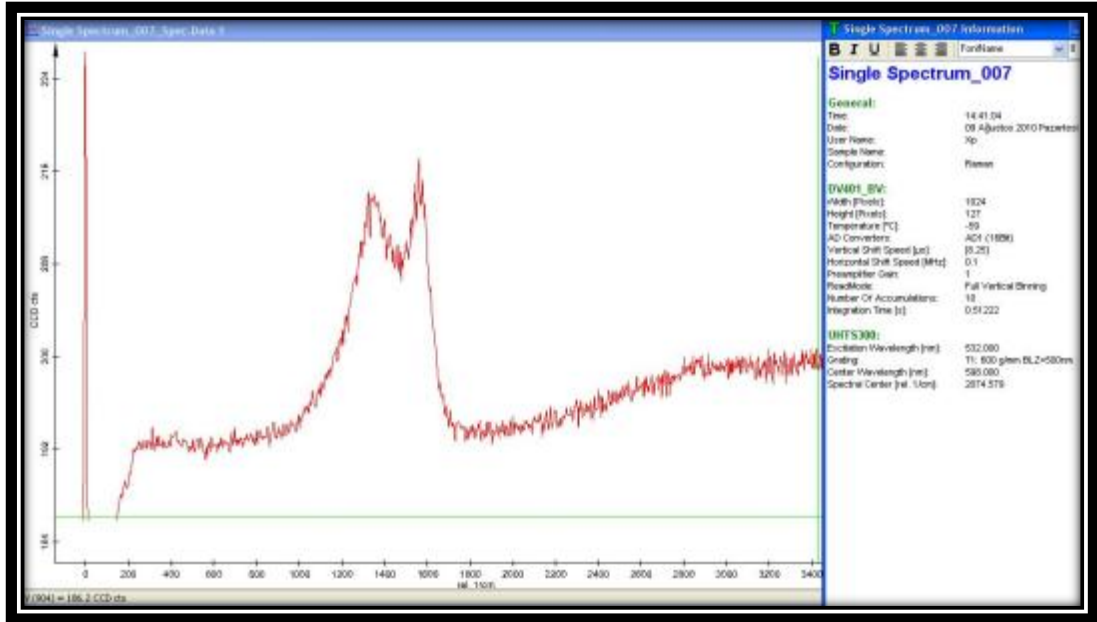


Figure 37. Raman spectrum of carbon fiber taken by WITec software

In fact, atoms and bonds are different in each material and this is resulted in having unique Raman spectrum. Therefore, identifying the structural changes on the surfaces of each material is very easy by investigating this own special Raman spectrum. Therefore, Raman spectra are scanned from 0 to 3400 cm^{-1} to detect the first-order D and G bands of the carbon fibers. “Origin Pro8” software program was used for data analyzing according to Lorentz curve fitting model that is defined as:

$$y = y_0 + \frac{2A}{\pi} \frac{\omega}{4(x-x_0)^2 + \omega^2} \quad (45)$$

where;

y_0 = baseline offset

A = total area under the curve from baseline

x_0 = center of the peak (cm^{-1})

ω = full width of the peak at half height “*FWHM*”.

Among these fitted parameters, the area “ A ” represents integrated intensity of the peaks which can be used in calculation of relative intensity ratios: I_D / I_T and I_G / I_T , where I_D is integrated intensity of the D-peak, I_G is integrated intensity of the G-peak and I_T is total integrated intensity of these two peaks “ $I_D + I_G$ ”.

Though there is one more fitting model “*Gaussian*” in the Origin program, the Lorentzian multiple peak fitting was chosen in this work with respect to some previous experimental studies [56, 79]. Since, there is no remarkable reason for deciding the type of fitting curve and Lorentzian fitting is usually preferred to use in analysis of disordered carbon crystal [80]. And, an example of fitted Raman spectra with its parameters is shown in Figure 38.

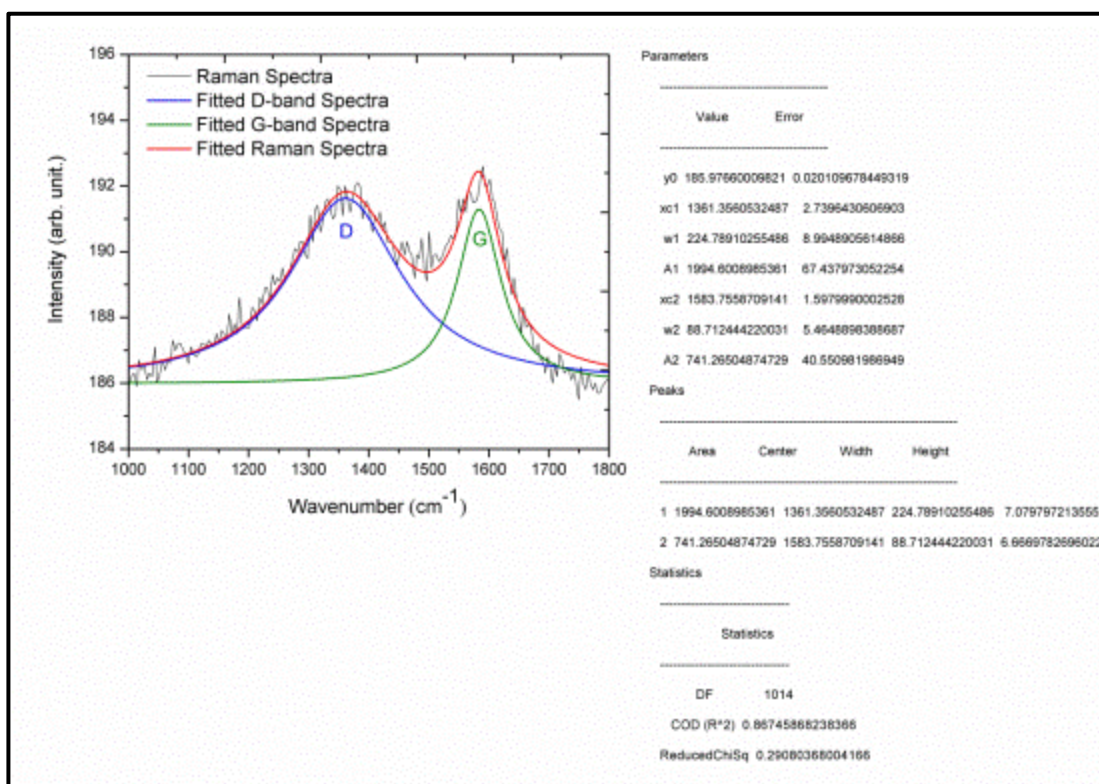


Figure 38. An example of Lorentzian multiple-peak fitted Raman spectra of a treated carbon fiber with its parameter results. Treatment conditions: single RF-N₂ discharge, 1 Torr, 200 Watt, 90 min

FT-IR Spectroscopy

Bruker Equinox 55 FT-IR spectrometer in the transmission mode shown in the following Figure 39 was used to analyze existence and types of chemical bonds in the crystalline structures of untreated and some treated carbon fibers listed in Table 6. At the beginning, a background “reference” spectrum without sample was obtained to measure percentage transmittance of the samples. Then, the scan range of light was set to Mid-IR “400 - 4000 cm⁻¹”. Again, all FT-IR spectrums were analyzed by using the Origin Pro8 software program.

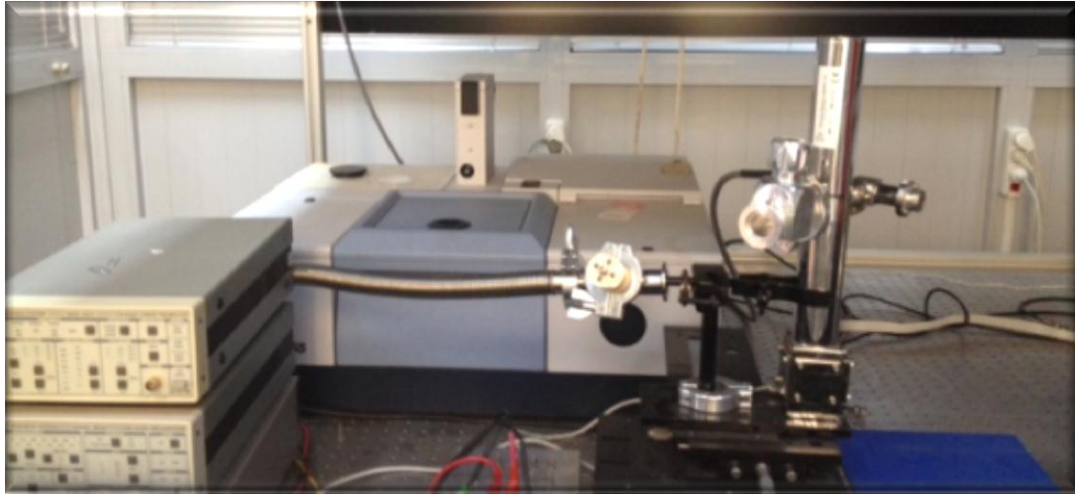


Figure 39. Photo of FT-IR spectroscopy system

The spectrometer is composed of five main parts: a sample box, interferometer that is controlled by a 632.8 nm - 1 mW He - Ne laser, a source box, a power supply box and a detector box. The frequency range of the spectrometer is 370 - 7500 cm^{-1} and its resolution is better than 0.5 cm^{-1} .

Measurement of Tensile Strain

5969MTS model Instron micromechanical tester machine shown in Figure 40 is used for tensile strain measurement of the treated and the reference carbon filaments listed in Table 5. The Instron universal mechanical tester is also called as “*pull tester*” that can measure tensile strain of the sample with its tensile static mode.

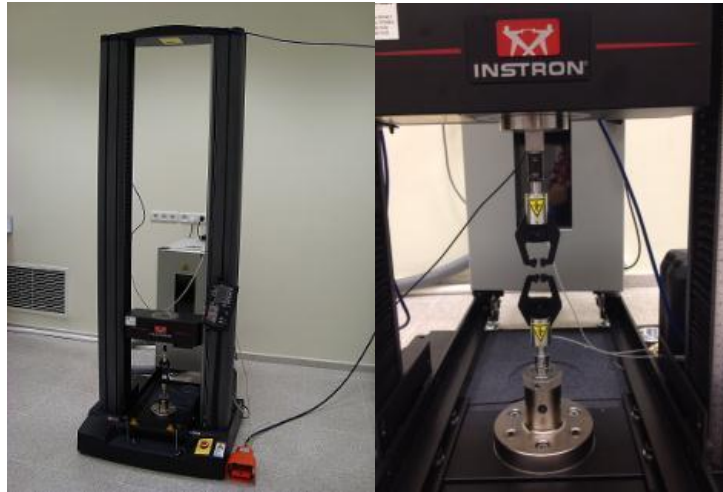


Figure 40. Photos of Instron micromechanical analyzer

The load cell connected to the jaws of the machine can resist on maximum 10N forces that supplies more sensitive measurement for very thin carbon filament samples. The distance between the jaws of the machine is set to 25 mm that is also equal to the length of prepared samples as seen in the Figure 41.

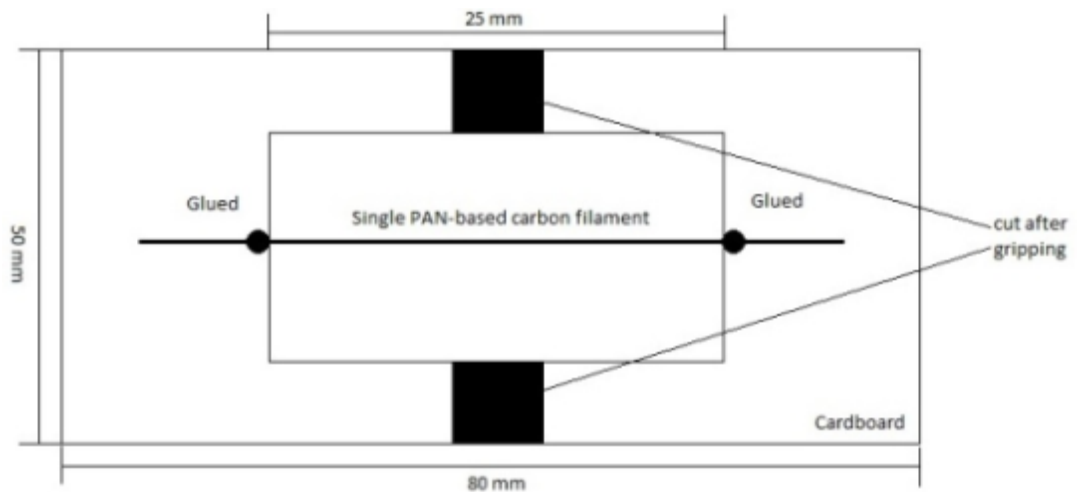


Figure 41. Schematic of cardboard designed for a single carbon filament tensile strain testing

For the strain measurement experiment, firstly, sample cardboard attached to the jaws. Secondly, the black parts of the cardboard shown in the Figure 41 are cut by scissors. Thirdly, all parts of the machine are balanced “zeroing force applied to the jaws” automatically. Then, the software program is opened and a special testing method is identified according to our sample properties. With the use of this method, an applied force versus extension graph that gives tensile strain of this sample shown in Figure 42 is obtained.

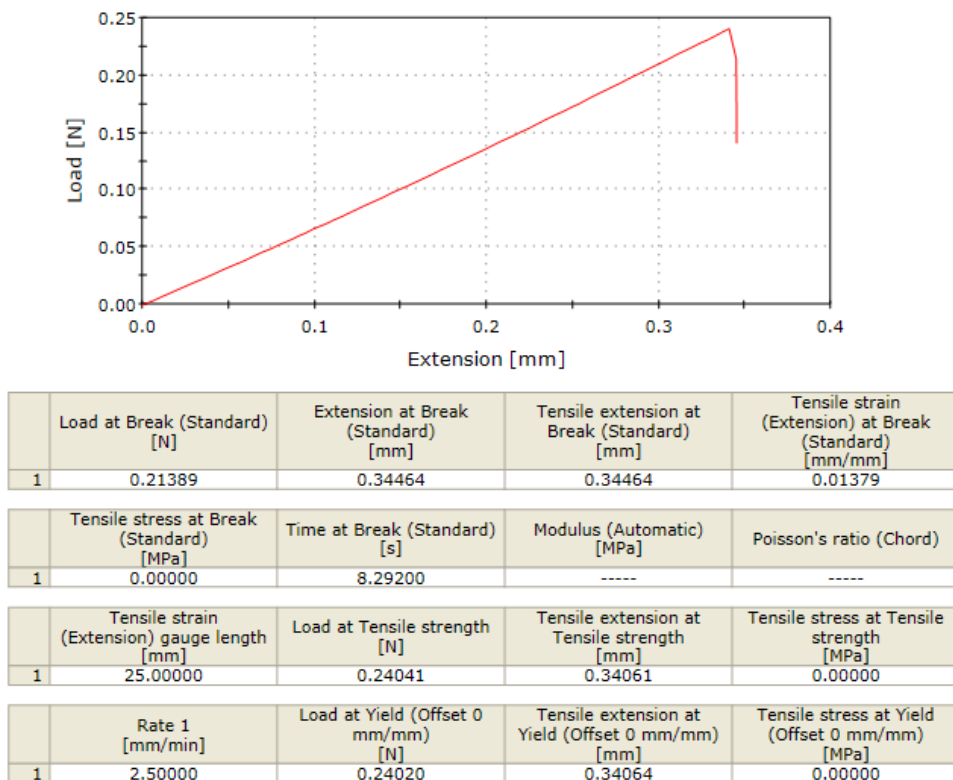


Figure 42. Force-extension graph and analysis results of untreated “as-received” carbon filament that are obtained by the use of Instron testing machine

CHAPTER 4

RESULTS AND DISCUSSION

Langmuir RF Probe

According to previous experimental studies, density of the plasma and electron temperature are in the range of $N \approx 10^{14} - 10^{19} \text{ m}^{-3}$ and $T_e \approx 1 - 10 \text{ V}$ where $T_e \gg T_i$ for weakly ionized low pressure “ $p \approx 1 \text{ mTorr} - 1 \text{ Torr}$ ” capacitive coupled RF discharges [1].

Langmuir Single RF Probe

Diagnostic of high frequency “40.68 MHz” single RF-CCP that were generated in the power range of $P = 50 - 200 \text{ Watt}$ and pressure range of $p \approx 0.1 - 0.8 \text{ Torr}$ was done by using Impedans Langmuir single probe. Some important experimental results are in the range of $N_e \approx 10^{13} - 10^{15} \text{ m}^{-3}$, $N_i \approx 10^{11} - 10^{17} \text{ m}^{-3}$, $kT_e \approx 3.3 - 37.5 \text{ eV}$. In addition, according to the Eqs. 1 and 2, pressure and power dependences of the electron current density square are shown in Figure 43 and Figure 44 for analysis of heating mechanism in the HF single RF-CCP.

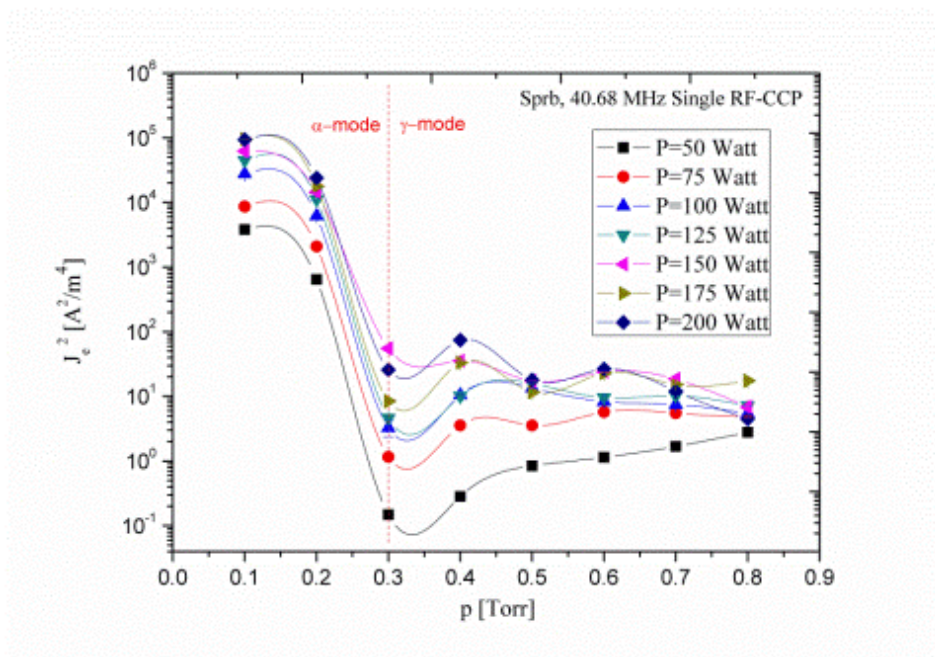


Figure 43. Electron current density square “ J_e^2 ” as a function of the gas pressure in the HF single RF mode

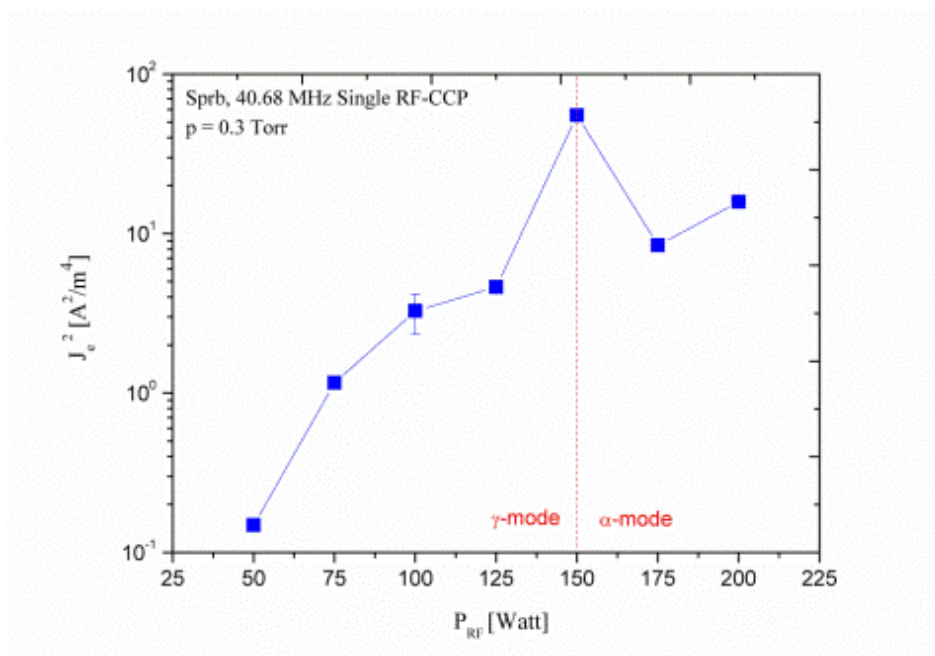


Figure 44. Electron current density square “ J_e^2 ” as a function of the HF-RF power in the single RF mode at $p = 0.3$ Torr

From the Figure 43, a sharp decrease in the electron current density is clearly seen when the nitrogen gas pressure is $p = 0.3$ Torr and then slight changes are observed with pressure. At low pressures “ $p < 0.3$ Torr”, low energetic electrons in the bulk plasma do not achieve to dc ambipolar potential barrier to pass through the sheath region and so they are heated by collisionless heating in the bulk plasma. When the value of the pressure becomes sufficiently high “ $p > 0.3$ Torr”, the electrons in the bulk plasma gains more energy and they move toward to the sheath region that collisional heating takes place [81, 82]. Because of this movement, electron current in the bulk plasma decreases. Therefore, the pressure “ $p = 0.3$ Torr” is $\alpha - \gamma$ heating transition point which means that the RF discharge generated at $p < 0.3$ Torr is in the α -mode “*collisionless or Stochasting*” whereas it is generated at $p > 0.3$ Torr is in the γ -mode “*collisional or Ohmic*”. In addition, from the Eqs. 1 and 2, there can be another transition point “ $\gamma - \alpha$ mode” that is related to the RF voltage “ V_{RF} ” or RF power “ P_{RF} ”. Therefore, the RF power dependence of J_e^2 in the RF plasma generated at $p = 0.3$ Torr is investigated as shown in Figure 44. From the Figure 44, $P = 150$ Watt is the $\gamma - \alpha$ mode transition point due to a sharp decrease in the value of the bulk discharge current after that power. Therefore, the generated RF-CCP at $P < 150$ Watt is in the γ - mode “*collisional or Ohmic*” while it generated at $P > 150$ Watt is in α - mode “*collisionless or Stochasting*” [83]. In collisional heating mode, high ionization in the bulk plasma takes place because of secondary electron emission from the electrodes [84] and so the generated electron current increases with power. However, when the RF power becomes 150 Watt, the generated electrons gain sufficiently high energy to escape from the bulk plasma toward to the sheath region. Therefore, the electron current that is in the bulk plasma region decreases and again only low energetic particles that are heated by collisionless collapse in the bulk plasma. Also, accuracy of the transition point analysis is proved by the investigation of pressure dependence of density and electron energy profile of the low energetic electrons in the bulk plasma [81] and pressure dependence of ion density as shown in Figure 45. Because, the energy of the low energetic electrons increases with pressure after being in the collisional regime and then density of these particles in the bulk plasma region

decreases due to achieving dc ambipolar potential barrier to pass through the sheath region [84].

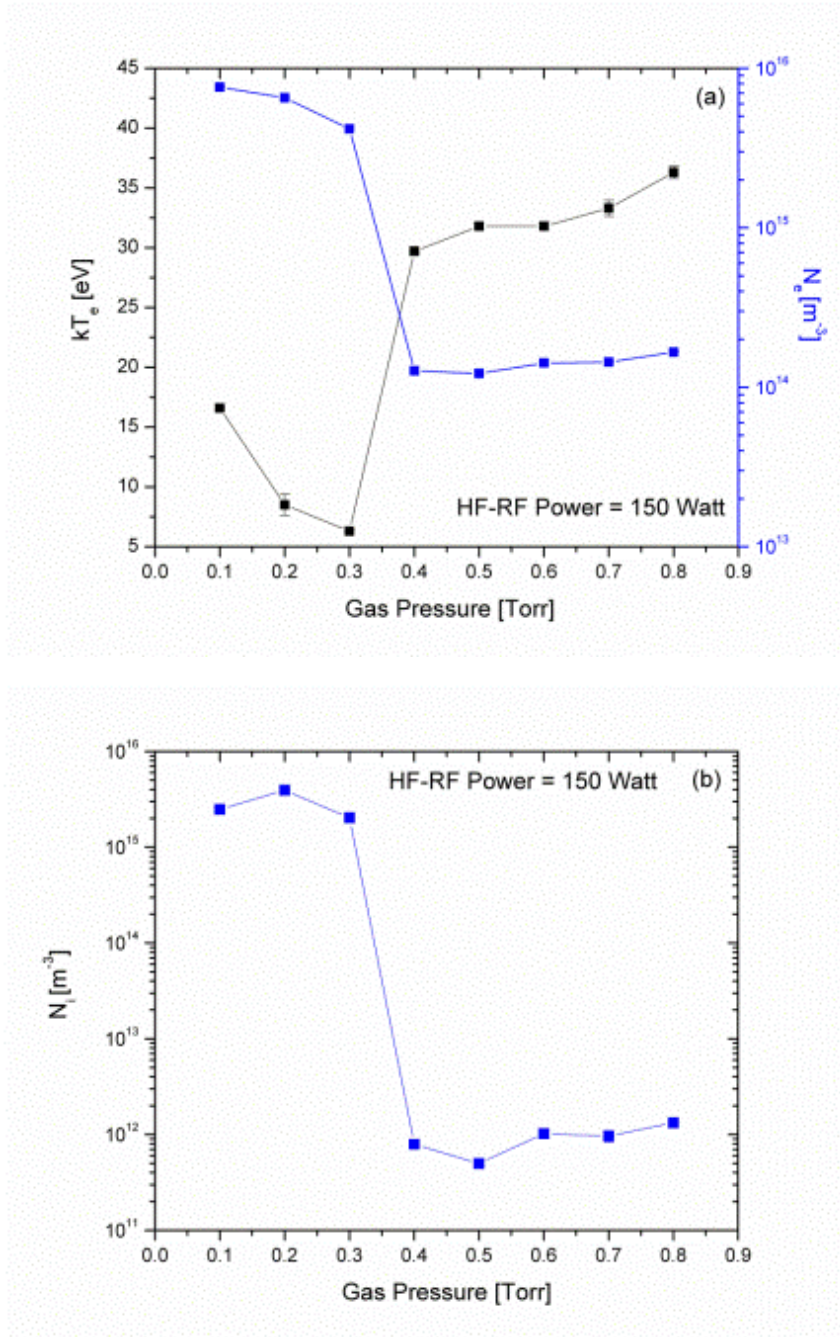


Figure 45. Nitrogen gas pressure dependence of a) density and temperature of electron and b) ion density in the bulk plasma at P = 150 Watt

Additionally, power dependence of density and electron energy profile of the low energetic electrons and ion density in the bulk plasma are examined in Figure 46. As compared to the pressure effect, power effect on heating mechanism is weak because the gas pressure is one of the most important RF discharge controlling parameter [81]. From the Figure 46-a, at RF powers “ $P < 150 \text{ Watt}$ ” for constant gas pressure “ $p = 0.3 \text{ Torr}$ ”, temperature of the low energetic particles that are heated by collisional heating in the bulk plasma decreases with power due to decrease in electric field strength in the bulk region and also high sheath voltage that causes cold electrons in the bulk region. Thus, the density of the electrons increases because of being imprisoned in dc ambipolar potential barrier [82]. At $P = 150 \text{ Watt}$, a small increase in temperature and a decrease in density are observed on account of heating mode transition “ $\gamma - \alpha$ ”. Then, when the powers are $P > 150 \text{ Watt}$, the decrease in electrons temperature and the increase in electron density are dramatically occur. From the Figure 46-b, the power dependence of the ion density is almost the same with that of electron density as shown in the Figure 46-a. Also, this similarity is shown in the Figure 45. The main reason of this is that the more electrons in the space mean the more collisions with other particles and that are resulted in more ion generation.

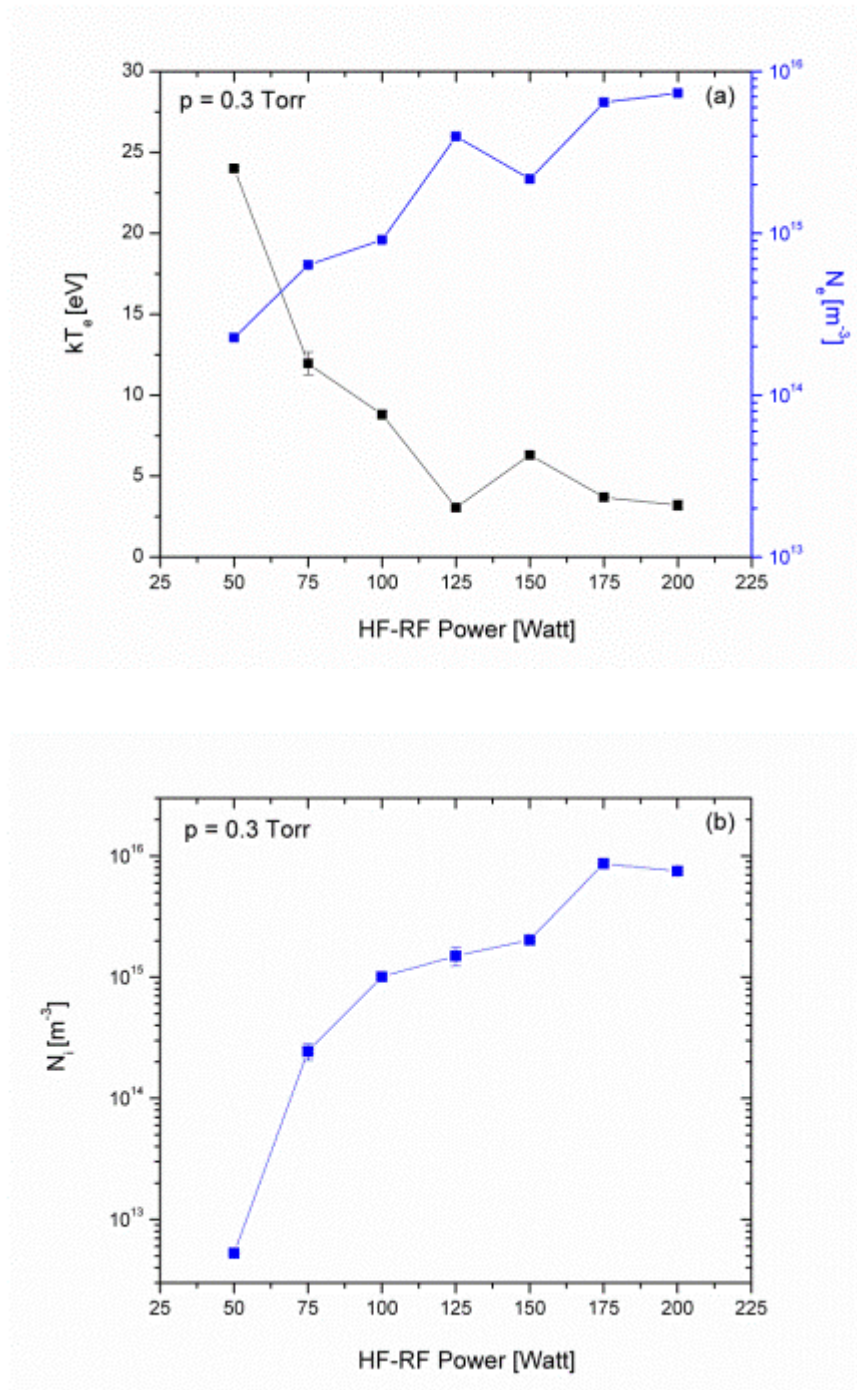


Figure 46. HF-RF power dependence of a) density and temperature of electron and b) ion density in the bulk plasma at $p = 0.3$ Torr

Langmuir Double RF Probe

In addition to a single probe analysis, all the experiments were also repeated with the Impedans Langmuir double probe. In fact, it is not possible to measure electron density and electron current density and so to analyze electron heating transition point in the RF-CCP by using double probe. The only measured important plasma parameters are N_i and kT_e . And, the experimental results are: $N_i \approx 10^{15} - 10^{16} \text{ m}^{-3}$, $kT_e \approx 4.77 - 12.2 \text{ eV}$. Also, as seen from Figure 47, the value of the ion density in the generated RF-CCP is high for all discharge conditions especially sharp increase is shown at $p = 0.3 \text{ Torr}$ as seen in the Figure 47-b. Moreover, the range of kT_e is smaller than that of the single probe because it is the energy of electrons located at the tail of the EEDF. In addition, from Figure 48, the electron energy increased after $p = 0.3 \text{ Torr}$.

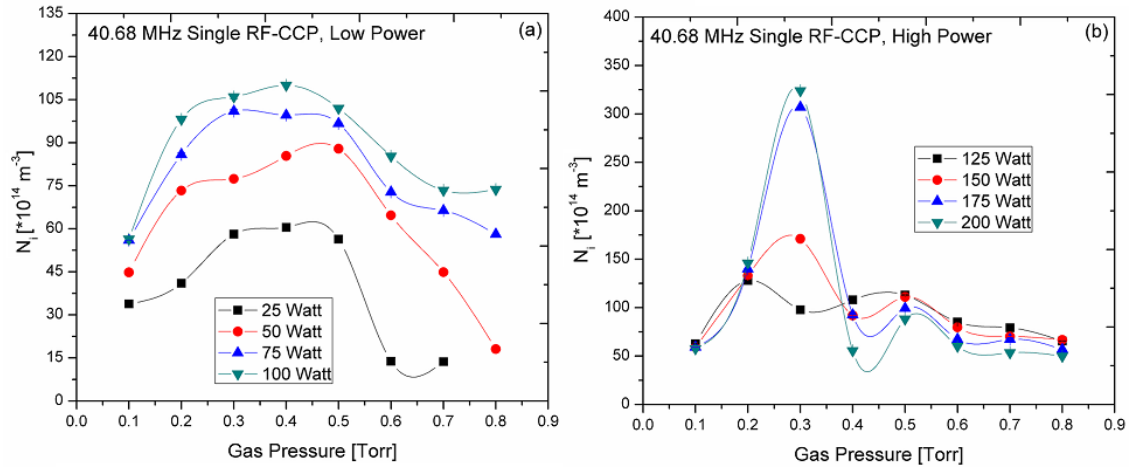


Figure 47. (a) Pressure and low HF-RF power dependence of ion density in a single RF plasma that measured by double probe and (b) pressure and high HF-RF power dependence of ion density in single RF plasma that measured by a double probe

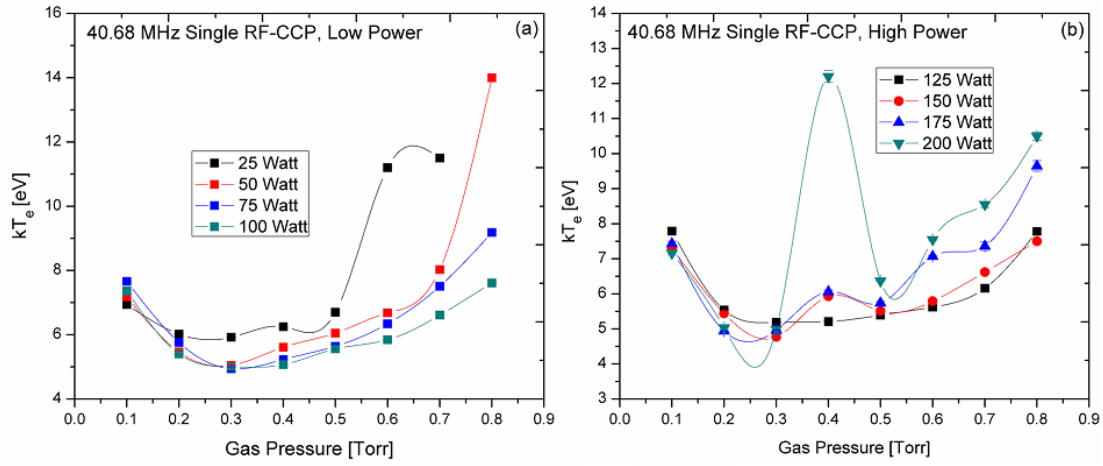


Figure 48. (a) Pressure and low HF-RF power dependence of energy of electrons in a single RF plasma that measured by a double probe and (b) pressure and high HF-RF power dependence of energy of electrons in a single RF plasma that measured by a double probe

Analysis of Physical Quantities

Disorder/Order Analysis after Single RF-CCP Treatment

Effects of applied N_2 pressure and HF-RF power

Short time ($t = 30$ min) treatment

At pressures " $p < 0.5$ Torr", there is no significant HF-RF power effect on structure whereas it is clearly seen at pressures " $p > 0.5$ Torr" as seen in Figure 49-a. Except at $P = 200$ Watt, the level of ordering structure increases with pressure.

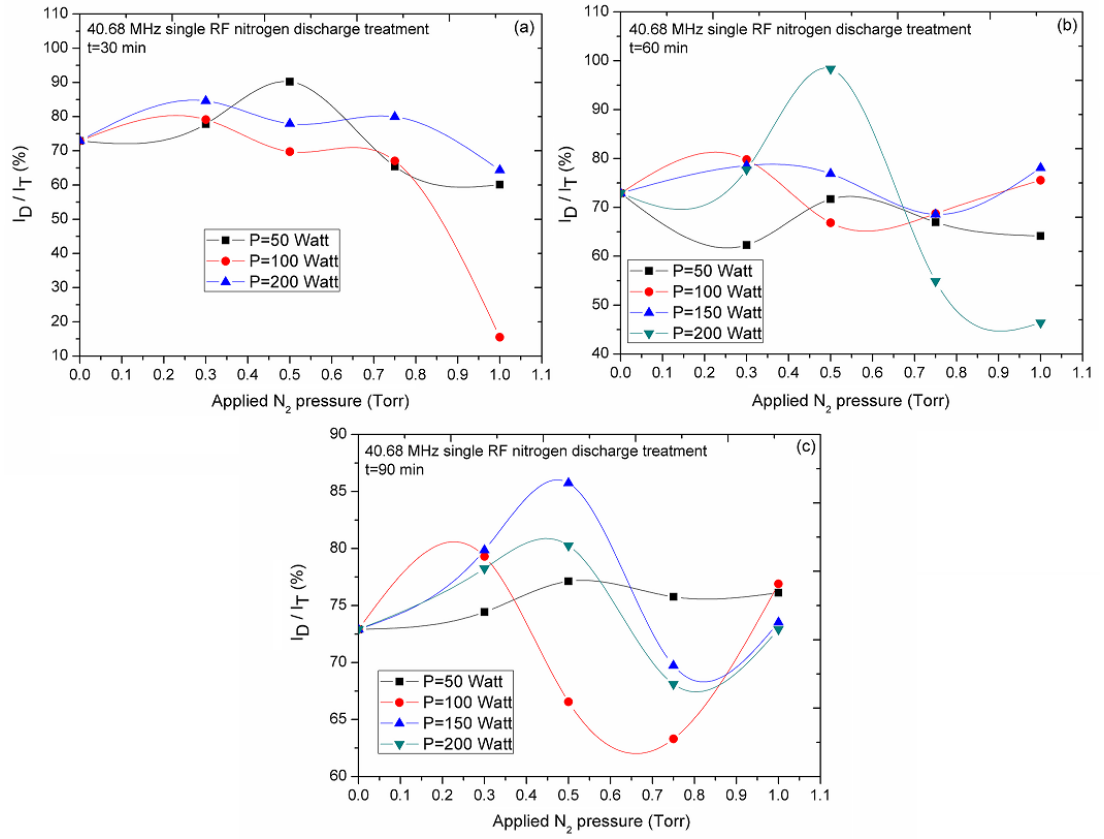


Figure 49. Effects of applied N_2 pressure and HF-RF power on the order/disorder structure of the carbon fibers treated under different treatment times; (a) 30 min, (b) 60 min and (c) 90 min

Long time ($t \geq 60$ min) treatment

As shown in Figure 49 (b-c), at pressures “ $p \leq 0.5$ Torr”, the level of disordering increases with HF-RF power due to collisionless “*non-Ohmic*” and low Ohmic electron heating while ordering level increases with HF-RF power when “ $p > 0.5$ Torr” because of high collisional “*Ohmic*” electron heating [85].

Effects of HF-RF power and treatment time

Low gas pressure ($p \leq 0.5$ Torr) treatment

As shown in Figure 50 (a-b), when the value of HF-RF power is increased during treatment process, the level of disordering in carbon fibers structure increases on account of being bombarded by high density vibrational excited particles [86, 87]. In fact, basal plane of the treated carbon fibers are destroyed by these excited species and so the number of carbon atoms in the edge plane of the fibers increases that resulted in high-level disordered structure [88].

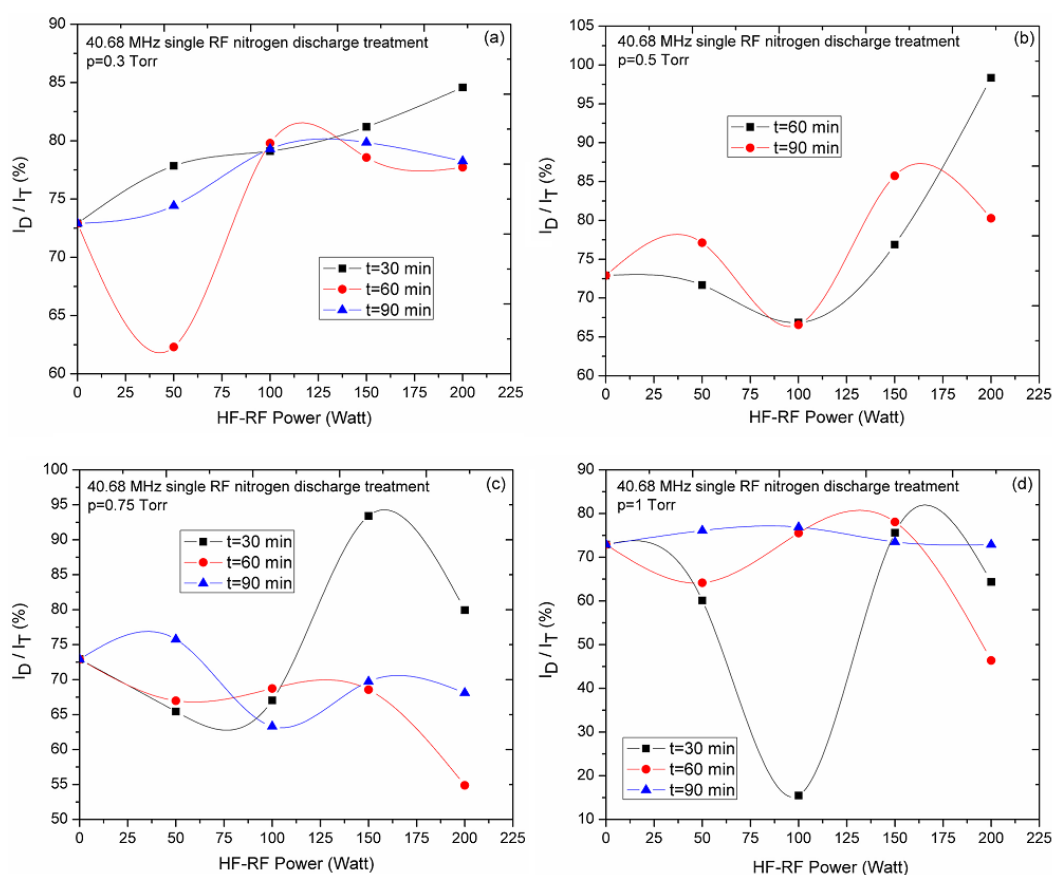


Figure 50. Effects of HF-RF power and treatment time on the order/disorder structure of the carbon fibers treated under different applied N_2 pressures; (a) 0.3 Torr, (b) 0.5 Torr, (c) 0.75 Torr and (d) 1 Torr

High gas pressure ($p > 0.5$ Torr) treatment

From Figure 50 (c-d), at $P \leq 100$ Watt, the degree of ordering in crystalline structure of carbon fiber treated under short time “ $t = 30$ min” increases with HF-RF power. On the other hand, the degree of disordering increases at $P > 100$ Watt treatment process. When treatment time becomes 60 min, ordering level increases with HF-RF power as seen in Figure 50 (c-d). In addition, almost none structural change is observed with HF-RF power at high pressure-90 min treatment.

Effects of applied N_2 pressure and treatment time

Low HF-RF power ($P \leq 100$ Watt)

From Figure 51-a, at pressures “ $p \leq 0.5$ Torr”, the level of disordering increases with pressure for 30 min treatment whereas it decreases when the treatment pressures are $p > 0.5$ Torr. With increasing treatment time to 60 min, ordered crystalline structure of carbon fibers are obtained. Moreover, 90 min is very long treatment time to observe structural changes. At 100 Watt treatment, structural effects of time and pressure are explicitly is seen when the pressures are $p > 0.5$ Torr as shown in Figure 51-b.

High HF-RF power ($P > 100$ Watt)

As shown in Figure 51-c, at pressures “ $p \leq 0.5$ Torr”, the amount of disordered structure increases with pressure. However, at pressures greater than 0.5 Torr, the degree of ordering increases. From Figure 51-d, at 200 Watt treatment, only the structure of the carbon fibers treated by 60 min changes. It becomes more disordered at pressures “ $p \leq 0.5$ Torr” and it is more-ordered with pressures “ $p > 0.5$ Torr”.

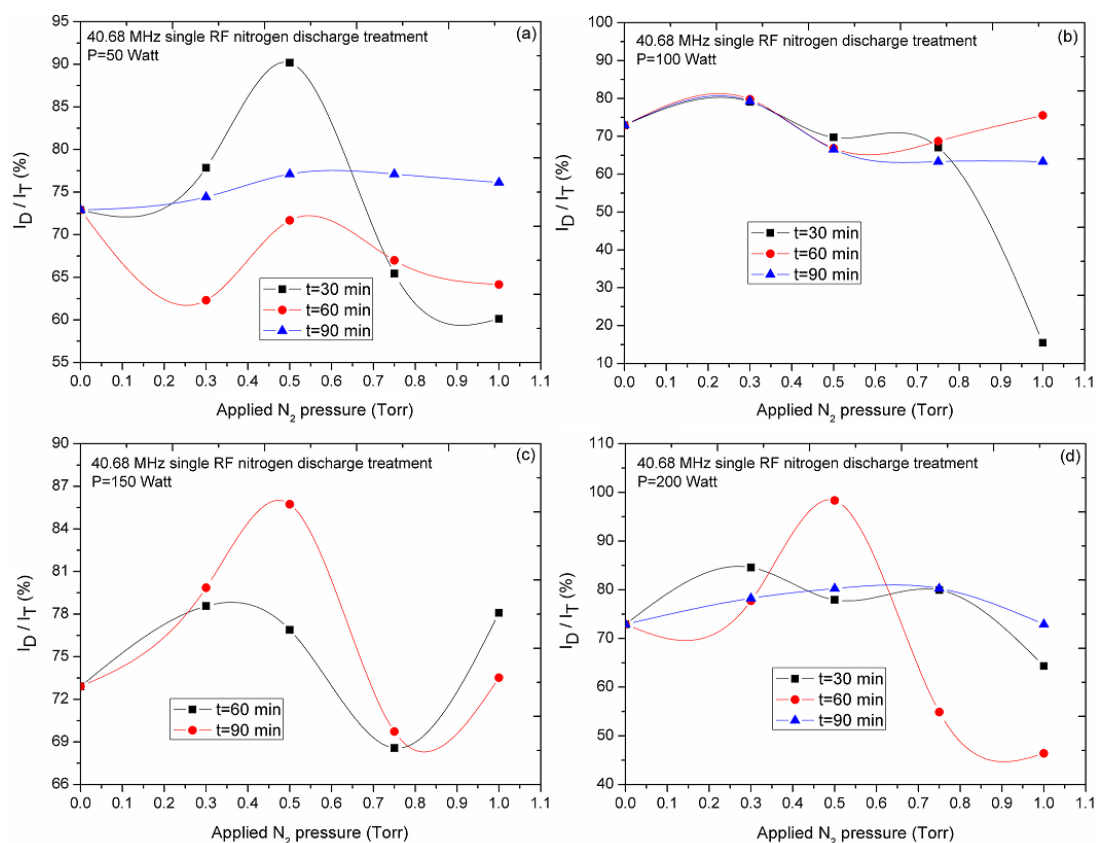


Figure 51. Effects of applied N_2 pressure and treatment time on the order/disorder structure of the carbon fibers treated under different HF-RF powers; (a) 50 Watt, (b) 100 Watt, (c) 150 Watt and (d) 200 Watt

Disorder/Order Analysis after Dual RF-CCP Treatment

Effects of applied N_2 pressure and LF-RF power

Short time treatment

As shown in Figure 52 (a-b), at $P = 50$ Watt treatment, the pressure effect on crystalline structure of carbon fiber is almost zero. From the Figure 52-a, the most pressure dependent LF-RF power for treatment applications is 100 Watt. The amount

of ordered structure of carbon fibers treated at this power increases with pressure. Also, at P = 200 Watt treatment, it increases when the pressures are $p > 0.5$ Torr.

From the Figure 52-b, at pressures “ $p \leq 0.5$ Torr”, the structure of the fibers treated by high LF-RF powers become more ordered with pressures. After $p = 0.5$ Torr, the level of disordering increases with pressures.

Long time treatment

The power effect of treatment process is clearly observed at pressures “ $p \leq 0.5$ Torr” as shown in Figure 52-c. Moreover, the highest effect belongs to 200 Watt treatment and these conditions increases the level of ordering structure. From Figure 52-d, at 60 min-high LF-RF powers treatment, the degree of ordering increases with pressures “ $p \leq 0.5$ Torr” whereas the degree of disordering increases with pressures $p > 0.5$ Torr.

Overall, as shown in Figure 52, it can be conclude that tendency of ordering with pressure is higher in dual RF-CCP treatment when compared to that in single RF-CCP treatment because of having high density and more energetic species [87].

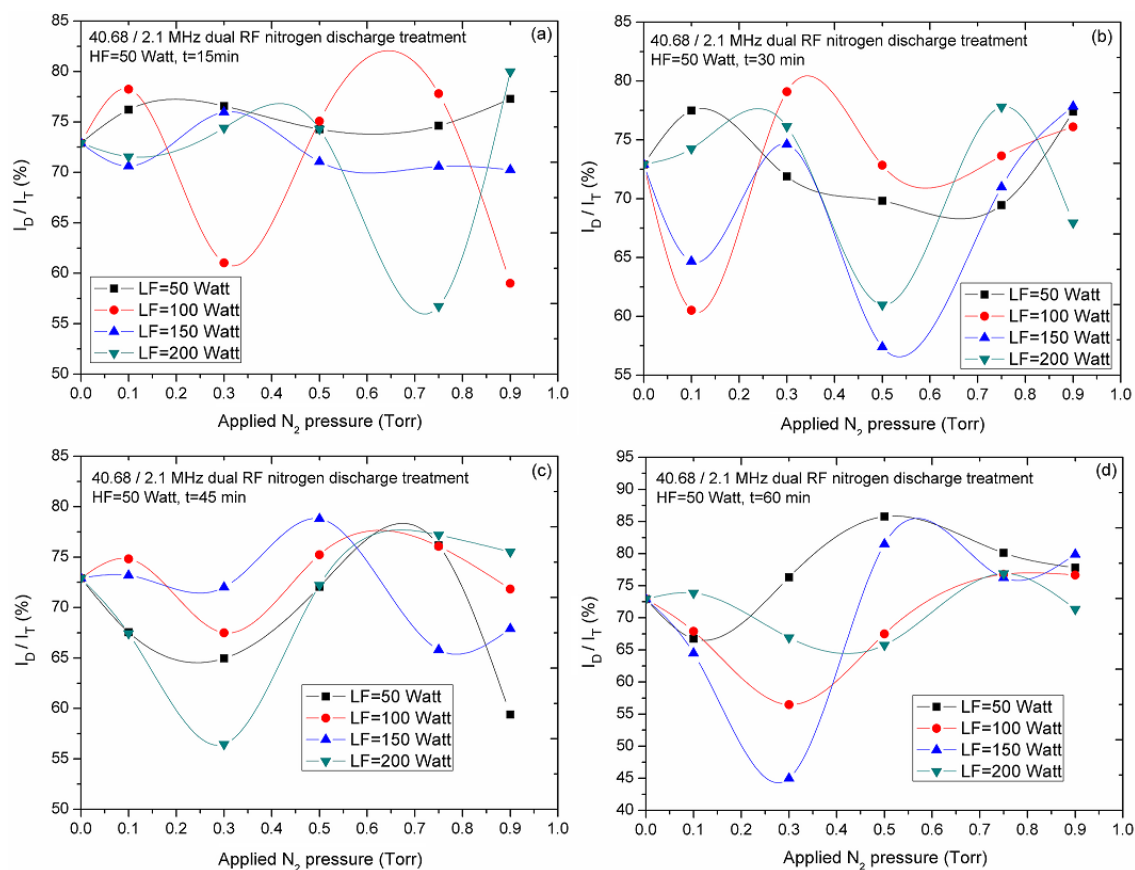


Figure 52. Effects of applied N_2 pressure and LF-RF power on the disordered/ordered structure of the carbon fibers treated under different treatment times; (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min

Effects of LF-RF power and treatment time

Low gas pressure ($p \leq 0.5$ Torr)

At $P \leq 100$ Watt treatment, the level of ordering increases with power as shown in Figure 53 (a-b). The effect of LF-RF power on being more-ordered can be explained by some discharge properties that are; having high sheath width, high potential, high electron temperature and high number of generated secondary electrons, more

energetic electrons, excitation and finality rotational temperature of nitrogen ions [87-89].

High gas pressure ($p > 0.5$ Torr)

As compared to the low pressure treatments, the LF-RF power effect of short time treatment is obviously pointed out with high pressures as shown in Figure 53 (d-e).

Also, from the Figure 53 (d-e), the level of ordering increases with low LF-RF power and high pressure; on the other hand, the level of disordering increases with high LF-RF power and pressure. The main reason of this can be a decrease in vibrational temperature of excited species due to high pressure and LF-RF power [87].

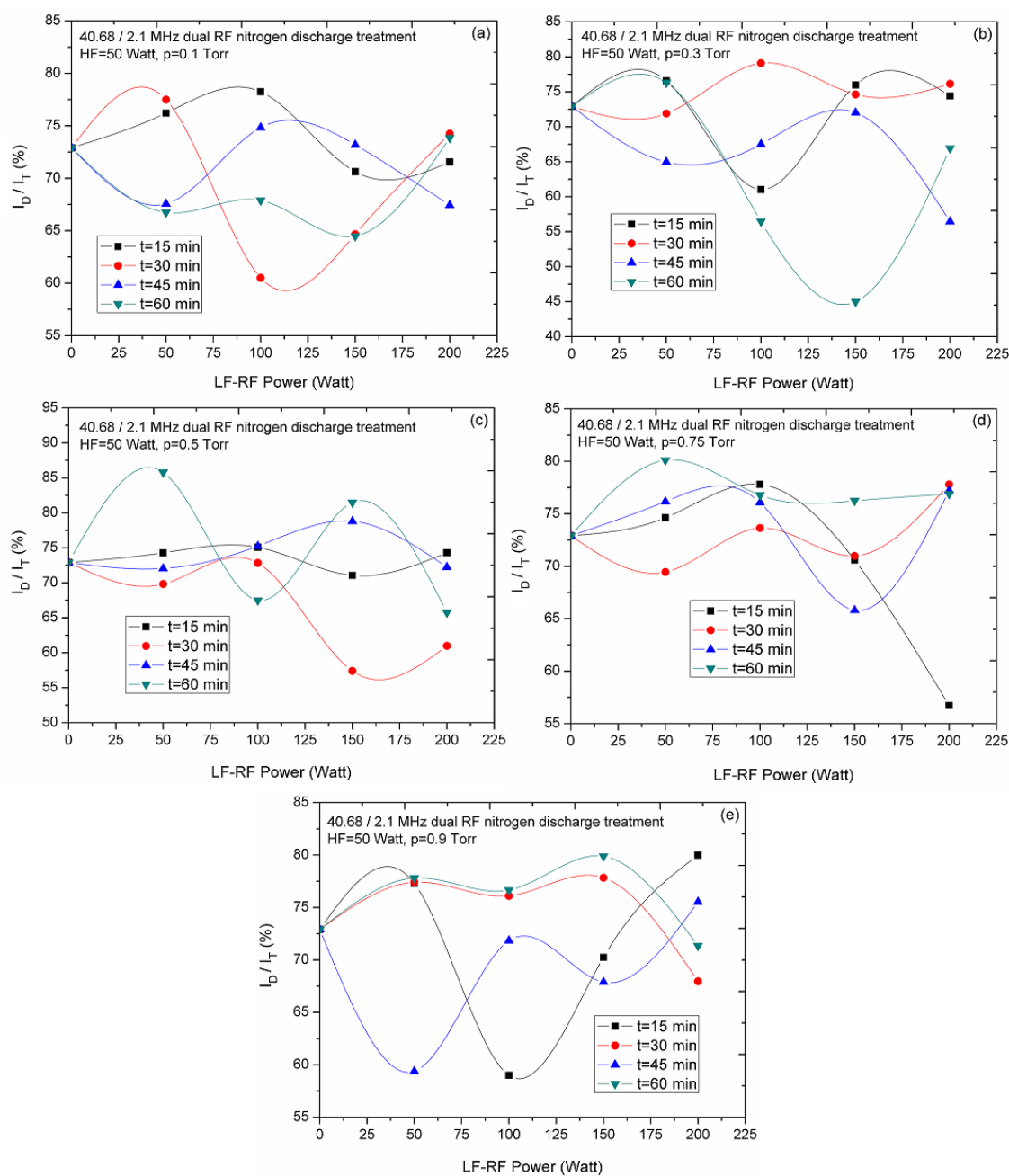


Figure 53. Effects of LF-RF power and treatment time on the disordered/ordered structure of the carbon fibers treated under different applied N_2 pressures; (a) 0.1 Torr, (b) 0.3 Torr, (c) 0.5 Torr, (d) 0.75 Torr and (e) 0.9 Torr

Effects of applied N₂ pressure and treatment time

Low LF-RF power ($P \leq 100$ Watt)

As in Figure 54-a, there is no significant short time treatment effect with pressure. However, at pressures “ $p \leq 0.5$ Torr”, the level of disordering in long time treatment process increases while the level of ordering increases with pressures “ $p > 0.5$ Torr”. Viewed from Figure 54-b, at pressures “ $p < 0.5$ Torr”, crystalline structures become more ordered with pressure whereas the level of disordering increases after $p = 0.5$ Torr.

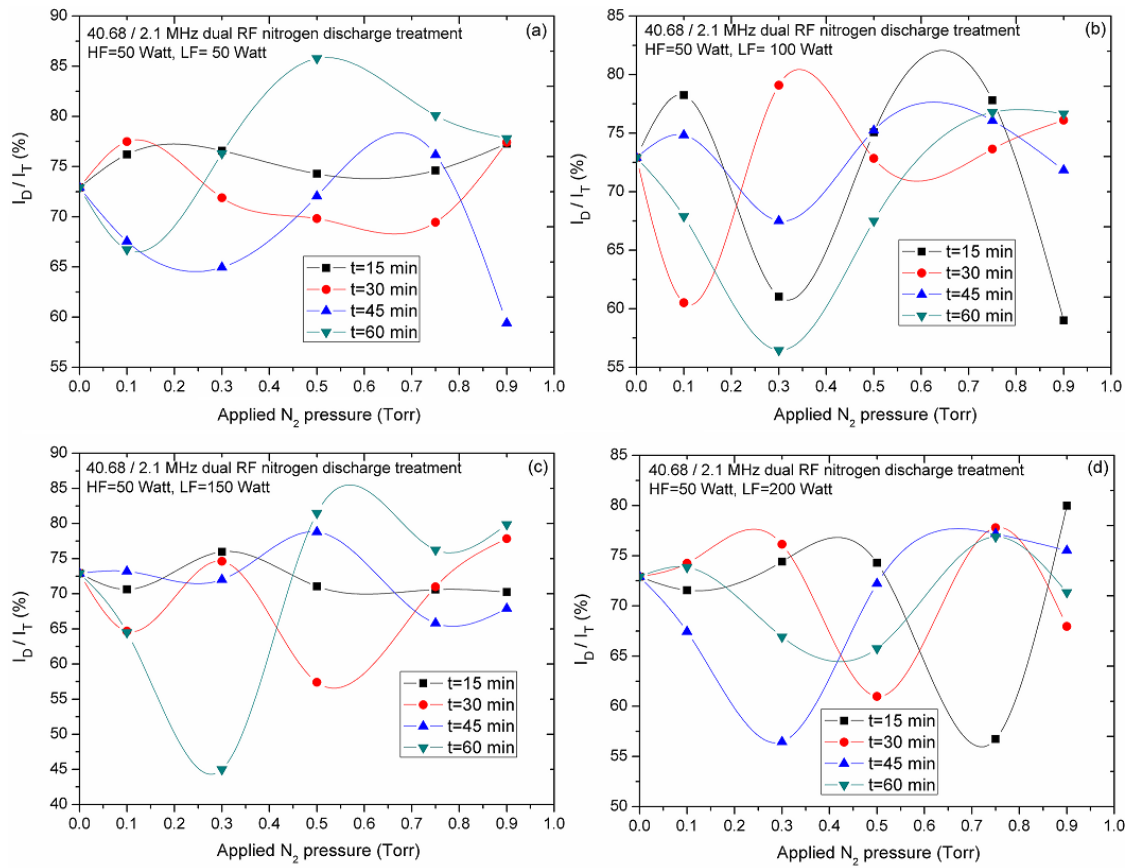


Figure 54. Effects of applied N₂ pressure and treatment time on disordered/ordered structure of the carbon fibers treated under different LF-RF powers; (a) 50 Watt, (b) 100 Watt, (c) 150 Watt and (d) 200 Watt

High LF-RF power ($P > 100$ Watt)

As in Figure 54 (c-d), the degree of ordering increases with pressures “ $p \leq 0.5$ Torr” while the degree of disordering increases with pressures “ $p > 0.5$ Torr”. In addition, only the effect of 60 min treatment with pressure is obviously seen in the Figure 54-c whereas the effect of all treatment times are clearly observed in the Figure 54-d.

Interfacial Property Analysis

Since the obtained results are very complicated and require more detailed work, only samples which show an increment higher than 8 % of order/disorder crystalline structure have been selected at this stage of our work, as in Table 3 and the fitted Raman-bands parameters of these fibers are shown in Table 4.

Table 3. RF plasma treatment processing conditions of HS unsized PAN-based carbon fibers.

Sample	Power (Watt)	Pressure (Torr)	Time (min)
<u>High Disorder</u>			
Single RF			
1	HF=200	0.5	60
2	HF=150	0.75	30
3	HF=50	0.5	30
4	HF=150	0.5	90
5	HF=200	0.3	30
6	HF=150	0.3	30
7	HF=200	0.5	90
Dual RF, HF =50 Watt			
8	LF=50	0.5	60
9	LF=150	0.5	60
10	LF=50	0.75	60
11	LF=200	0.9	15
12	LF=150	0.9	60
13	LF=100	0.3	30
14	LF=150	0.5	45
15	LF=100	0.1	15
<u>High Order</u>			
Single RF			
16	HF=100	1	30
17	HF=200	1	60
18	HF=200	0.75	60
19	HF=50	0.3	60
20	HF=100	0.75	90
21	HF=50	1	60
22	HF=200	1	30
Dual RF, HF =50 Watt			
23	LF=150	0.3	60
24	LF=200	0.3	45
25	LF=100	0.3	60
26	LF=200	0.75	15
27	LF=150	0.5	30
28	LF=100	0.9	15
29	LF=50	0.9	45
30	LF=200	0.5	30

Table 4. Lorentz-fitted parameters of D and G Raman bands of untreated (as-received) and treated fibers listed in the Table 3.

Carbon Fiber	$x_0\text{-D}$ (cm^{-1})	$x_0\text{-G}$ (cm^{-1})	ω_D (cm^{-1})	ω_G (cm^{-1})	ω_D/ω_G	I_D/I_G	I_D/I_T (%)	I_G/I_T (%)	L_a (nm)
Untreated	1362	1584	225	89	2.53	2.69	72.91	27.09	7.14
<u>High Disorder</u>									
Sample 1	1437	1560	926	68	13.72	59.46	98.35	1.65	0.32
Sample 2	1388	1566	603	96	6.27	14.17	93.41	6.59	1.36
Sample 3	1367	1562	527	97	5.44	9.19	90.19	9.81	2.09
Sample 4	1355	1560	384	96	4.01	6.01	85.74	14.26	3.20
Sample 5	1350	1572	335	77	4.35	5.49	84.58	15.42	3.50
Sample 6	1365	1589	293	84	3.50	4.32	81.20	18.80	4.45
Sample 7	1349	1561	298	103	2.89	4.07	80.26	19.74	4.73
Sample 8	1345	1569	354	77	4.62	6.03	85.78	14.22	0.32
Sample 9	1355	1569	323	83	3.92	4.40	81.48	18.52	4.37
Sample 10	1352	1580	282	84	3.35	4.03	80.11	19.89	4.77
Sample 11	1363	1586	279	86	3.26	4.00	79.99	20.01	4.81
Sample 12	1354	1575	289	84	3.44	3.97	79.88	20.12	4.84
Sample 13	1350	1569	289	86	3.35	3.78	79.09	20.91	5.08
Sample 14	1348	1569	279	86	3.25	3.72	78.80	21.20	5.17
Sample 15	1363	1583	270	89	3.03	3.60	78.25	21.75	5.34
<u>High Order</u>									
Sample 16	1351	1560	4	16	0.25	0.18	15.49	84.51	104.85
Sample 17	1353	1560	41	33	1.26	0.87	46.39	53.61	22.21
Sample 18	1359	1554	92	64	1.42	1.22	54.88	45.12	15.80
Sample 19	1354	1562	160	86	1.86	1.65	62.30	37.70	11.63
Sample 20	1350	1554	151	86	1.76	1.73	63.31	36.69	11.14
Sample 21	1355	1558	161	89	1.82	1.79	64.15	35.85	10.74
Sample 22	1353	1560	168	87	1.93	1.81	64.36	35.64	10.65
Sample 23	1355	1561	56	45	1.27	0.82	44.99	55.01	23.51
Sample 24	1356	1558	105	69	1.52	1.30	56.45	43.55	14.83
Sample 25	1354	1558	109	73	1.50	1.30	56.46	43.54	14.82
Sample 26	1354	1559	100	65	1.53	1.31	56.73	43.27	14.66
Sample 27	1357	1560	119	68	1.75	1.35	57.40	42.60	14.26
Sample 28	1372	1582	182	114	1.59	1.44	59.00	41.00	13.35
Sample 29	1377	1584	164	97	1.70	1.46	59.39	40.61	13.15
Sample 30	1351	1559	148	86	1.73	1.56	60.98	39.02	12.30

Generally, as shown in the Table 4, central peak positions “ x_0 ” of the both Raman bands significantly were shifted to the left or right with the different treatment conditions.

This is a sign of changes in bond modulus, stress, fiber modulus [90] and also in crystallite size of the fibers [43]. In addition, the width of G-peak of some treated carbon fibers shrunk due to an increase in fiber modulus [38] and having more-ordered molecular structure [57]. Also, the ratio " I_G/I_T " and crystallite size of these high-ordered samples increased as seen in the Table 4 due to an increase in fiber modulus after treatment processes [38]. Moreover, diminution in the ratios " ω_D/ω_G and I_D/I_G " shows an increase in applied tensile strain of the high-ordered carbon fibers [56].

When the samples that were treated with the use of single HF "40.68 MHz" RF-CCP are analyzed in detail, it is realized that the crystalline microstructure "*observing the value of I_D/I_G and that of the L_a* " of the fibers is significantly changed after the plasma treatments. Even though, the single LF "13.56 MHz" RF-CCP treated carbon fibers in the experiment of Sarraf and et al. had similar ordering crystalline structure because of slight difference in I_D/I_G and L_a [8]. The reason of this is the close relationship between these high structural changes in fibers treated with single HF RF-CCP nitrogen treatment and electron heating mechanism in the discharge. From the Table 4, in general, Ohmic electron heating in the discharge at high pressure " $p \geq 0.5 \text{ Torr}$ " is resulted in large changes in crystallite size of the treated carbon fibers. The crystallite size mostly decreases with low Ohmic heating. And, when the pressure becomes very high, crystallite size increases because of high Ohmic electron heating. However, from the Table 4, it can be seen also some changes in crystallite size of the fibers treated at 0.3 Torr low pressure. The reason of this exception is being mode transition " $\alpha - \gamma$ " pressure in our plasma system. At $p = 0.3 \text{ Torr}$ pressure, the discharge is in γ - mode "*Ohmic heating*" with the low power " $P < 150 \text{ Watt}$ " whereas it turns out again α -mode "*non - Ohmic*" with high power " $P \geq 150 \text{ Watt}$ ". Therefore, the fibers treated at 0.3 Torr - 50 Watt have high crystallite size because of Ohmic electron heating while the fibers treated at 0.3 Torr - 150 Watt have low crystallite size although there exist non-Ohmic electron heating in the discharge.

Tensile Strain Analysis

Tensile strain of some samples listed in Table 5 was tested to learn the effects of plasma treatment conditions “*discharge parameters*” on mechanical properties of the PAN-based carbon fibers. And, the tested results that are average of four measurements are shown in Figure 55.

Table 5. Treatment conditions of the samples, which tensile strain were tested

Sample	Power (Watt)	Pressure (Torr)	Time (min)
Untreated			
S-1	HF= 50	0.3	60
S-2	HF= 100	0.3	60
S-3	HF= 150	0.3	60
S-4	HF= 200	0.3	30
S-5	HF= 200	0.3	60
S-6	HF= 50	0.5	30
S-7	HF= 50	0.5	60
S-8	HF= 200	0.5	60

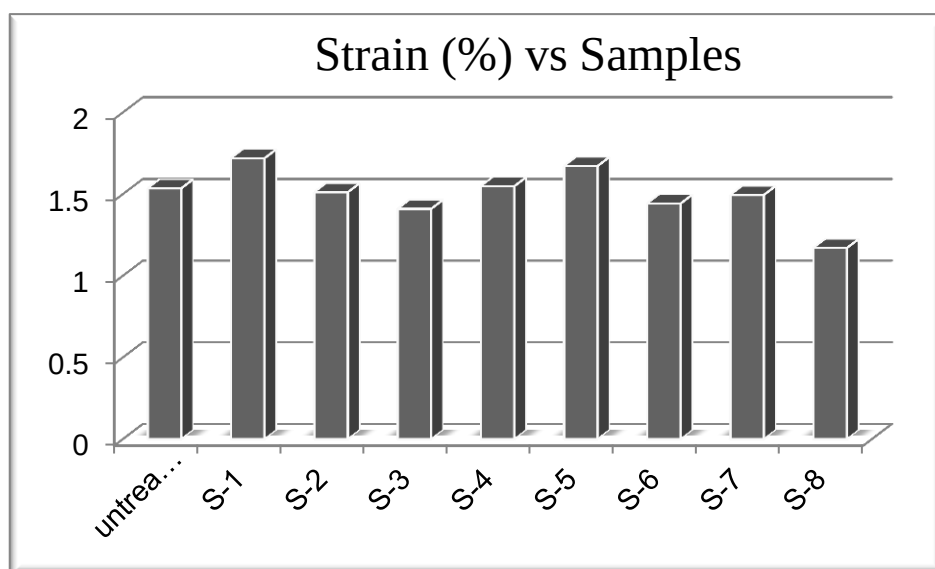


Figure 55. A chart showing tensile strain value of the samples listed in the Table 5

From the Figure 55, tensile percentage strain of the S-1 and the S-5 increased while that of the others decreased. The reason behind these differences is related to the plasma treatment conditions. Moreover, after plasma treatment, the highest strengthened “~24 %” carbon sample is the S-8 while the highest weakened “~12 %” carbon sample is S-1.

Formerly, Dr. Chang investigated the effect of oxygen and ammonia discharge treatment on interfacial properties of the carbon fiber. It was found that the carbon fiber strengthen 21 % after $t = 20$ min oxygen discharge treatment while it was 1.6 % strengthen with $t = 20$ min ammonia treatment [9]. And, Sarraf and et al. modified the carbon fiber surfaces to understand the effect of inductively coupled “*high density*” discharge on tensile strength of the carbon fibers. For argon plasma treatment, the tensile strength increased as 25 % after $t = 10$ min and it decreased as 9 % after $t = 20$ min. For oxygen plasma treatment, 12 % increment after $t = 2$ min, 28 % increment after 5 min and 73 % increment in the tensile strength were observed [8]. When our experimental results are compared with the previous studies, it can be mentioned that it is possible to strengthen and to weaken the PAN-based carbon fiber samples by using high frequency RF nitrogen discharge under different processing conditions. Also, the nitrogen RF-CCP treatment is more effective than the ammonia RF-CCP treatment to strengthen carbon fibers. On the other hand, the inductively coupled low frequency RF plasmas are more suitable than the capacitively coupled high frequency RF plasmas to change mechanical properties of the carbon fiber in a very short time interval because of supplying more dense discharge.

Additionally, the relation between the Raman band peaks and the applied percentage strain of the carbon fiber filaments were investigated as shown in Figure 56. And, it was observed that there exist an inverse relation between the D-band peak location and the strain whereas there is a linear relation between the G-band peak and the carbon fiber strain. Moreover, R-square values in the Figure 56 is very low, this can be happen when less number of data is used [56].

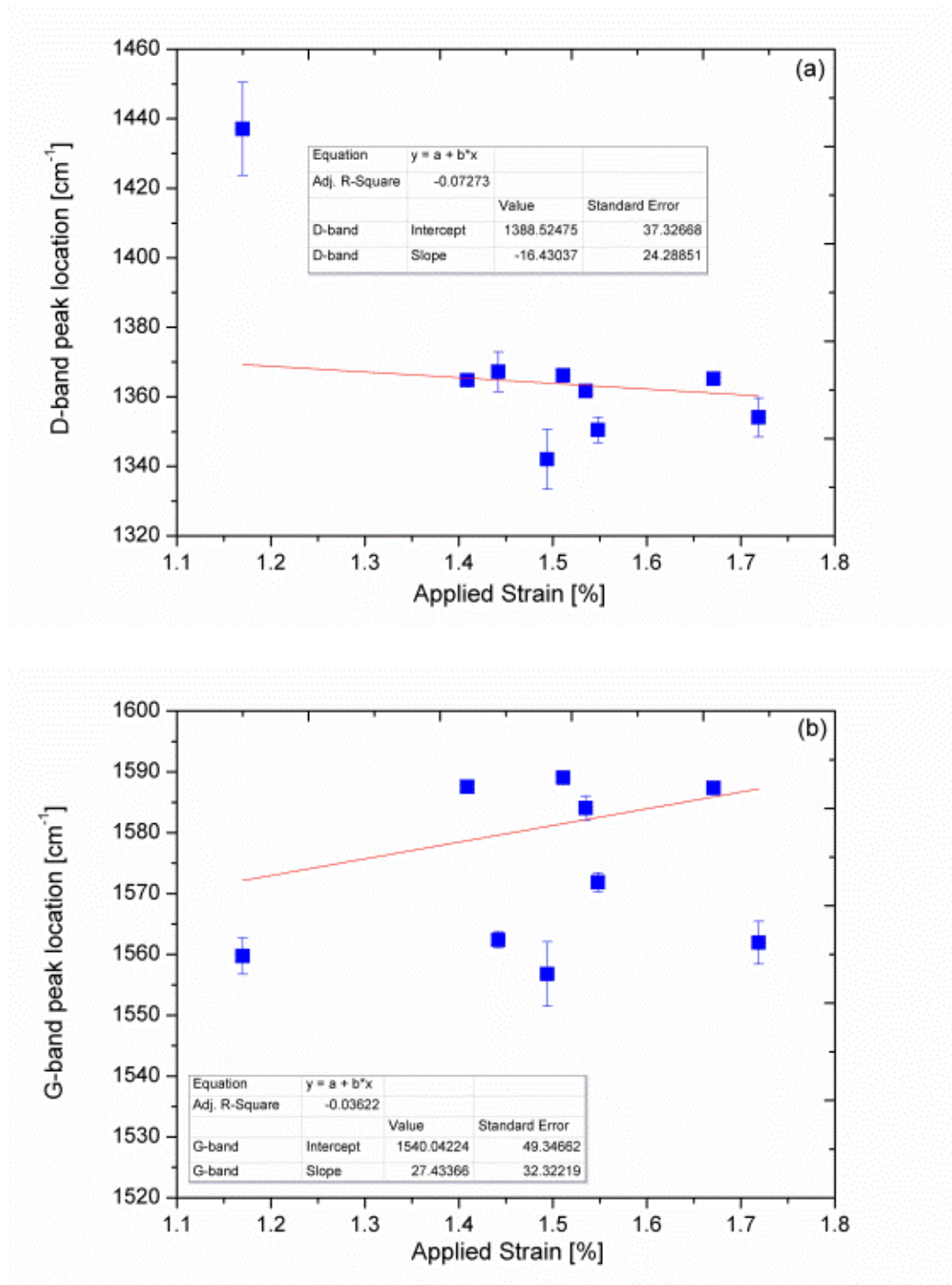


Figure 56. The relation between peak locations of the a) D and b) G bands and tensile strain of the carbon fiber filaments listed in the Table 5

Also, it is possible to calculate the values of Grüneisen parameter of the Raman bands by putting the relations in the Figure 56 into the Eqs. 43 and 44.

From the Figure 56-a, $\frac{\Delta\omega_D}{\varepsilon} \approx -16.4 \text{ cm}^{-1}/\%$ and $\omega_D^0 \approx 1437 \text{ cm}^{-1}$ and when we insert these values into the Eq.15, the Grüneisen parameter of D-band becomes $\gamma_D \approx 1.6$.

From the Figure 56-b, $\frac{\Delta\omega_G}{\varepsilon} \approx 27.4 \text{ cm}^{-1}/\%$ and $\omega_G^0 \approx 1560 \text{ cm}^{-1}$ and by putting these values into the Eq. 16, the Grüneisen parameter of G-band is calculated as $\gamma_G \approx -2.5$.

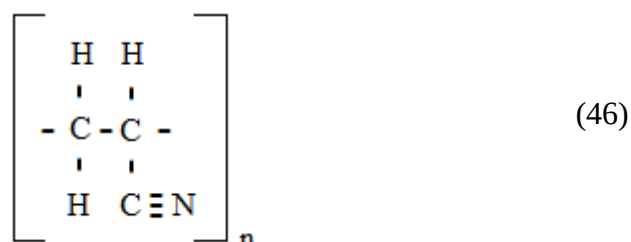
Functional Group Analysis

Chemical bond analysis of some carbon fiber samples listed in Table 6 was done by using FT-IR spectral method, which the results are also shown in the Table 6.

Table 6. FT-IR results of untreated and some treated carbon fibers.

Samples	Wavenumber (cm ⁻¹)	Functional Group
Untreated	1539.20	C=C
	1653.00	C=N
	2355.09	C≡N
	3500-4000	Strechng vibrations between H and other atoms having mass 19 or less (N-H, C-H or others)
0.3T-100W-60 min	1540.16	C=C
	1653.00	C=N
	2355.09	C≡N
	3500-4000	Strechng vibrations between H and other atoms having mass 19 or less (N-H, C-H or others)
0.3T-200W-30 min	2355.09	C≡N
0.3T-200W-60 min	1653.96	C=N
	2355.09	C≡N
0.5T-50W-30 min	1539.20	C=C
	2357.02	C≡N
	3500-4000	Strechng vibrations between H and other atoms having mass 19 or less (N-H, C-H or others)
0.5T-50W-60 min	1653.00	C=N
	2355.09	C≡N
	3500-4000	Strechng vibrations between H and other atoms having mass 19 or less (N-H, C-H or others)
0.75T-200W-60 min	1653.96	C=N
	2354.13	C≡N
	3500-4000	Strechng vibrations between H and other atoms having mass 19 or less (N-H, C-H or others)

The general chemical formula of the PAN-based carbon fiber is;



However, as seen from the Table 6 and Figure 57, functional groups in the untreated “as - received” PAN-based carbon fiber are different from those in the Eq. 46. The main reason of this mostly can be the value of temperatures during the production of PAN-based carbon fiber.

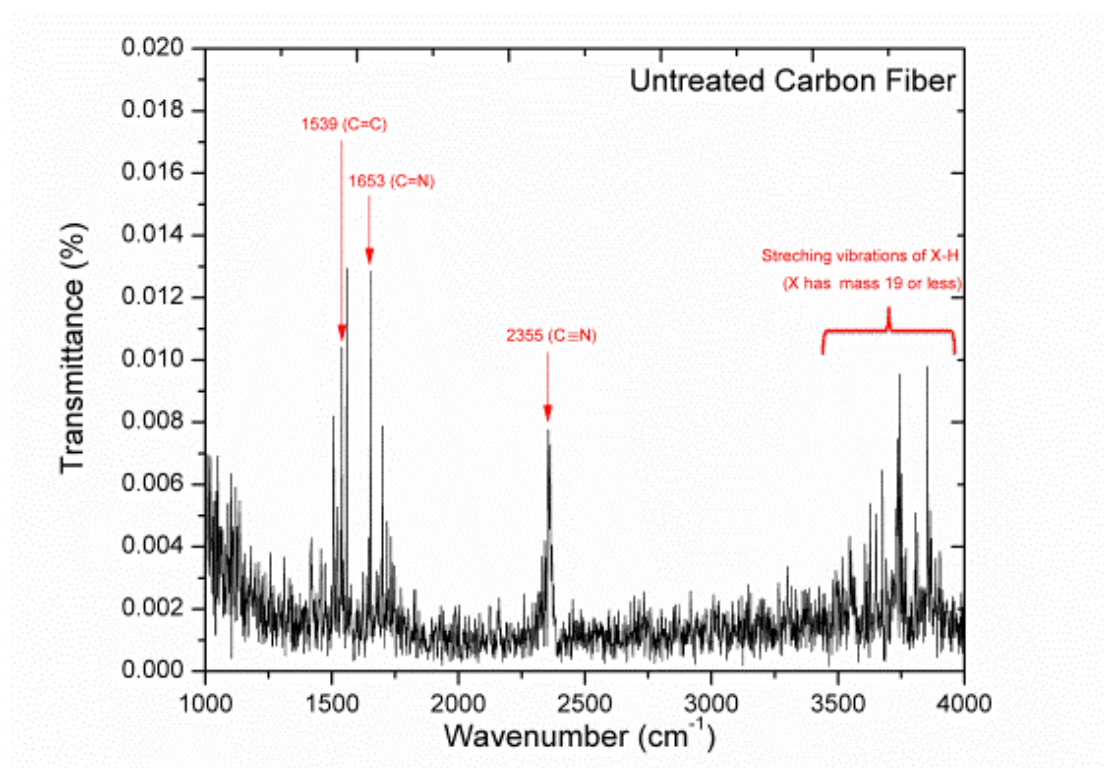


Figure 57. FT-IR spectrum of untreated unsized PAN-based carbon fiber

In addition, from the Table 6, type of the functional groups changed with different treatment conditions “*discharge parameters*” when compared to the groups in the untreated fiber. Therefore, for a more accurate analysis, the connection between FT-IR results and plasma properties are investigated deeply.

Firstly, by increasing pressure “ $p > 0.3 \text{ Torr}$ ”, the C=C bond is disappeared and only carbon to nitrogen bonds are generated. The main reasons of this are existence of more energetic particles in the plasma and nitrogen enrichment. When the carbon fiber is bombarded with these high energetic particles, the bonds are broken easily and then the carbon atoms are combined with the nitrogen atoms that exist more in the plasma environment. Secondly, the significant effect of treatment time in molecular rearrangements was observed in carbon fiber structure. As inferred from the Table 6, the carbon fiber treated at 0.3 Torr - 200 Watt - 30 min has C $\equiv$ N bond whereas the carbon treated at 0.3 Torr - 200 Watt - 60 min has C=N bond. Additionally, the C=C bond is disappeared in the fiber structure that treated at 0.5 Torr - 50 Watt when treatment time increases from 30 to 60 min. Again, the reason of this time effect is being exposed to high density nitrogen gas and being bombarded with more energetic particles. Lastly, some weak peaks showing stretching vibrations between H and N or C “*N-H or C-H*” were observed in the range of 3500 - 4000 cm^{-1} as seen in the Table 6.

CHAPTER 5

CONCLUSION

In conclusion, when compared with the previous works, this thesis points out unexpected effects of high frequency single and dual nitrogen RF-CCP treatment processes on structural ordering/disordering, on crystalline microstructure “ I_D/I_G and L_a ” and also on some properties of the unsized HS PAN-based carbon fiber. Especially, the changes in tensile strain and chemical functional groups of some fibers that were treated by using single HF nitrogen RF-CCP were observed.

High frequency single RF-CCP has more impressive effect on carbon fiber’s crystalline structure and tensile strain than low frequency “13.56 MHz” RF discharge because of its electron heating “*mode -transition*” mechanisms that are shown at $p = 0.3$ Torr “ $\alpha - \gamma$ ” and at $P = 150$ Watt “ $\gamma - \alpha$ ”. Order/disorder structural effect of HF single RF-CCP can be summarized as follows; in short time treatment process that is generated at low pressures, the degree of disordering increases by HF-RF power on account of an increase in excitation and rotational temperatures of neutral nitrogen molecular gas and also non-Ohmic electron heating. On the contrary, in long time treatment process that is generated at high pressures, the degree of ordering increases with HF-RF power due to Ohmic electron heating. Moreover, it can be pointed out that $t = 90$ min is too long time in HF single RF discharge treatment process to observe structural changes at very high pressure. Furthermore, in-plane crystallite size “ L_a ” of the treated fibers and the level of ordering structure increase with high Ohmic plasma. They are also significantly affected by electron heating transition points in HF single RF-CCP. Besides, tensile strain of some treated carbon fibers were tested and their results show that it can be possible to obtain the highest “24 %”

increment in hardness and “12 %” increment in relaxation of the treated fiber after HF single RF discharge treatment process. According to the relations between tensile strain and the Raman band shifts, the Grüneisen parameter of D-band “ γ_D ” is calculated as “1.6” while the Grüneisen parameter of the G-band “ γ_G ” is found as “-2.5”. Additionally, the existence of chemical functional groups in the treated fiber structures is affected by the plasma treatment conditions “*physical changes in the plasma*”.

In this thesis, only the effect of HF dual RF-CCP on crystalline structure was investigated because of experimental problems and they reveal that; in general, discharge treatment process of HF nitrogen dual RF supplies more-ordered carbon fiber structure than that of the HF nitrogen single RF. In short time treatment process that is generated at high pressures, the level of ordering increases with low LF-RF power by reason of high vibrational and rotational temperature of nitrogen molecular ion. On the other hand, it decreases with high LF-RF power and pressure due to having less vibrational temperature of nitrogen ions. In long treatment process that is generated at low pressures, high tendency of ordering is observed with LF-RF power. In addition, the in-plane crystallite size of the treated fibers that have ordered structure increases while the ratios “ ω_D/ω_G and I_D/I_G ” decrease. On the contrary, the in-plane crystallite size of the treated fibers that have disordered structure decreases while the ratios “ ω_D/ω_G and I_D/I_G ” increase.

REFERENCES

- [1] M. A. Lieberman and A. J. Lichtenberg, *Principles of plasma discharges and materials processing*, New York: Wiley, 1994.
- [2] M. A. Montes-Moran, A. Martinez-Alonso and et al., *Effects of plasma oxidation on the surface and interfacial properties of ultra-high modulus carbon fibres*, Comp. Part A: Appl. Sci. and Manufac., vol. 32, pp. 361 - 371, 2001.
- [3] R. Li, L. Ye and et al., *Application of plasma technologies in fibre-reinforced polymer composites: a review of recent developments*, Comp. Part A: Appl. Sci. and Manufac., vol. 28, pp. 73 - 86, 1997.
- [4] Q. H. Yuan, Y. Xin and et. al., *Effect of low-frequency power on dual-frequency capacitively coupled plasmas*, J. Phys. D: Appl. Phys., vol. 41, no. 205209, 2008.
- [5] S. Helhel, *Analysis of dual frequency confined capacitively coupled plasma at low power*, Inter. J. of Infr. and Milli. Waves, vol. 27, no. 4, pp. 615 - 629, 2006.
- [6] S. Chand, *Review: Carbon fibers for composites*, J. of Mater. Sci., vol. 35, pp. 1303 - 1313, 2000.
- [7] F. Liu, H. Wang and et al., *Effect of microstructure on the mechanical properties of PAN-based carbon fibers during high-temperature graphitization*, J. Mater. Sci., vol. 43, pp. 4316 - 4322, 2008.
- [8] H. Sarraf, P. Louda and et al., *Surface modification of carbon fiber*, J. Ach. Mater. Manufac. Enginee., vol. 25, pp. 24 - 30, 2007.
- [9] T. C. Chang, *Plasma surface treatment in composites manufacturing*, J. Indust. Tech. vol. 15, pp. 1 - 7, 1999.
- [10] A. Bogaerts, E. Neyts and et al., *Gas discharge plasmas and their applications*, Spectrochimica. Acta. Part B, vol. 57, pp. 609 - 658, 2002.

- [11] V. Nehra, A. Kumar and et al., *Atmospheric non-thermal plasma sources*. Inter. J. of Enginee., vol. 2, issue 1.
- [12] A. Ganguli and R. D. Tarey, *Understanding of plasma sources*, Current Science, vol. 83, no. 3, 2002.
- [13] E. Wagenaars, *Plasma breakdown of low-pressure gas discharges*, Eindhoven University of Technology - PhD Thesis, 2006.
- [14] Chapter 6: Currents, Filaments and Pinches, http://www.thunderbolts.info/eg_draft/eg_chapter_6.htm, last visit: February 2014.
- [15] R. F. Bunshah, *Handbook of deposition technologies for films and coatings*, Noyes, New Jersey, 1994.
- [16] H. Conrads and M. Schmidt, *Plasma generation and plasma sources*, Plasma Sources Sci. Technol., vol. 9, pp. 441 - 454, 2000.
- [17] Y. P. Raizer, M. N. Shneider and et al., *Radio - frequency capacitive discharges*, CRC Press LLC, ISBN 0-8493-8644-6, 1995.
- [18] R. D'Agostino, P. Favia and et al., *Advanced plasma technology*, Wiley - VCH Verlag GmbH & Co. KGaA, ISBN 978-3-527-40591-6, 2008.
- [19] L. M. Isola, B. J. Gomez and et al., *Determination of the electron temperature and density in the negative glow of a nitrogen pulsed discharge using optical emission spectroscopy*, J. Phys. D: Appl. Phys., vol. 43, 2010.
- [20] E. Abdel-Fattah and H. Sugai, *Electron heating mode transition observed in a very high frequency capacitive discharge*, Appl. Phys. Lett., vol. 83, no. 8, 2003.
- [21] W. Jiang, X. Xu and et al., *Heating mechanisms and particle flow balancing of capacitively coupled plasmas driven by combined dc/rf sources*, Phys. of Plasmas, vol. 15, no. 033502, 2008.

- [22] N. P. Lockwood, *Investigation of radio frequency discharges and Langmuir probe diagnostic methods in a fast flowing electronegative background gas*, Ohio, Air University - PhD Thesis, 2007.
- [23] L. Xiang - Mei, S. Yuan-Hong and et al., *Driving frequency effects on the mode transition in capacitively coupled argon discharges*, Chin. Phys. B vol. 20, no. 6, 2011.
- [24] R. Schrittwieser, C. Ionita and et. al., *Probe methods for direct measurements of the plasma potential*, Rom. J. Phys., vol. 50, nos 7 - 8, pp. 723 - 739, 2005.
- [25] N. P. Lockwood, *Investigation of radio frequency discharges and Langmuir probe diagnostic methods in a fast flowing electronegative background gas*, Ohio, Air University - PhD Thesis, 2007.
- [26] F. F. Chen, *Langmuir probes in RF plasma: surprising validity of OML theory*, Plasma Sources Sci. Technol., vol. 18, no. 035012, 2009.
- [27] S. Ji. Oh, S. Ju. Oh and et. al., *Radio frequency-compensated Langmuir probe with auxiliary double probes*, Rev. Sci. Instrum., vol. 81, no. 093501, pp. 1 - 4, 2010.
- [28] Impedans, *ALP System™ Langmuir Probe Installation & User Guide. pdf*, Copyright © 2007 - 2011 Impedans Ltd.
- [29] R. H. Huddleston and S. L. Leonard, *Plasma diagnostic techniques*, Academic Press INC., New York, London, 1965.
- [30] F. F. Chen and J. P. Chang, *Lecture notes on principles of plasma processing*, Kluwer Academic/ Plenum Publishers, New York, ISBN 0-306-7497-2, 2003.
- [31] A. Karamcheti and C. Steinbruchel, *Parametrization of Laframboise's results for spherical and cylindrical Langmuir probes*, Vac. Sci. Technol. A, vol. 17, no.5, pp. 3051 - 3056, 1999.

- [32] G. Narasimhan and C. Steinbruchel, *Analysis of Langmuir probe data: Analytical parametrization, and the importance of the end effect*, Vac. Sci. Technol. A, vol. 19, no. 1, pp. 376 - 378, 2001.
- [33] S. Klagge and M. Tichy, *A contribution to the assessment of the influence of collisions on the measurements with Langmuir probes in the thick sheath working regime*, Czech. J. Phys. Sect. B, vol. 35, no. 9, pp. 988 - 1006, 1985.
- [34] X. Huang, *Review: Fabrication and properties of carbon fibers*, Materials, vol. 2, pp. 2369 - 2403, 2009.
- [35] T. A. Edison, U. S. Patent 223, 398, 1880.
- [36] Graphite as solid lubricant, http://www.substech.com/dokuwiki/doku.php?id=graphite_as_solid_lubricant, last visit: February 2014.
- [37] P. Morgan, *Carbon fibers and their composites*, Taylor & Francis, 2005.
- [38] N. Melanitis, P. L. Tetlow and et al., *Characterization of PAN-based carbon fibers with laser Raman spectroscopy .1. Effect of processing variables on Raman band profiles*, J. Mater. Sci., vol. 31, pp. 851 - 860, 1996.
- [39] S. Yoshimura, R. P. H. Chang (Eds.), *Supercarbon: synthesis, properties and applications*, Springer, ISBN 3-540-64379-6, 1998.
- [40] K. Lafdi, and M. A. Wright, *Carbon fibers: In handbook of composites*, 2nd Ed.; Peters, S.T., Ed.; Chapman & Hall: London, UK, p. 169, 1998.
- [41] M. Endo, *Structure of mesophase Pitch-Based carbon fibers*, J. Mater. Sci. vol. 23, pp. 598 - 605, 1988.
- [42] One Step Forward toward Characterization: Some Important Material Properties to Distinguish Biochars, <https://www.soils.org/publications/jeq/abstracts/41/4/1001?access=0&view=article>, last visit: February 2014.
- [43] K. Morita, Y. Murata and et al., *Characterization of commercially available PAN-based carbon fiber*, Pure & Appl. Chem., vol. 58, no. 3, pp. 455 - 468, 1986.

- [44] L. M. Marilyn and S. Kumar, *The processing, properties and structure of carbon fibers*, JOM, pp. 52 - 58, 2005.
- [45] D. L. Chung, *Carbon fiber composites*, Butterworth-Heinemann: Boston, MA, USA, pp. 3 - 65, 1994.
- [46] J. R. Ferraro, K. Nakamoto and et al., *Introductory Raman spectroscopy*, Amsterdam; Boston, Academic Press, 2003.
- [47] Raman: theory and instrumentation, http://www.ccmr.cornell.edu/igert/modular/docs/Raman_Scattering.pdf, last visit: February 2014.
- [48] P. Morgan, *Carbon fibers and their composites*, Taylor & Francis CRC Press, Cambridgeshire, UK, 2005.
- [49] G. Turrell and J. Corset, *Raman microscopy: developments and applications*, Elsevier Academic Press, 1996.
- [50] R. L. McCreery, *Raman spectroscopy for chemical analysis*, John Wiley & Sons, ISBN 0-471-25287-5, 2000.
- [51] XI. Raman Spectroscopy, <http://users.abo.fi/mhotokka/mhotokka/lecturenotes/ms04.d/ms04-raman-eng.pdf>, last visit: July 2013.
- [52] A. C. Ferrari, *Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects*, Elsevier Solid State Commun., vol. 143, pp. 47 - 57, 2007.
- [53] H. C. Lin., S. T. Shiue and et al., *Effects of radio-frequency powers on the properties of carbon coatings on optical fibers prepared by plasma enhanced chemical vapor deposition*, Surface & Coatings Technology, vol. 202, pp. 5360 - 5363, 2008.
- [54] J. C. Chen and I. R. Harrison, *Modification of polyacrylonitrile (PAN) carbon fiber precursor via post-spinning plasticization and stretching in dimethyl formamide (DMF)*, Carbon, vol. 40, pp. 25 - 45, 2002.

- [55] T. M. G. Mohiuddin, A. Lombardo and et al., *Uniaxial strain in grapheme by Raman spectroscopy: G peak splitting, Grüneisen parameters and sample orientation*, Phys. Rev. B, vol. 79, no. 205433, pp. 1 – 8, 2009.
- [56] F. D. Jr. Blum, *Condition assessment of carbon fiber composites using Raman spectroscopy*, Columbia, University of Missouri - Ms Thesis, 2009.
- [57] N. Oya and D. J. Johnson, *Longitudinal compressive behavior and microstructure of PAN-based carbon fibers*, Carbon, vol. 39, pp. 635 - 645, 2001.
- [58] I. M. Robinson, M. Zakikhani and et al., *Strain dependence of the Raman frequencies for different types of carbon fibres*, J. of Mater. Sci. Letters, vol. 6, no. 10, pp. 1212 - 1214, 1987.
- [59] L. G. Cançado, K. Takai and et al., *General equation for the determination of the crystallite size L_a of nanographite by Raman spectroscopy*. Appl. Phys. Lett. vol. 88, no. 16, pp. 163106 - 163109, 2006.
- [60] H. Miyagawa, T. Mase and et al., *Comparison of experimental and theoretical transverse elastic modulus of carbon fibers*, Carbon, vol. 44, pp. 2002 - 2008, 2006.
- [61] K. Sato, R. Saito and et al., *D-band Raman intensity of graphitic materials as a Function of laser energy and crystallite size*, Preprint submitted to Elsevier Science, 2009.
- [62] T. Ungar, J. Gubicza and et al., *Size and shape of crystallites and internal stresses in carbon blacks*, Elsevier Composites: Part A, vol. 36, pp. 431 - 436, 2005.
- [63] L. B. Nohara, G. P. Filho and et al., *Evaluation of carbon fiber surface treated by chemical and cold plasma processes*, Materials Research, vol. 8, no. 3, pp. 281 - 286, 2005.

- [64] H. Miyagawa, D. Kamiya and et al., *Strain measurement for Raman-inactive substrates with PbO thin films using Raman coating method*, J. Mater. Sci., vol. 34, pp. 105 - 110, 1999.
- [65] S. Reich, H. Jantoljak and et al., *Shear strain in carbon nanotubes under hydrostatic pressure*, Phys. Rev. B, vol. 61, no. 20, 2000.
- [66] C. Thomsen and S. Reich, *Ab initio determination of the phonon deformation potentials of grapheme*, Phys.Rev. B, vol. 65, 2002.
- [67] M. S. Amer and L. S. Schadler, *Stress concentration phenomenon in graphite/epoxy composites: Tension/compression effects*, Comp. Sci. and Tech., vol. 57, no. 8, pp. 1129 - 1137, 1997.
- [68] Introduction to Fourier Transform Infrared Spectrometry, <http://mmrc.caltech.edu/FTIR/FTIRintro.pdf>, last visit: February 2014.
- [69] G. Washer and Jr. F. Blum, *Raman spectroscopy for the nondestructive testing of carbon fiber*, Res. Lett. in Mater. Sci., 2008.
- [70] F. A. Settle, *Handbook of instrumental techniques for analytical chemistry*, A Simon & Schuster Company, New Jersey, ISBN 0-13-177338-0, 1997.
- [71] S. M. Saufi and A. F. Ismail, *Development and characterization of polyacrylonitrile (PAN) based carbon hollow fiber membrane*, Songklanakarin J. Sci. Technol., vol. 24, pp. 843 - 854, 2003.
- [72] Brochure Manual, http://serenips.com/R601_FACT_SHEET.htm, last visit: February 2014.
- [73] SEREN, AT-6 Automatic Matching Network Operator's Manual, http://mfc.engr.arizona.edu/documents/PECVD%20manuals/6200080000_AT6_OPER_MAN_V1_02.pdf, last visit: February 2014.
- [74] Brochure Manual, http://serenips.com/AT3FACT_SHEET.htm, last visit: February 2014.

- [75] IRFS: Eoropean Man-made Fibres Association, <http://www.cirfs.org/manmadefibres/fibrerange/Carbon.aspx>, last visit: August 2013.
- [76] DowAksa: Products - Continuous carbon fiber properties, <http://www.dowaksa.com/products>, last visit: August 2013.
- [77] UNAM Bilkent University: SNOM + Raman Microscope, http://www.nano.org.tr/sr_microscope.html, last visit: August 2013.
- [78] WITec: High - Resolution optical and scanning probe microscopy systems, <http://www.witec.de/assets/Downloads/raman/WITecCatalogueHighRes.pdf>, last visit: August 2013.
- [79] R. Li, L. Ye and Y. W. Mai, *Application of plasma technologies in fibre-reinforced polymer composites: a review of recent developments*, Comp. Part A: Appl. Sci. and Manufac., vol. 28, no. 1, pp. 73 - 86, 1997.
- [80] M. J. Matthews, M. A. Pimenta and et. al., *Origin of dispersive effects of the Raman D band in carbon materials*, Phys. Rev. B, vol. 59, pp. R6585 - R6588, 1999.
- [81] Q. H. Yuan, G. Q. Yin and et. al., *Effects of gas pressure on 60/13.56 MHz dual-frequency capacitively coupled plasmas*, Phys. of Plasmas, vol. 18, no. 053501, pp. 1 - 5, 2011.
- [82] S. K. Ahn and H. Y. Chang, *Role of low-frequency power in dual-frequency capacitive discharges*, App. Phys. Lett., vol. 95, no. 111502, pp. 1 - 3, 2009.
- [83] W. Jiang, X. Xu and et. al., *Heating mechanisms and particle flow balancing of capacitively coupled plasmas driven by combined dc/rf sources*, Phys. of Plasmas, vol. 15, no. 033502, pp. 1 – 5, 2008.
- [84] H. Park, S. J. You and et. al., *Correlation between excitation temperatures and electron temperature with two groups of electron energy distributions*, Phys. of Plasmas, vol. 17, no. 103501, pp. 1 – 4, 2010.

- [85] H. C. Kim and J. K. Lee, *Mode transition induced by low-frequency current in dual-frequency capacitive discharges*, Phys. Rev. Lett., vol. 93, no. 8, 2004.
- [86] X. J. Huang, Y. Xin and et. al., *Analysis of optical emission spectroscopy in a dual - frequency capacitively coupled CHF₃ plasma*, Phys. of Plasmas, vol. 16, no. 043509, 2009.
- [87] X. J. Huang, Y. Xin and et. al., *Spectroscopic study on rotational and vibrational temperature of N₂ and N₂⁺ in dual-frequency capacitively coupled plasma*, Phys. of Plasmas, vol. 15, no. 113504, 2008.
- [88] M. A. Montes - Mora'n and R. J. Young, *Raman spectroscopy study of HM carbon fibres: effect of plasma treatment on the interfacial properties of single fiber/ epoxy composites Part I: Fibre characterization*, Carbon, vol. 40, pp. 845 - 855, 2002.
- [89] P. Chabert and N. S. J. Braithwaite, *Physics of radio frequency plasmas*, Cambridge University Press, New York, 2011.
- [90] V. K. Mitra, M. R. William and et al., *A laser Raman study of the stress dependence of vibrational frequencies of a monocrystalline polydiacetylene*, The J. of Chem. Phys., vol. 66, no. 6, pp. 2731 - 2736, 1977.

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name: ERÖZBEK-GÜNGÖR, Ümmügül

Nationality: Turkish “T.C.”

Date and Place of Birth: 2 Agust 1981, Wien-AUSTRIA

Marital Status: Married to Özgür GÜNGÖR

Phone: +90 312 210 43 09

Fax: +90 312 210 22 91

e-mail: ummugul55@gmail.com and ummugul@metu.edu.tr

EDUCATION

Degree	Institution	Year
PhD	Physics Dept., METU	2009 – Present
MS	Physics Dept., METU	2006 - 2009
BS & MS	Physics Education Dept., METU	1999 - 2005
“Without thesis”		
BS	Physics Dept., METU	2000-2004
“Double Major”		

WORK EXPERINCES

Position	Field	Institution	Year
BS Student	<u>Project:</u> Qualitative and spectral analysis of metal entities by arc plasma	Physics Dept. METU	2003-2004
BS Student	<u>Project:</u> Teaching eleventh level physics with daily life examples	Physics Education Dept. METU	2004-2005
Teacher	Physics and science	Eryaman Platin Dershanesi	2005-2006
Private Tuition	Physics, chemistry, math and geometry		2005-2012
Project Assistant “MS Student”	<u>Tübitak Project:</u> Development of a compact time-domain terahertz spectrometer using photoconductive antenna detection method	Physics Dept. METU	2008-2009
Research Assistant “PhD Student”	Surface modification , RF plasma, carbon fiber, high frequency single and dual capacitively coupled RF plasma, plasma diagnostic, Langmuir probes, optical emission spectroscopy “OES”, laser induced breakdown spectroscopy	Physics Dept. METU	2012- Present

SKILLS

Laboratory Skills: Usage of Raman spectroscopy, plasma chamber, turbo and rotary vacuum pumps, single and dual Langmuir probes, 13.56, 40.68, 2.1 MHz RF power supplies, lasers, optical elements and mechanical tester device

Computer Skills: Advance usage of all Microsoft Office programs, OriginLab “Data analysis and graphing software” and internet

Languages: English “Intermediate and B2 level certificate was taken by TÖMER-Ankara University” and French “Beginner”

PUBLICATIONS AND CONFERENCES

1. Ümmügöl E. Güngör, Sinan K. Bilikmen and Demiral Akbar, *High frequency capacitively coupled RF plasma discharge effects on the structure of PAN-based carbon fiber*, Manuscript accepted, Journal of Theoretical and Applied Physics, 2013
2. Demiral Akbar, Ümmügöl E. Güngör, Sinan K. Bilikmen, *Study of high radio frequency plasma discharge effects on carbon fiber using Raman spectroscopy*, Manuscript waiting for response, Surface and Coatings Technology, 2013
3. Ümmügöl E. Güngör and Sinan K. Bilikmen, *The Effects of High Frequency RF Capacitively Coupled Plasma on Tensile Strain and Functional Groups of PAN-based Carbon Fiber*, Abstract submitted for Poster Presentation, 1st International Middle East Plasma Science (IMEPS) Conference, Belek-Antalya, TURKEY, 2014
4. Halil Berberoğlu, K. Efe Eseller, Ümmügöl Erözbek Güngör, Sinan Bilikmen, “*Lazer uyarımlı plazma spektroskopisi ile kalitatif toprak analizi*”, Poster Presentation, Fotonik 2013, Ankara, TURKEY, 2013

5. K. E. Eseller, E. Yurdanur-Taşel, H. Berberoğlu, Z. Yurtkuran, Ü. E. Güngör, S. Bilikmen, “*Monitoring non-pathogenic yeast growth by laser induced breakdown spectroscopy*”, Poster Presentation, 7th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy, Bari, ITALY, 2013
6. Ü. Erözbek Güngör, D. Akbar and S. K. Bilikmen, “*Surface modification of PAN-based carbon fiber using single and dual high frequency RF-PECVD*”, Oral Presentation, 64th Annual Gaseous Electronics Conference, Salt Lake City, Utah, USA, vol. 56, no. 15, 2011
7. D. Akbar , Ü. Erözbek Güngör and S. K. Bilikmen “*Surface modification of carbon fiber with high frequency single and dual RF capacitive coupled plasma*”, Poster Presentation, GEC&ICRP Paris, France Conference, vol. 55, no. 7, 2010
8. Ümmügül Erözbek Güngör, “*Development of a Time-Domain Terahertz Spectrometer: using Photoconductive Antenna Detection Method*”, Book, LAMBERT Academic Publishing, 2010

AWARDS

FI-LIPS Group, “*Honorable Mention: Fiber optic laser system (FOLS)*”, New Ideas New Works-Competition in SSM Category “*Yeni Fikirler Yeni İşler Yarışması - Savunma Sanayii Kategorisinde*”, Ankara, TURKEY, 2013

HOBBIES

Movies, Cycling, Driving, Swimming, Pilates, Yoga

REFERENCES

	Institution	E-mail
Prof. Dr. Sinan K. Bilikmen	Physics Dept., METU	bilikmen@metu.edu
Assoc. Prof. Dr. Demiral Akbar	Hacettepe Tecnopolis	dakbar@hacettepe.edu.tr
Dr. Halil Berberoğlu	Physics Dept., METU	halilb@metu.edu
Assist. Prof. Dr. K. Efe Eseller	Elec. Electr. Engineering Dept., Atılım University	efe.eseller@atilim.edu
Assoc. Prof. Dr. Hakan Altan	Physics Dept., METU	haltan@metu.edu