Depiction of the Ambipolar-State of the Gas-Substrate Interphase of the Electron Cyclotron Resonance – Microwave – Chemical Vapor Deposition (ECR-MW-CVD) Method and Its Influence over the Properties of Vapor-Deposited Hydrocarbon Films

by

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Biographical Sketch

Jesús M. García-Figueroa — Jesús — obtained a master's of engineering in chemical engineering at the University of Puerto Rico–Mayaguez in 2012. He did a double bachelor's degree in chemistry and chemical engineering and a minor in manufacturing, management, and business technology enterprises at the University of Puerto Rico–Mayaguez in 2009. His most recent contribution is the first depiction of the ambipolar-state of the electron cyclotron resonance – microwave – chemical vapor deposition (ECR-MW-CVD) method. He also was the first to analyze the costs of a local bioproducts processing plant using microalgae biomass as feedstock at the detailed design level. His projects have been sponsored by the Air Force Research Laboratories, the American Institute of Chemical Engineers, the American Nuclear Society, Bristol Myers Squibb, the MasterCard Foundation, the National Science Foundation, the Sloan Foundation, the University of Puerto Rico, the University of Rochester, the U.S. Department of Defense, the U.S. Department of Education, and the U.S. Department of Energy. Jesús' interests are engineering, enterprises, sciences, management, and technology, and connect processes and their products through the virtues of the scientific method.

Publications:

1. García-Figueroa JM, Harding DR. Relationship between the Gas-Phase Reactions Occurring within an Electron Cyclotron Resonance- (ECR) Microwave- (MW) CVD Process and the Properties of Hydrocarbon Films. PowerPoint presented: 2019 MRS Fall Meeting & Exhibit; December 1-6, 2019; Boston, Massachusetts, United States of America. Available from: García-Figueroa's website at: https://inquchild09.wixsite.-com/inquchild09/in-rochester.

2. García-Figueroa JM, Harding DR. Effect of High Ion and Electron Densities and Substrate Temperature on the Properties of Glow-Discharge-Polymer Films. Poster presented at 22nd Target Fabrication Conference; March 12-16, 2017; Nevada National Security Site, Nevada, United States of America. Available from: García-Figueroa's website at: https://inquchild09.wixsite.com/inquchild09/in-rochester.

Abstract

The content of this study provides evidence of the non-collisional, transient, discrete, discriminant, and susceptible nature of the electron cyclotron resonance — microwave — chemical vapor deposition (ECR-MW-CVD) method ambipolar-state's character, its relationship to the processing conditions in an ECR-MW-CVD system, and its influence over the properties of hydrocarbon films. More important, the results of this study qualify the ECR-MW-CVD method for upgrading shells for laser fusion experiments at ≤ 200ºC and provide first-hand knowledge of how to use the ECR-MW-CVD method ambipolar-state's character to deposit specialty types of hydrocarbon films. In this study, hydrocarbon films were deposited on silicon substrates using a home-built ECR-MW-CVD system, methane, and hydrogen and were characterized via x-ray, Raman, and Fourier transform infrared spectroscopies, scanning electron and probe microscopies, photography, nano-indentation, gravimetry, ellipsometry, and 1-D measurements. Beyond dissecting the ECR-MW-CVD method ambipolar-state's character and uncovering its role in dictating the properties of hydrocarbon films deposited in an ECR-MW-CVD system, this study concludes by suggesting ways to keep exploring aspects from the concept 'ambipolar-state' of the ECR-MW-CVD method for the benefit of humanity.

Contributors and Funding Sources

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List of Symbols

Symbols Shown in Chapter 2

Symbol	Name	Unit
σ_s	Plasma's Conductivity	S/m
B_x	Magnetic Field	Ns/m or Gauss
dv_e/dt	Acceleration of the Electron or Electron's Velocity Rate	m/s^2
e^2	Elementary Charge Unit equal to 1.602×10^{-19}	C
$E_{\|\|}$	Electric Field	N/C
f_{ce}	ECR-MW Source's Oscillation Frequency	Hz
F_e	Force of Moving Electron	N
m_e	Electron's Mass, equal to 9.109×10^{-31}	kg
n_e	Electron's Density of the Plasma	m^{-3}
Q	Electron's Charge	C
Q/m_e	1.758×10^{11}	C/kg
V	Ionization Potential	eV or Volts
v_e	Electron's Velocity	m/s
r_e	Electron's Gyration Radius	m or mm

List of Symbols (Continue)

Symbols Shown in Appendix A

Symbol	Name	Unit
Com	Number of Compounds	—
Kn^{-1}	The Reciprocal Knudsen Number (RKN)	—
F	Degrees of Freedom	—
L	Characteristic Length of the ECR-MW-CVD System, 0.1016.	m
λ	Mean Free Path	m
μ	Viscosity	Pa-s
M	Molecular Weight	g/mol
P	Pressure	Pa
P_x	Pressure in the Point x	Pa
P_1	Pressure in the Point 1	Pa
P_2	Pressure in the Point 2	Pa
Ph	Number of Phases	—
R	Gas Constant Law, 8.314	$J\ K^{-1}\ mol^{-1}$
RKN_x	Reciprocal Knudsen Number in the Point x	—
RKN_1	Reciprocal Knudsen Number in the Point 1	—
RKN_2	Reciprocal Knudsen Number in the Point 2	—
T	Temperature	K

Symbols Shown in Appendix B

Symbol	Name	Unit
ρ_{Film}	Density of a Film	g/cm^3
$\rho_{Substrate}$	Density of a Substrate	g/cm^3

List of Symbols (Continue)

Symbols Shown in Appendix C

Symbol	Name	Unit
A	First Coefficient of Cauchy's Layer Model	—
B	Second Coefficient of Cauchy's Layer Model	μm^2
C	Third Coefficient of Cauchy's Layer Model	μm^4
λ	Wavelength, 0.55	μm
$n(\lambda)$	Refractive Index	—

Symbols Shown in Appendix D

Symbol	Name	Unit
A_{sp}	Area of Carbon sp Hybridized Bonds	pts^2
A_{sp^2}	Area of Carbon sp^2 Hybridized Bonds	pts^2
A_{sp^3}	Area of Carbon sp^3 Hybridized Bonds	pts^2
A_{Square}	Area of a Square	pts^2
A_T	Total Area Counted in the Analysis	pts^2
$A_{Triangle}$	Area of a Triangle	pts^2
F_{sp}	Fraction of Carbon sp Hybridized Bonds	—
F_{sp^2}	Fraction of Carbon sp^2 Hybridized Bonds	—
F_{sp^3}	Fraction of Carbon sp^3 Hybridized Bonds	—
H	Height	pts
W	Width or Base	pts

Chapter 1

Introduction

1.1. Purpose of the Study

The study explains why and how an electron cyclotron resonance – microwave – chemical vapor deposition (ECR-MW-CVD) system was selected as a method to deposit a variety of thin films at temperatures ≤ 200ºC to make specific types of capsules needed for laser-fusion experiments[1 – 5]. The explanation of how the unique plasma properties of the ECR feature affect the deposited-film properties is provided through the depiction of the ECR-MW-CVD method ambipolar-state's character — or sum of properties or characteristics — that define the ambipolar-state of the ECR-MW-CVD method at the gas-substrate interphase and how such ambipolar-state's character allows the molecular balance between the species that form the film at the gas-substrate interphase. The study also offers empirical evidence of how the system's processing conditions affect the ECR-MW-CVD method ambipolar-state's character and how the ECR-MW-CVD method ambipolar-state's character influences the properties of hydrocarbon films.

1.2. Roadmap of the Study

The study consists of a construction and commissioning phase, an experimentation phase, and a verification-by-proof cause-and-effect phase. The construction and commissioning phase consists of build, test, and qualify an ECR-MW-CVD system. The experimentation phase has two stages. Its first stage consists of depositing hydrocarbon films at selected conditions using the ECR-MW-CVD system. Its second stage consists of characterizing hydrocarbon films using multiple methods to determine if and how the processing variables affect the properties of the deposited films. The verification-by-proof cause-and-effect phase consists of matching the processing conditions of the system to the properties of the film using spreadsheets, images, and research literature.

1.3. Importance of the Study

Capsules containing the fuel for laser-fusion experiments must be low density and comprise of low-atomic-number elements (preferably only carbon and hydrogen), be like spheres with an out-of-round less than 0.2%, and possess higher-atomic number atoms such as silicon to help inhibit relativistic electrons from pre-heating the fuel[2 – 6,] Most important, the surface needs to be smooth to limit Rayleigh-Taylor induced hydrodynamic instabilities from compromising the compression of the deuterium-tritium fuel to produce a high neutron yield[3].

Today, these capsules are made using cylindrical inductively coupled plasma processes known as glow discharge polymerization (GDP) — processes that can vapor-deposit hydrocarbon films in a low-pressure low-thermal-equilibrium plasma. Nonetheless, there is interest in enhancing the capabilities of those GDP processes to make capsules with strength equal to or less than 200 GPa from elements with atomic-number equal to or less than 15.

An ECR-MW-CVD method might assist in the enhancement of current GDP processes by vapor-depositing hydrocarbon films on top of low-density spherical plastic shells at less than 200ºC[6 – 9]. However, the method can not be approved for making shells until the fusion community understands how it works, why it works as it does, and how to control it to vapor-deposit desirable types of shells. Thus, this study focussed on explaining to the fusion community what types of capsules they can get through the depiction of the ECR-MW-CVD method ambipolar-state character backed up with evidence from a space parameter analysis of hydrocarbon films made at a specific condition.

1.4. Features of the ECR-MW-CVD System Used in this Study

The ECR-MW-CVD system has five main components — three of these are a vacuum chamber, a gas manifold, and a commercial ECR-MW source; the other two are a heater and DC high-voltage supply. The ECR-MW source generates waves at 2.45 GHz, the electron resonance frequency at a magnetic field of 875 Gauss[9, 10]. The ECR-MW source heats the species inside the system by stripping electrons from the atomic species

and confining them to cyclonically motion around lines of magnetic field[9, 10]. That type of confinement makes it possible to ionize more molecules per unit volume, or to increase the degree of ionization energy per molecule, in the system without adding thermal heat. This phenomenon allows the films to be deposited[- at low temperatures[7] with properties that otherwise only could be achieved at much higher temperatures. Nonetheless, the heater[11, 12], and voltage supply[12] provided supplemental heat and biased the polarity of the substrate to increase the kinetic energy of the depositing radicals[7 – 12].

1.5. Other Components of Interest of the Study

1.5.1. Features of the Films Deposited in the Study

The type of film deposited in this study is hydrocarbon film, a matrix of carbon and hydrogen different from a polymer because there is no associated chain length; the structure is best thought of as a solid solution[6 – 8, 11, 13, 14]. These materials have a high degree of molecular complexity associated with their matrix, as well as a wide variety of characteristics[6 – 8, 13]. For example, their microstructure can have varying degrees of crystallinity embedded in an amorphous structure, depending upon the carbon-to-hydrogen ratio,[6, 10,] and the energetics of the absorbed species at the interphase, which is typically controlled by the temperature of the substrate. Moreover, the microstructure can be tuned, energizing the atomic species absorbed onto the surface using the high ion energy density source of the ECR-MW-CVD system.

1.5.2. The Deposition of Hydrocarbon Films

The ECR-MW-CVD system deposited various types of films suitable for making shells for laser fusion experiments. The data from the characterization techniques showed that these films were from 0.2 to 9.8 μm-thick, their refractive indices were from 1.2 to 1.6, their densities were-up to 1.8 g/cm^3, and their hardnesses and stresses were from 0.3 to 12.1 GPa and from 5.2 to 180 GPa. It also showed that these films possessed roughness ranging from 4 to 430 nm-rms over an area of 10,000 μm^2. However, at pressures < 3 Pa, no deposition was achieved as the plasma conditions favored etching or desorption over deposition or nucleation, and there was no film growth observed at pressures > 7 Pa.

The hydrocarbon films deposited in this study used methane gas as the limiting reactant and hydrogen as dilution gases. Other gas combinations are known to form hydrocarbon films, but this study was limited to these two gases to limit the complexity of the gas- and surface chemistries that occur[6]. All the syntheses were at substrate temperatures ≤ 200ºC and pressures between 2.6 – 7.0 Pa. Films were deposited on silicon (1,0,0) and Kapton HN film[16]. Depositions were done by changing ECR-MW powers, ECR-MW voltage-to-current ratios or resistances, gas pressures, and methane-to-hydrogen ratios[9, 10]. Also, by changing the substrate temperature and electrical bias of the substrates[10 – 12].

1.5.3. The Verification-by-Proof Cause-and-Effect Phase

The verification-by-proof cause-and-effect phase was a two-stage–process that combined research literature with software. The first step was to arrange the data corresponding to the independent and dependent variables into matrices, graphics, or images. This step employed multiple spreadsheet calculations, basic statistics, image processing, and illustration techniques to record, manage, and analyze the data. The second step was to use these matrices and visual arrangements to verify cause-and-effect between the dependent and independent variables. In this step, the observations were backed up using literature related to the ECR-MW-CVD technique[9 – 12], hydrocarbon films[6, 7], laser fusion experiments[1 – 5], and each characterization methodologies used to measure the films' properties.

The study classified the system's processing parameters and the films' properties into three types of variables: independent-variables, dependent-variables, and mixed-variables, where the term mixed-variables refers to those variables that are neither fully independent nor dependent variables. The main independent variables were the substrate temperature, the percentage of methane, the total gas pressure, the processing time, ECR-MW voltage-to-current ratio — or ECR-MW resistance, and the ECR-MW power. Ancillary independent variables were the substrates and the heater temperature. The dependent variables were the thickness, stress, roughness, hardness, density, color, and coating uniformity of the films. The mixed variables were the surface's chemistry and the refractive indices of the films.

1.6. Overview of the Relationship between the ECR-MW-CVD Method, its Ambipolar-State's Character, and the Properties of Vapor Deposited Films

In any vapor deposition method, films are grown according to five phenomena: diffusion, inter-diffusion, desorption, step-nucleation, and 3D-nucleation. Figure 1.6-1 shows the action of these phenomena in the formation of the films[17].

How and which of these phenomena predominate to form a specific type of film is exclusive of each VD method. This statement is true for physical vapor deposition (PVD), where the species inside the plasma are only ionized to bombard a target that ablates and form the film, or for chemical vapor deposition (CVD), where the species inside the gas or plasma react to form ionized radicals, and then, reacted to form the film[6, 7, 10, 18].

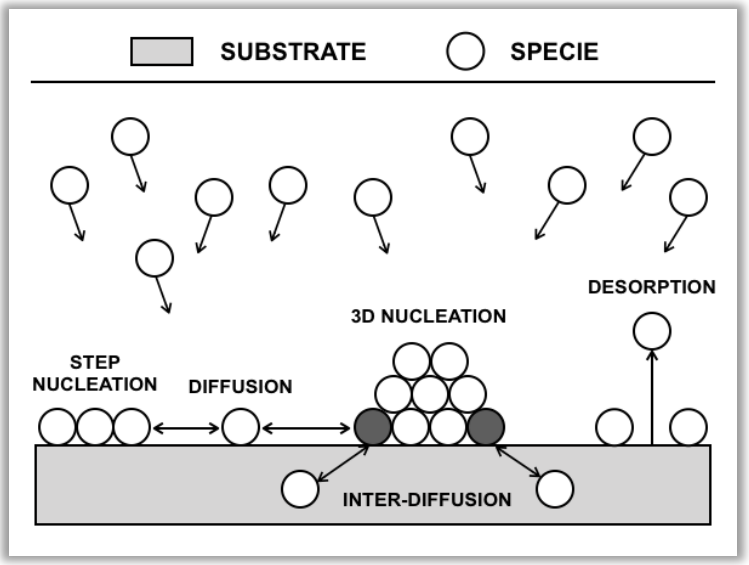

Figure 1.6-1. Atomic transfer phenomena happening in VD methods[17].

In the electron cyclotron – microwave – chemical vapor deposition (ECR-MW-CVD) method, the species inside the plasma are ionized using a moderate electron density and ion energy source. As a result, films can grow at low deposition temperatures due to the moderately high density of energized ions that results from a moderated density of energized electrons inside an ECR-MW plasma[6, 7, 9 – 11, 19 – 21].

The features of the ECR-MW-CVD method make that method a complementary approach for vapor-deposit films for laser fusion experiments. Currently, these films are deposited on plastic shells via plasma-assisted chemical vapor deposition (PA-CVD) and to helical discharge resonation (HDR). While the ECR-MW-CVD, PA-CVD, and HDR have provided similar electron-plasma confinement, the HDR's source delivers lower ion energy to the species in the plasma than the source of an ECR-MW-CVD's course does. Likewise, the ECR-MW-CVD's source gives lower ion energy to the species in the plasma than the PA-CVD's source does[2, 9, 10, 17, 20, 21]. The moderate ion bombardment and electron confinement of the ECR-MW-CVD's source makes an ECR-MW-CVD system deposit films with moderate strengths, hardnesses, and densities[17] that are smoother than those films deposited via PA-CVD or HDR[6, 11, 16 – 18].

Nevertheless, the most important thing of the ECR-MW-CVD method is its ambipolar-state's character, which dictates how the plasma species interact at the gas substrate interphase to form a film[9, 14, 17, 21]. The concept 'ambipolar' refers to the balanced coexistence of the species with opposite characteristics — such as a proton vs. an electron — at the gas substrate interphase. For the specific case of the ECR-MW-CVD method, the ambipolar-state's character of an ECR-MW-CVD system makes the ECR-MW plasma

to be neutrally charged[22, 23]. What is more, the ambipolar-state is transient, in part because of the transient nature of conductivity in the substrate during the deposition process and because of the conditions at which films are deposited. Furthermore, the ECR-MW-CVD method ambipolar-state's character should also be discrete, discriminant, and thus, susceptible to any change in the plasma condition within the ECR-MW-CVD method because of the moderate ion energy and electron density produced by the ECR-MW plasma source.

Ironically, regardless of the ECR-MW-CVD method ambipolar-state's character exists, and it must be depicted no one has ever validated its existence experimentally. The ambipolar-state's character of the ECR-MW-CVD method makes films grow as they do inside an ECR-MW system. Furthermore, research literature shows that the transient, discrete, discriminant, and susceptible of the ambipolar-state's character of the ECR-MW-CVD method can be influenced by intrinsic and extrinsic conditions in the ECR-MW environment. That justifies why the deposition parameters of the ECR-MW-CVD system can be manipulated to control the properties of films while these are deposited.

1.7. The Rest of this Manuscript

The rest of this manuscript shows in more detail the role of the ambipolar-state's character of the ECR-MW-CVD method and its influence on the properties of vapor-deposited films deposited at low energy and near-ambient substrate temperatures. It provides empirical knowledge for making films with a broader range of properties from the perspective of the ambipolar-state's character of the ECR-MW-CVD method.

In addition to that, the rest of this manuscript offers supporting evidence that qualifies the ECR-MW-CVD method as part of the GDP processes to make capsules for laser fusion experiments. In short, it shows that the ECR-MW-CVD method can deposit films with moderate-high densities and modulus at near-ambient substrate temperatures in a controllable way like no other VD method did[1 – 5].

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