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John Carlson
Macalester College, jcarls10@macalester.edu

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MACALESTER COLLEGE

Dissociative Excitation of H2 in an RF Plasma

Abstract

Plasma-enhanced chemical vapor deposition is a widely used method for depositing thin films. In order to optimize the properties of the films, it is important to understand the plasma processes that occur during film growth. In this research we use optical emission spectroscopy in order to measure the spectral emission lines of a plasma produced with hydrogen gas. In conjunction with other measurements and modeling, these measurements can provide insight to the electron energy distribution of the plasma.

Keywords

plasma, thin film, hydrogen, electron temperature

Cover Page Footnote

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INTRODUCTION

Thin film applications arise in numerous fields, and are responsible for many of the technological advances that our society takes advantage of. These fields include everything from photovoltaics to medicine transport in a human body. Despite the wide range of uses that thin films can be applied to, the bioprocesses that occur during film growth and modification are not well known. Because of this lack of understanding, it is more difficult to truly optimize the films for specific uses. In our research we wanted to further the understanding of the plasma chemistry and physics in order to optimize thin film applications. In plasma processing, elementary processes such as ionization, dissociation, excitation, gas-phase chemical reactions, and ion bombardment are closely related to the plasma parameters and therefore plasma diagnostics are important in understanding the mechanisms of material processing [1]. The ability to understand the chemistry and physics that occurs during a plasma discharge would allow us to measure and model the reactive species involved during thin film growth and modification. The radiation produced in the visible spectral range of the plasma originates from atomic and molecular transitions [2]. Through the use of optical emission spectroscopy, it is possible to measure the electron kinetics of the plasma through the measurement of the hydrogen gas dissociation, excitation, and photon release during a steady state discharge. We needed to carefully analyze the kinetic processes contributing to populate and depopulate excited states of the species in the plasma in order to determine the plasma characteristics [3]. While our findings are a key component into discovering the chemistry and physics occurring in a thin film plasma, it is important to note that this approach to plasma analysis is relatively

rare. As a result, this research leaves us with unanswered questions and requires to rethink our approach to the analysis of the data.

METHODOLOGY

1. Matching Network

The circuit (Figure 1) used to power a plasma discharge needs to be designed a specific way in order to ensure the discharge will maintain a plasma while simultaneously protect the components from the large powers needed to create a plasma. The initial power is supplied by an alternating current generator that has an output impedance of 50 Ω. The power from this generator feeds through a coaxial cable with stray capacitance of 57 pF and stray inductance of 0.16 μH into the matching network system. The matching network consists of a variable inductor, variable capacitor, and a coupling capacitor with values of 0.39 μH, 534 pF, and 0.1 μH, respectively. The power then traveled through a second coaxial cable with a stray capacitance of 142 pF and a stray inductance of 0.40 μH, until it finally reaches the upper electrode of the discharge system.

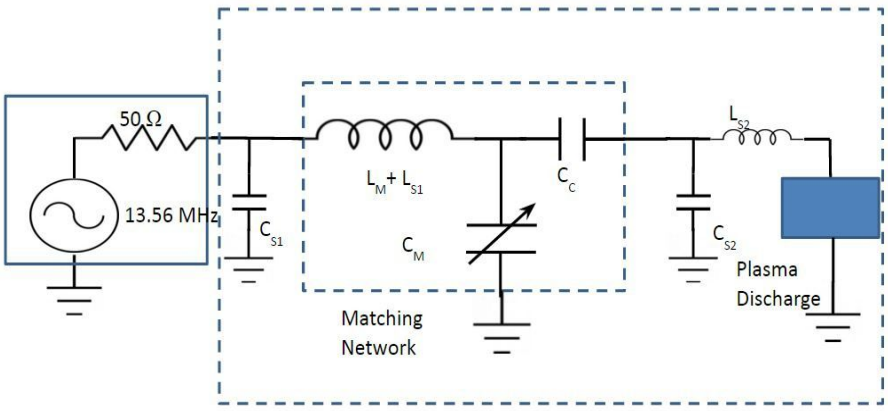


Figure 1. Schematic showing entire circuit design. Small dashed box denotes contents of matching network. Large dashed rectangle represents the components whose total must equal 50 Ω in order for no reflected power.

The matching network plays an integral part in the success of the discharge circuit design. It is designed to protect the power supply from overheating and damaging itself by matching the output impedance with the impedance of the plasma discharge. In this sense it eliminates any reflected power that could travel back to the power supply. If reflected power back to the power supply reached zero, we knew that the power supply was safe and able to produce plasmas for long periods of time. Assuming we had reached zero reflected power, we could derive the impedance provided by the discharge itself in order to learn more about its properties.

2. Optical Emission Spectroscopy

Optical emission spectroscopy was used to provide insight into the movements and particle interactions of the electrons present in the plasma. The great advantages of plasma spectrometry are the simple experimental set-up and that it provides a non-invasive and *in situ* diagnostic method [2]. In order to do this, we measure the spectral lines produced by dissociative excitation of the hydrogen gas and the resulting de-excitation of hydrogen molecules through photon release. The general approach is to compare relative emission intensities that are excited by electrons from different parts of the electron energy distribution function [4]. In our research we compared H_α and H_β emission intensities. To ensure we measured accurate results we focused on the center of the discharge, which we took to be the point of highest intensity of light emissions. Then we used a lens to refract escaping light back to the Ocean Optics spectrometer. Finally, we acquired the data and

produce light spectrums that we could analyze. To ensure we measured the correct relative intensities of light, the spectrometer sensitivity was calibrated using a tungsten halogen lamp with known light spectrum.

Our research focused on the dissociative excitation reactions of hydrogen molecules due to the relatively simple nature of hydrogen, and the well-known properties of the hydrogen dissociation process. In particular, we chose to focus our measurements on the spectral emissions of H_α and H_β, the first of the Balmer emission lines for hydrogen. This decision came about because both peaks are relatively pronounced in hydrogen, and the cross sections of both excitation processes. The reactions shown below visualize the dissociative excitation in which we can measure.

$$e^- + H_2 \rightarrow H + H^* + e^- \qquad H_\alpha \text{ excitation} \tag{1}$$

$$e^- + H_2 \rightarrow H + H^{**} + e^- \qquad H_\beta \text{ excitation} \tag{2}$$

Both reactions begin when an electron collides with molecular hydrogen and dissociates it, simultaneously exciting one hydrogen atom. The difference depends on whether the excited hydrogen is excited to the first or second excited state, which is determined by the energy of the electron, or the electron temperature, that collided with the molecule. Once excited, the hydrogen atom releases the energy in the form of a photon and returns to the ground state. The process and known wavelengths for both H_α and H_β are listed below.

$$H^* \rightarrow H + h\nu \quad (656.3\ nm) \qquad H_\alpha \text{ emission} \tag{3}$$

$$H^{**} \rightarrow H + h\nu \quad (486.1\ nm) \qquad H_\beta \text{ emission} \tag{4}$$

Knowing these wavelengths and processes enables us to determine the intensities of the light at each wavelength, and make inferences of the average electron temperature of the plasma.

RESULTS AND DISCUSSION

1. Matching Network Examination

Performing the circuit analysis using the matching network and discharge impedances, we were able to calculate the impedance of the discharge itself to be -16j. Due to the negative imaginary term present in the impedance, the discharge system must act as a capacitor. From this, we determined the total capacitance to be 733 pF. However, it was previously calculated that the electrodes alone have a capacitance of about 8 pF. This implies that the majority of the capacitance is not dependent upon the electrodes, but rather an artifact the entire system. We then determined that the entire chamber reacts capacitively to the powered electrode. Figure 2 shows a visualization of all the places that chamber was acting capacitively. Literature suggests this problem is solved with the addition of an inductor, which would counteract the impedance brought on by the grounded chamber.

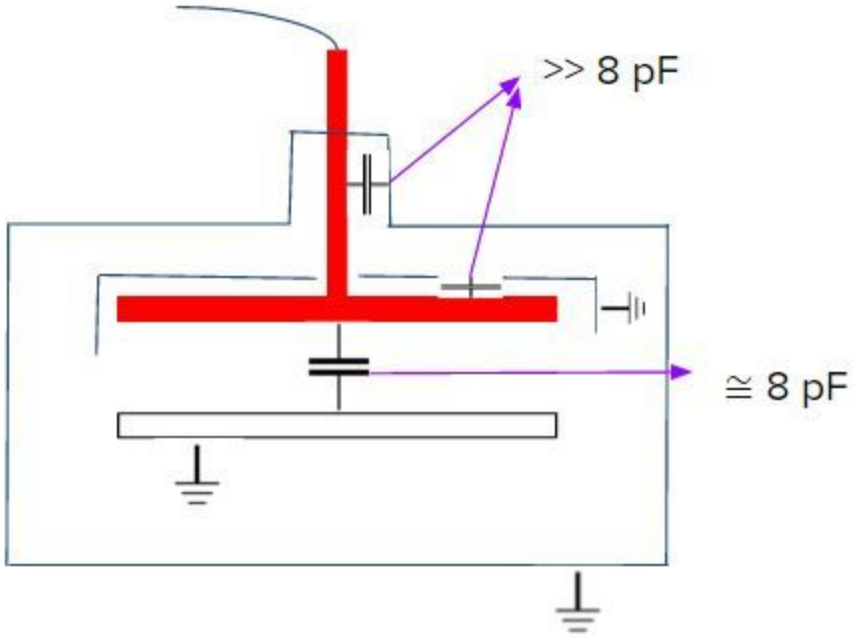
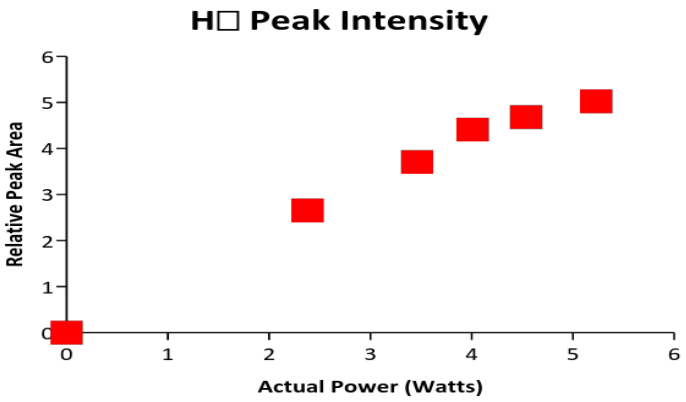


Figure 2. Simplified schematic of chamber showing all the possible places for capacitive effects to occur. Red denotes powered. The capacitance produced by interactions with the chamber walls and the electrode shield are much greater than the capacitance produced between the two electrodes.

2. Optical Emission Spectroscopy Results

From the results produced using optical emission spectroscopy, we found the peak areas to determine the relative emission intensities of both H_α and H_β. Figure 3 shows this calculation as a function of power delivered to the discharge for both emission processes.



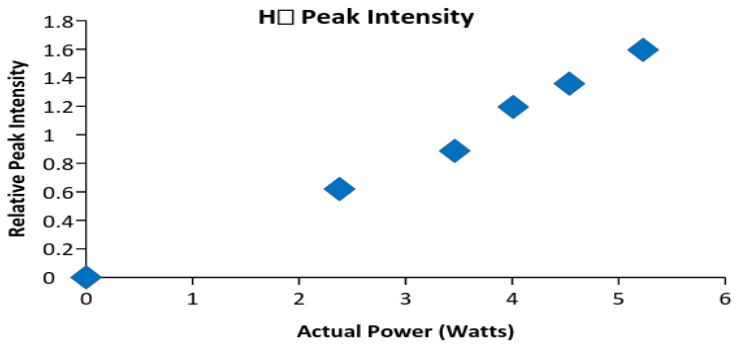


Figure 3. Plots showing H_α (red) and H_β (blue) relative peaks area on the y-axis versus actual power delivered to the discharge on the x-axis.

Both the H_α peak intensity as well as the H_β peak intensity shows a linear relationship at lower powers. This implies that the power delivered to the discharge is proportional the the peak intensity for low powers. However we cannot apply this to the whole plot because there seems to be a slight leveling off of the peak area, especially in the H_α plot.

In order to apply our plot findings, the rate constant for dissociative excitation that is dependent upon the energy of the electrons in the plasma is

$$\nu_{de} = C \int_{E_{th}}^{\infty} \sigma_{de}(E) f(E) dE$$

where $\sigma_{de}(E)$ is the cross section for dissociative excitation and $f(E)dE$ is the electron energy distribution, which we took to be a Maxwellian function. $\sigma_{de}(E)$ can also be thought of as the probability of the reaction occurring at a given energy, while $f(E)dE$ can be thought of as the probability that the electron has that energy. By assuming that photon emission is the exclusive de-excitation for excited hydrogen, we can then set the dissociative excitation rate ν_{de} equal to the emission rate of the the plasma, and take it to be proportional to the intensity for H_α and H_β measured using optical emission spectroscopy.

Then we can take the ratio of the two hydrogen emissions using the formula

$$\frac{I_\alpha}{I_\beta} = \frac{\int_{E_{th\alpha}}^{\infty} \sigma_\alpha(E) f(E) dE}{\int_{E_{th\beta}}^{\infty} \sigma_\beta(E) f(E) dE}$$

and use the relative peak intensities from Figure 3 in order to create a ratio of the H_α and H_β peak intensities, as seen in Figure 4.

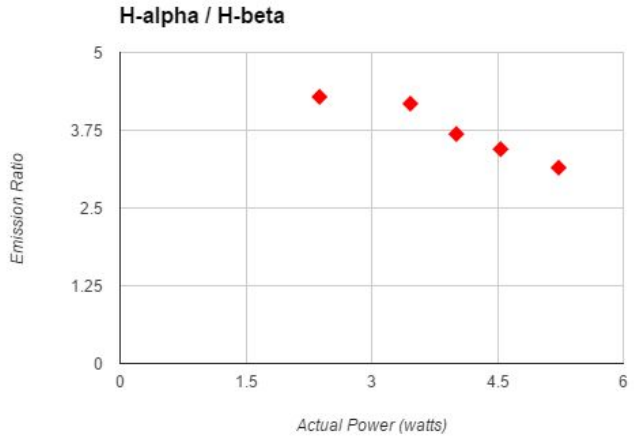


Figure 4. Plot showing the ratio of H_α over H_β. The x-axis is power delivered to the discharge in watts, and the y-axis is the emission ratio in arbitrary units.

From the plot we can see that the ratio of emission decreases as power increases. This implies that the rate of H_β emissions is increasing at a faster rate than H_α emissions as power increases. This finding matches the theoretical data predicted in Figure 6 below, where we expect intensities of both H_α and H_β to increase as electron energy increases. However, due to the higher cross section of H_β, the rate of H_β should increase at a faster rate. From this similarity, it is clear that power delivered to the discharge has some effect on the average electron energy of the plasma.

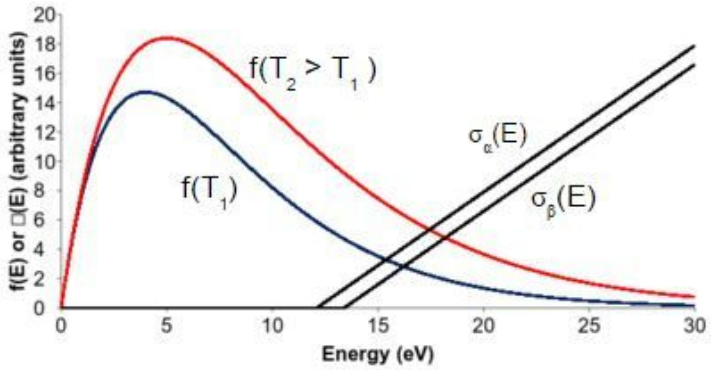


Figure 6. Plot showing cross sections σ_{α} and σ_{β} intersecting with the Maxwellian average electron energy function *f(E)*. The x-axis is energy in electron-volts and the y-axis is the function *f(E)*, known in this case as the probability the electrons has the correct amount of energy.

SUMMARY AND CONCLUSIONS

Conclusions

While our conclusions resulted in results that correspond to the expected results, more research is required in order to make conclusions about the data. The main reason for this is due to a complication involving a non-zero baseline around the H_{β} peak that accounts for approximately 15 to 20 percent of the peak area. One possibility for this baseline is an accumulation of many peaks in such a small area resulted in an overlap effect that hides the true data when plotted on a spectrum. Another possibility we discussed involves light from the discharge that has been scattered, resulting in a baseline glow effect that covers a wide range of wavelengths. More research is required to examine the true cause of the effect, and we will need a comprehensive model for the kinetics of the plasma in order to truly understand.

Future Work

The main concern of the research stemmed from the baseline complications surrounding

the H_β emission peak. One popular method of combatting this issue is to take advantage of a practice called actinometry. This practice involves adding a small amount of noble gas, usually argon, to the hydrogen plasma. This produces pronounced, well known argon excitation peaks. Because argon has a much greater cross section than hydrogen, these peaks eliminate any baseline error that may be in the spectrum. However, the issue with this practice is we are not sure how argon influences the electron kinetics of hydrogen. Along with this, it is not well known how argon affects the energy distribution of the plasma.

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