CHARACTERIZATION OF BCl_3, SF_6, and BCl_3/SF_6 PLASMAS USING LANGMUIR PROBE MEASUREMENTS

BY

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ABSTRACT

A Langmuir probe study in BCl_3, SF_6, and mixtures of BCl_3/SF_6 capacitively-coupled plasmas is presented. In this study, energy distribution functions, electron temperatures (and average electron energy) and electron, positive ion, and negative ion densities were determined as a function of process conditions such as RF power, chamber pressure, and SF_6 percentage in the total flow.

It has been previous observed that the etch rate of GaAs increased when SF_6 was added to BCl_3 plasmas, and that this increase was due to increased dissociation of BCl_3 and subsequent increases in Cl and Cl_2 densities, along with a possible reduction in recombination of reactive etching species via formation of BClF and BCl_2F. It was hypothesized that this effect was primarily due to an increase in electron temperature (or average electron energy) as a result of electron attachment heating with the addition of SF_6.

In a pure BCl_3 plasma at 50 mTorr and 150 W power the electron density was determined to be approximately 1.1×10^9 cm^{-3} and the electron temperature was near 3.2 eV. Under the same conditions in a pure SF_6 plasma, the electron density was 4.1×10^8 cm^{-3} and the electron temperature was 5.5 eV. With the addition of only 10% SF_6 to the BCl_3 plasma, the electron density rapidly decreased to 5.7×10^8 cm^{-3}, and the electron temperature sharply increased to about 4.3 eV (a ~1.1 eV increase). This is characteristic of electron attachment heating, whereby low energy electrons attach to species within the plasma, and the average electron temperature of the fewer remaining electrons must increase in order to sustain the same power dissipation.

These results therefore confirm that the increased dissociation and enhancement in GaAs etch rate with the addition of SF_6 to BCl_3 plasmas was due to electron attachment heating.

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Chapter 1

Introduction

1.1 Background

Semiconductor device fabrication of gallium-arsenide (GaAs), gallium-nitride (GaN), and other III-V compounds is dramatically expanding from the last decade. The drive for the development of these semiconductors is for applications when high gain and low noise at high frequencies are a necessity. These new compounds offer higher electron mobility and a wider direct band gap as compared to silicon (Si) based technologies.

The traditional field effect transistor, usually made from silicon, is called a metal-oxide-semiconductor field-effect transistor (MOSFET). This transistor uses an electron channel region that is doped with impurities to generate mobile electrons in the layer. The drawback to using a MOSFET is a slow down of electrons because they collide with the dopant impurities. Newer, smarter devices find ways to resolve this contradiction of using doped materials. The High Electron Mobility Transistor (HEMT) and uses heterojunction technology and undoped layers for the electron channel instead of doped regions.

A heterojunction is a junction between two materials with different band gaps. Commonly used materials for HEMTs are GaAs with AlGaAs, although GaN with AlGaN is also promising due to its high-power performance. One critical step in fabricating GaAs based field effect transistors (FETs) is the recessing of the gate region. This requires an etching process to remove a thin layer of n^+GaAs. After the

removal of n^+GaAs, the etching process must stop at or in the underlying AlGaAs layer.

Several different plasma processing systems are in use today to etch wafers in industry. The primary plasma sources for wafer fabrification include a capacitively-coupled plasma (CCP), inductively-coupled plasma (ICP), and electron-cyclotron resonance (ECR). Varying other systems, including double plasma (D.P.) and DC plasma sources are still in use, but do not meet high yield expectations of industry and are now primarily in use for investigative purposes. A gaseous electronics conference (GEC) reference cell (operated at 13.56 MHz) is seen often in research, and the historical design is an attempt to give researchers a baseline experimental apparatus. With this rapidly changing field even this baseline system is frequently updated by research groups to operate in the inductively-coupled mode.

1.2 Selective Etching

Selectivity in etching is the relative etch rate between two different materials that are exposed to an etchant gas. For HEMT devices, these two materials are the desired layer that is to be etched and the underlying layer. Another type of selective etching is between a substrate, and a patterning material such as a photoresist. High selectivity is desired on the layer that is to be etched over the other material, to help ensure uniformity.

A selective dry etch process, whereby the thin layer of n^+GaAs is removed with high selectivity over etching the AlAs or AlGaAs stop layer is ideal to meet

HEMT device fabrication requirements. Etch depth uniformity across a wafer during the gate recess process is an important factor in determining the threshold voltage, uniformity of the devices, and overall performance of the integrated circuit (IC). In a reactive ion etch system (RIE), the uniformity of etching is not exact across an entire wafer and there can also be inherent nonuniformities in the substrate layers. With a high etch selectivity plasma; there are few drawbacks if wafer regions are exposed to the etchant for a longer period of time than is required to achieve device uniformity.

There are three basic mechanisms for achieving selectivity of one material over another. One or more of these mechanisms may be present when selectively etching: selective formation of an etch-inhibiting layer (i.e. using a fluorocarbon plasma to selectively etch SiO_2 over Si where polymer films readily deposit on all surfaces, however SiO_2 surfaces can be etched via volatile formation of CO, CO_2, and COF_2), non-reactivity of one material in the plasma chemistry (i.e. removal of a resist film in an O_2 plasma which does not etch an underlying Si or SiO_2 layer), and non-volatility of a reaction product (i.e. formation of a non-volatile product on the surface of an underlying layer). In a RIE chamber, chlorinated plasmas readily etch GaAs, and fluorinated plasmas do not [2]. For the heterojunctions GaAs over AlAs or AlGaAs, a mechanism for selectivity is that the underlying layer forms non-volatile AlF_3 with an etching plasma containing chlorinated (to etch GaAs) and fluorinated species (to form a non-volatile reaction product on an underlying layer of AlAs or AlGaAs).

Previous etching plasmas for GaAs over AlGaAs included CCl_2F_2 in the chemistry [3]. There are a few problems when using CCl_2F_2 plasmas. The first being polymer formation when using a carbon plasma [4]. Another drawback when using CCl_2F_2 is the inability to control the chlorine to fluorine gas ratio, which directly affects selectivity [5, 6]. There are several possible chemistries to attempt to selectively etch materials like GaAs or GaN with different gas ratios. For the chlorinated chemistries one could use Cl_2, BCl_3, or $SiCl_4$. The fluorinated chemistries include F_2, SF_6, SiF_4, or NF_3. Plasmas containing BCl_3 and SF_6 have been used at the KU PRL to selectively etch GaAs over AlAs [5]. However, the addition of SF_6 to BCl_3 caused a somewhat counterintuitive increase in the GaAs etch rate. The addition of Langmuir probe diagnostics to other existing plasma diagnostic techniques was necessary to further explain this effect.

1.3 Langmuir Probe Studies

To characterize plasma chemistries, there are several tools and techniques to determine the properties of the plasma. A microwave interferometer gives an approximation to the bulk electron density. Optical emission spectroscopy can give relative concentrations if actinometry is applied and the electron temperature is constant. Mass spectrometry can give approximate neutral species measurements that are useful to determine the relative concentration of these species and the percent dissociation of parent gas molecules in the plasma. For complex plasmas, like BCl_3/SF_6, there are many species and reactions taking place, requiring a combination

of several diagnostic tools and techniques to provide a good understanding of the plasma properties and mechanisms associated with etching.

The primary experimental instrumentation used in this thesis is a Langmuir probe. It is a relatively easy tool to use in an ideal case plasma, like pure Helium. However, for complex plasmas there are several operational guidelines that must be followed to properly determine plasma properties. A Langmuir probe can give estimations of plasma density, electron density, positive ion density, negative ion density, electron temperature, and average electron energy. The mass of each species must be known when determining densities. For electrons, this is a well known value. However, even in plasmas containing a diatomic molecule it is not well known or easy to attain the average mass of the positively or negatively charged ions.

Several factors limit the ability to measure each plasma property with a Langmuir probe. One such factor is the ability to clean the probe tip after exposure during a data sweep in the processing gas. There are several literature experiments involving the study of simple, electropositive plasma discharges, typically in single noble gas chemistries [7-11]. However, these studies do not have to incorporate the rigorous the probe cleaning techniques that are involved in the less studied, electronegative, and corrosive gases like Cl_2, BCl_3, and $SiCl_4$.

In increasing order of difficulty (in electropositive discharges), the plasma properties that classical Langmuir probe techniques can measure are: floating potential (V_f), plasma potential (V_p), characteristic electron temperature (kT_e), and electron density (N_e). The difficulty in measuring kT_e and N_e are equal in

electronegative discharges due to their reliance on the same distribution function. In comparison to classical Langmuir probe techniques, it is even harder to estimate positive ion densities when dealing with their portion of the I-V (current vs. voltage) curve. Iteration techniques coupled with theories are often required; Laframboise, OML (orbital-motion-limited), ABR (Allen, Boyd, and Reynolds), and BRL (Bernstein and Rabinowitz, and further refined by Laframboise) theories only yield estimates of electron and positive ion density within about 40% of microwave density measurements [11, 12]. Furthermore, estimates of the electron energy probability function (EEPF) and the electron energy distribution function (EEDF) are very difficult to obtain, due to the low signal to noise ratio required for the analysis of the second derivative of the I-V probe characteristic. Finally, for electronegative plasmas the determination of the negative ion densities depends upon the EDF (energy distribution function, which consists of electrons and negative ions) and is rarely reported. For this reason, as well as the difficulty in approximations to the mass of the ion(s), data concerning plasmas containing negative ions are by far the most difficult.

Amemiya presented theoretical and experimental extensions of the electrostatic probe technique in an electronegative plasma [13]. These experiments were fundamental in obtaining a method for plasma parameters by use of a Langmuir probe in an electronegative plasma. Besides the identification of features in the second derivative of the current, Amemiya also discussed negatively charged metastable species which must be discriminated from the peak caused by negative ions.

No experiments using a Langmuir probe in BCl_3/SF_6 plasmas have been previously reported. Again, this may well be due to the difficulty in obtaining an EDF, complex discharge chemistry, and the intricate plasma physics. With the exception of my coworker, B. Pathak, the closest Langmuir probe studies to this work are in plasmas containing noble gas mixtures with SF_6 and plasma chemistries involving the addition of Cl_2, N_2, and/or Ar to BCl_3. B. Pathak recently investigated He, N_2, and BCl_3/N_2 plasmas by use of a Langmuir probe and his work was instrumental in establishing a premise for application of probe theory in corrosive, electronegative plasmas [1].

Chapter 2

Motivation, Literature Review, & Objectives

This chapter contains the motivation for this work, a review and discussion of the literature, and the objectives of this research. The first part describes the motivation for the use of a Langmuir probe to investigate mechanisms associated with the increase in GaAs etch rate with the addition of SF_6 to BCl_3. Included is a summary of work performed by Y.S. Lee in BCl_3/SF_6 plasmas at the KU PRL for the selective etching of a particular heterojunction substrate comprised of GaAs over AlAs. The second part is a literature review of Langmuir probe investigations in BCl_3 and SF_6 plasmas. This part also covers a literature review of electron collisions in BCl_3 and SF_6 plasmas. The final part includes the overall objectives of this research for the Langmuir probe studies.

2.1 Motivation

2.1.1 Background on Selective Etching of GaAs over AlGaAs or AlAs

Smolinsky et al. investigated plasma etching of GaAs and its oxide in sixteen reagents [2]. In their research, the only reagents to etch GaAs were chlorinated; CCl_4, CCl_2F_2, PCl_3, HCl, Cl_2, and $COCl_2$. With the exception of CCl_2F_2 (where the dissociated chlorine was responsible for etching), no fluorine containing plasmas etched GaAs or its oxide. This is due to a presumed high-activation energy barrier of GaF_3 and the non-volatility of the fluorine-based product(s) [14].

The vapor pressure and boiling points for Ga and As chlorides and fluorides are presented in Table 2-1. Chlorine based plasmas form volatile etching products with Ga and As. Fluorine based plasmas only form volatile etching products with As. As a result, mixtures of BCl_3 and SF_6 are useful as selective etch plasmas to remove GaAs but not AlGaAs or AlAs via non-volatile AlF_3 formation. In the Introduction chapter of this work, selective etching of the heterojunctions, GaAs over AlGaAs or AlAs, is discussed. The mechanisms for etching these heterojunctions using chlorinated and fluorinated plasmas to remove GaAs and not AlGaAs or AlAs are also included. The mixtures for this work include BCl_3 and SF_6, and they are effectively used to selectively etch GaAs over AlAs and AlGaAs [5, 15-18].

Table 2-1 Volatility of possible chloride and fluoride etch products of GaAs [14].

Etch product	**Vapor Pressure at 75^{0}C (Torr)**	**Boiling or sublimation temperature (^{0}C)**
$AsCl_3$	199	130
AsF_5	39225	-53
AsF_3	1110	58
$GaCl_3$	14.5	201
GaF_3	Insignificant	950

The first group to apply selective dry etching of GaAs over AlGaAs was Hikosaka et al. [3]. They used a gas mixture of CCl_2F_2/He and showed an increase in GaAs etch rate by increasing power and composition of CCl_2F_2. With the selectivity

reported (≥200:1), and good etch uniformity on the wafer, dry etching of heterojunctions showed promise compared to that of wet etching.

Salimian et al. was the first group to independently control the fluorine to chlorine ratio for the selective etching for GaAs over $Al_{0.29}Ga_{0.71}As$. The importance of controlling this ratio is the direct impact on selectivity, which is highly desired for creating heterojunctions [14]. The plasma chemistry used was $SF_6/SiCl_4$, which was shown to be superior to CCl_2F_2 due to the elimination of polymer buildup with carbon containing plasmas, and higher selectivity (500:1).

Guggina et al. reported on the selective reactive ion etching of GaAs over varying mole fraction $Al_xGa_{1-x}As$ in $SiCl_4/SiF_4$ plasmas [19]. The results showed that the presence of the AlF_3 etch inhibiting layer was dependent on the aluminum concentration in the $Al_xGa_{1-x}As$ layer. Higher concentrations of aluminum quickened the formation of the inhibiting layer; however the results also showed that at higher self-bias voltages, the AlF_3 would be sputtered at a higher rate, thus dropping selectivity which was reported as high as 500:1.

Kao et al. studied the selective reactive ion etching of double recessed pseudomorphic GaAs HEMTs in BCl_3/SF_6 plasmas and reported a selectivity greater than 600:1 [16]. Juang et al. reported faster etch rates of the III-V materials GaAs, AlGaAs, InP, InGaAs, and InGaAsP in $Cl_2/BCl_3/Ar$ plasmas as compared to $CCl_2F_2/BCl_3/Ar$ [20]. Hays et al. selectively etched $GaAs/Al_{0.22}Ga_{0.78}As$ under ICP (inductively coupled plasma) source and RIE system conditions using BCl_3/SF_6 plasmas, and the authors suggested that etch selectivity in RIE was superior to that of

ICP due to higher atomic fluorine concentration and higher ion flux in the ICP system [15]. The authors also commented that the higher ion flux may be causing desorption of the otherwise involatile etch products that improve selectivity.

Hays et al. also compared ICP and RIE systems in BCl_3/NF_3 plasmas [21]. Both systems were reported with lower selectivity than in his previous investigation with BCl_3/SF_6, however the etched surface morphology improved with the use of BCl_3/NF_3 plasmas. The authors commented that with SF_6 plasmas, sulfur contamination was most likely contributing to the surface residue, and an additional in-situ or ex-situ cleaning step may be required.

J. W. Lee et al. investigated the etching of GaAs over $Al_{0.2}Ga_{0.8}As$ with $BCl_3/SF_6/N_2/He$ chemistry in an ICP system [17]. They reported a dramatic increase in etch rate with the addition of a small amount of He to a SF_6/BCl_3 plasma, and a resultant increase in selectivity. The addition of N_2 to BCl_3/SF_6 plasma enhanced their sidewall passivation, and produced a very anisotropic pattern transfer without a significant decrease in etch rate. With a $BCl_3/SF_6/N_2/He$ plasma, the authors reported excellent anisotropy, clean surfaces, reasonably fast etch rate, and a selectivity >200:1 with etch rate of 1500Å/min.

Each of these scientists noticed a change in selectivity and etch rate for the addition of one gas to another (i.e. SF_6 added to BCl_3 and SF_6 added to $SiCl_4$). These observations of etch rate enhancement and changes in selectivity initiated investigations as to the cause. Several plasma diagnostic tools and techniques must be employed to adequately characterize the plasmas.

2.1.2 Etching and Diagnosis of GaAs using BCl_3/SF_6 Plasmas

Y.S. Lee chacterized BCl_3/SF_6 plasmas used for selective etching of GaAs/AlAs; this section contains a summary of his work [5, 17, 22].

It is well known that chlorine based plasmas etch GaAs, however for the addition of SF_6 to BCl_3 there is an etch rate enhancement [18, 23]. This enhancement was previously investigated by Y.S. Lee using microwave interferometry, optical emission spectrometry (OES), and a quadruple mass spectrometry (QMS) [5]. The enhancement in etch rate of GaAs in a BCl_3/SF_6 plasma can be seen in Figure 2.1. At this power and pressure, the etch rate maximum occurs around 55% SF_6.

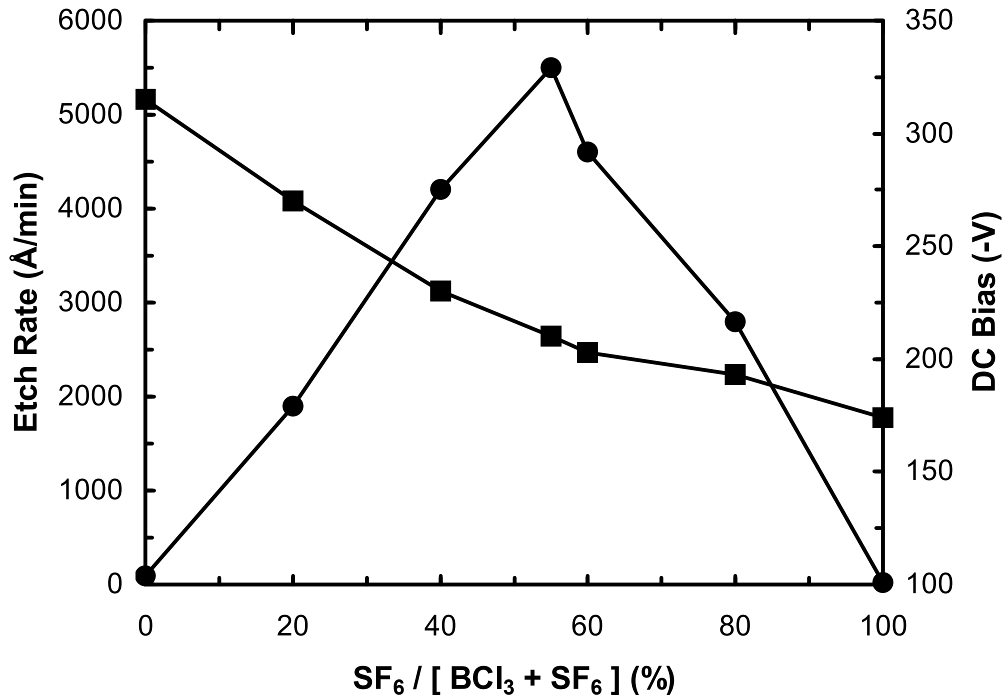


Figure 2-1 Etch rate of GaAs as a function of percent SF_6 in the flow for constant power (150 W, 50 mTorr, 20 sccm). DC bias is also shown [5].

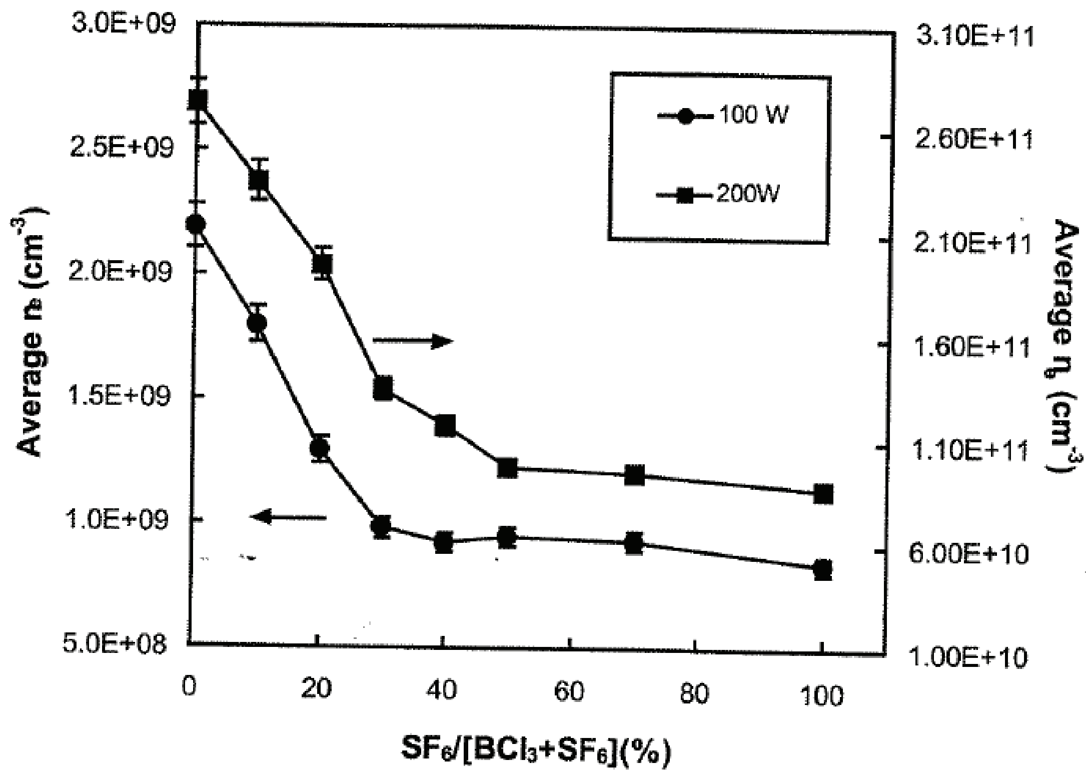


Figure 2-2 Averaged electron density as a function of SF_6 percentage in the flow (50 mTorr, 20 sccm BCl_3+SF_6) [5].

The microwave interferometry results from Y.S. Lee show a decrease in electron density for the addition of SF_6 to BCl_3. Figure 2.2 shows this drop in electron density as a function of composition at 100 and 200 W for constant pressure of 50 mTorr. This can be explained by the higher electronegativity of SF_6 as compared to BCl_3 (and not shown, the drop in DC bias for constant power). Y.S. Lee also noticed in BCl_3/SF_6 plasmas that at constant DC bias, the addition of SF_6 "results in higher power requirements to keep a constant DC bias. This can be explained by the results from the electron density measurements in which the electron density decreases with added SF_6 due to electron attachment."

Electron attachment heating is a mechanism that results in an abrupt decrease in electron density and a corresponding abrupt increase in electron temperature [24-28]. Low energy electrons attach to species within the plasma, increasing the average electron energy and this increase does not scale from the pure gas values [24]. The fewer remaining electrons must sustain the same power dissipation, thus increasing their average energy [23]. The Ar OES results from Y.S. Lee show a steady increase in the Ar excited state emission intensity as SF_6 is added to a BCl_3 plasma even though the argon concentration was constant. Since the electron density decreases with increasing SF_6 percentage, this is an indication that there may be electron attachment heating.

Appearance mass spectrometry results of neutrals from Y.S. Lee are shown in Figure 2.3 and percent dissociation measurements of BCl_3 are presented in Figure 2.4. The percent dissociation of BCl_3 was defined as the QMS intensity difference of BCl_3 signal between plasma on and off. At a power of 200W and 70% SF_6, there is almost complete dissociation of BCl_3. This also correlates with the maxima of the Cl_2 and Cl signals. This indicates that the addition of SF_6 enhances the dissociation of BCl_3 and increases the formation of Cl_2 and Cl etching species [5]. QMS measurements were not taken of the positive ions due to the equipment restriction of not being able to place the orifice close enough to the chamber. As a result, any charged species would have recombined into a neutral species prior to entering the mass spectrometer.

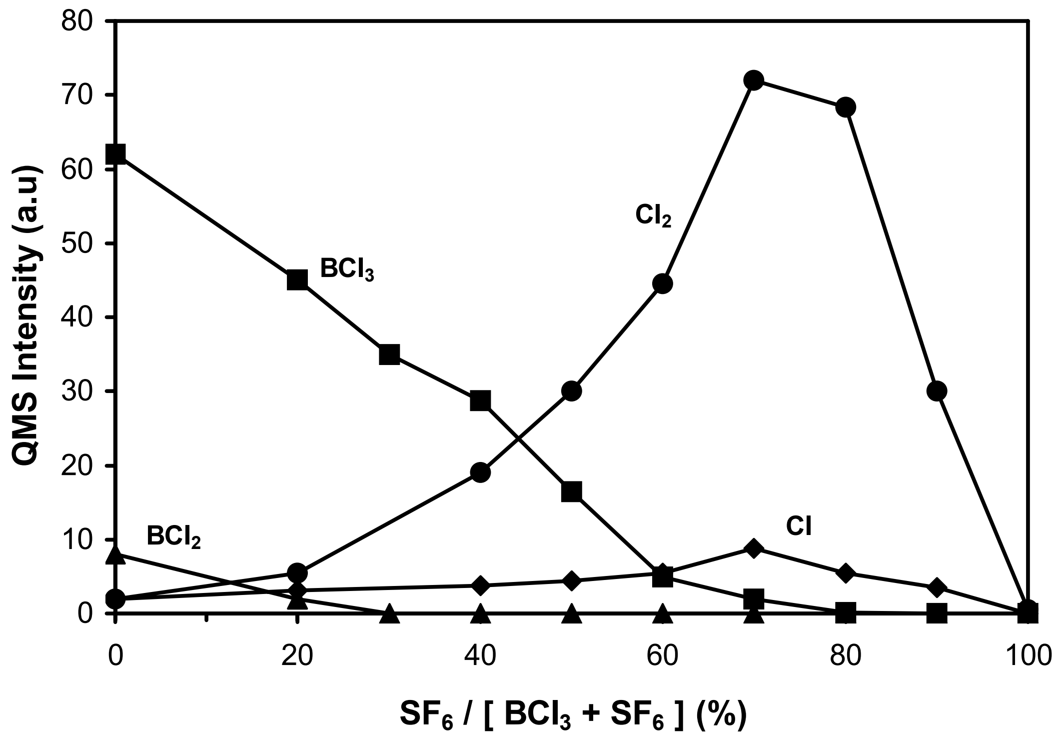


Figure 2-3 QMS intensities of BCl_3, BCl_2, Cl_2 and Cl as functions of SF_6 percentage in the flow (200W, 50 mTorr, 20 sccm) [5].

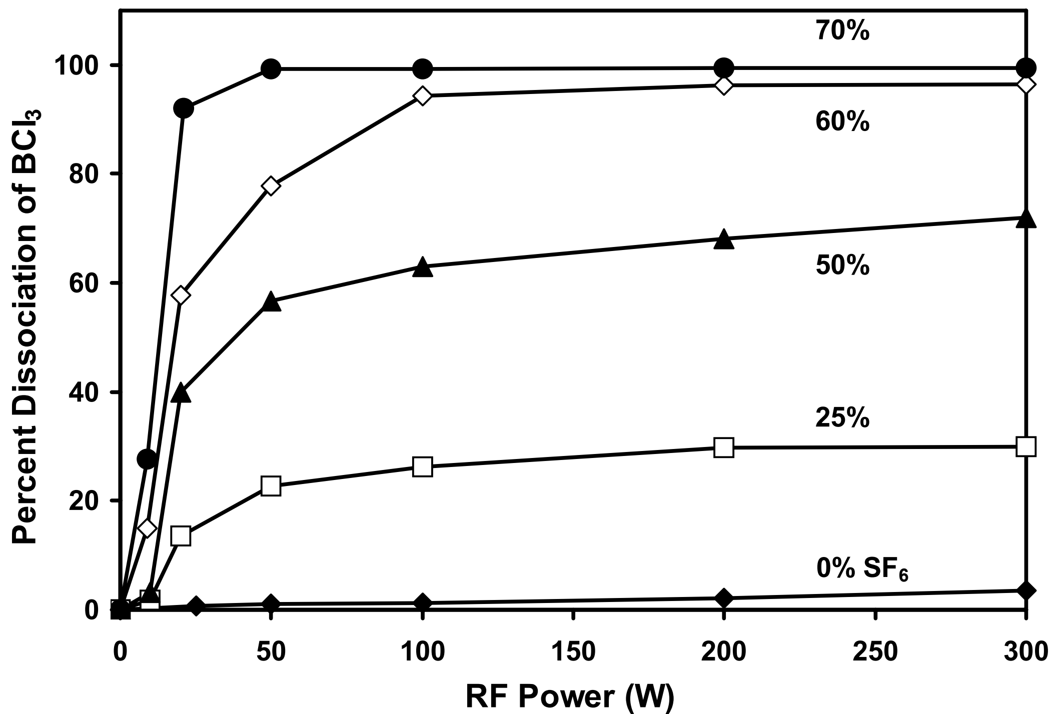


Figure 2-4 Dissociation of BCl_3 as a function of RF power with SF_6 percentage a parameter (50 mTorr, 20 sccm) [5].

Another factor that can increase etch rate is a mechanism that inhibits the loss of reactive etch species in the plasma. Y.S. Lee observed the formation of BClF and BCl_2F at varying isotopes using mass spectrometry and his results are presented in Figure 2.5 and Figure 2.6. These figures show that the QMS intensity of BClF and BCl_2F peaks around 30% SF_6, so that the addition of SF_6 to BCl_3 does in fact create fluorinated BCl_x molecules which would help to prevent the recombination of Cl or Cl_2 etching species.

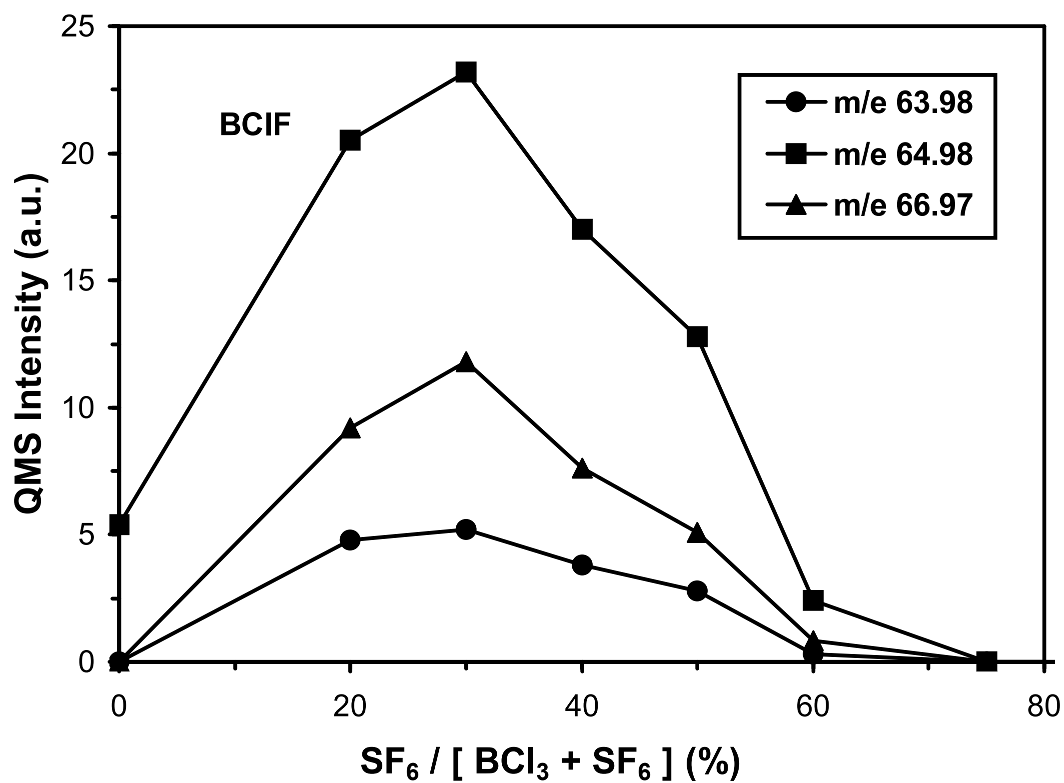


Figure 2-5 QMS intensities of BClF for different isotopes of chlorine and boron as functions of SF_6 percentage in the flow (200W, 50 mTorr, 20 sccm) [5].

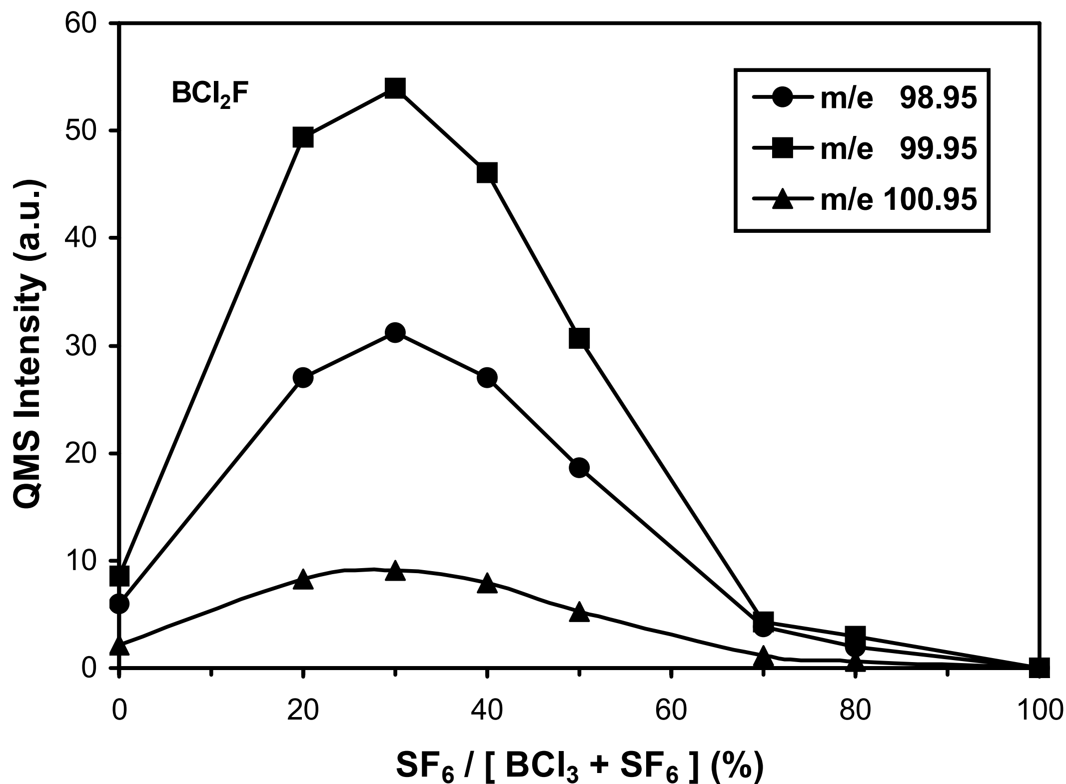


Figure 2-6 QMS intensities of BCl_2F for different isotopes of chlorine and boron as functions of SF_6 percentage in the flow (200W, 50 mTorr, 20 sccm) [5].

As a summary of the work by Y.S. Lee on the characterization of BCl_3/SF_6 plasmas as a result of SF_6 addition: there is an electron density decrease, more reactive etching species (Cl and Cl_2) are formed, and the formation of BClF and BCl_2F may reduce the recombination of these reactive etching species. An electron density decrease should lower the dissociation of BCl_3 and production of etch species Cl and Cl_2 and hence etch rate. A reduction in recombination of reactive etching species alone cannot explain the etch rate increase for the addition of (*a quasi-diluent)* SF_6 to BCl_3.

As evidenced by the electron density decrease, electron attachment is present by adding a more electronegative gas, SF_6, to BCl_3. It is again proposed that a mechanism of electron attachment heating can simultaneously explain an increase in etch rate (with similar trend in active etching species) by a decrease in electron density (via electron attachment heating of low energy electrons) resulting in a consequent increase in electron temperature (and average electron energy). This electron attachment heating phenomena has not been previously studied in BCl_3/SF_6 plasmas and can readily explain these occurrences by an increase in energetic electrons available to dissociate BCl_3. Fortunately a cost effective diagnostic probe technique to measure electron temperature exists where other techniques and tools cannot (microwave phase measurements, OES, and QMS)

2.2 Literature Review

2.2.1 Langmuir Probe Studies focused on BCl_3 Plasmas

Langmuir probe studies in ICP and CCP discharges have primarily focused on noble and inert gases. The bridge between using a Langmuir probe in electropositive to electronegative plasmas has rarely been crossed; primarily due to the corrosive nature of electronegative plasmas and the formation of negative ions. The literature does not cover Langmuir probe studies in plasmas containing mixed chemistries of BCl_3 and SF_6. Three pieces of literature cover Langmuir probe studies in BCl_3, for pure and mixed chemistries containing Cl_2, N_2, and/or Ar [29-31]. Recently, a fourth

piece was added by my colleague, B. Pathak, which includes Langmuir probe studies in mixtures of BCl_3 with N_2 [1].

Fleddermann and Hebner wrote three papers investigating various mixtures of BCl_3 , Cl_2, N_2, and Ar [30, 32, 33]. Of these three papers, only one mentioned the use of a Langmuir probe, however they did not publish the probe results because of concerns about reproducibility and accuracy. Nonetheless, these three papers are relevant to BCl_3 chemistries.

The first paper presented electron density and negative ion densities of Cl_2 and BCl_3 containing plasmas in a GEC reference cell operated in the inductively coupled mode [32]. The electron density measurements were performed using a microwave inteferometer and negative ion densities were observed with laser photodetachment coupled with microwave interferometry. The authors state that, "For all gas mixtures, the electron density was proportional to the total input power. With the exception of 100% Cl_2, the electron density was independent of pressure regardless of the gas mixtures studied. For all gas ratios, Cl^- densities were in the low 10^{11} cm^{-3} range; no evidence of significant densities of other negative ion species was found." For the case of 100% BCl_3, the negative ion density was also found to be proportional to input power, and independent of pressure.

Fleddermann and Hebner continued their experiments in Cl_2 and BCl_3 containing plasmas by investigating relative BCl densities using laser-induced fluorescence (LIF) and plasma-induced emission (PIE) [33]. These studies show that BCl densities are independent of power; however by comparing the relative intensity

increase with PIE compared to the electron density increase of the previous study, they suggest that the electron energy distribution function (EEDF) may be changing with power. The relative density of BCl radicals and excited states in all gases were seen to increase approximately linearly over the pressure range of 6 to 40 mTorr.

The third work cited for Hebner and Fledderman published LIF coupled with Langmuir probe results to further diagnose metastable chlorine ions, Cl^{+*}, in ICP source mixtures of BCl_3, Cl_2, N_2, and Ar [30]. The results show that energy transfer from long lived nitrogen states and argon metastables can enhance the decomposition of BCl_3. The Langmuir probe results in plasmas containing nitrogen were not published because of concerns about reproducibility and accuracy. However, electron temperature, electron density, plasma potential, and normalized ion saturation current were reported for BCl_3/Cl_2 plasmas at various radial positions within the chamber. In general, the radial distributions of electrons, Cl^{+*}, and ion saturation current were in good agreement.

G. Franz wrote a comprehensive analysis of BCl_3, Cl_2, and Ar capacitively coupled plasmas using Langmuir probe studies combined with OES, self-excited electron resonance spectroscopy (SEERS), and impedance characteristics of the discharge [29]. Franz states that, “Below a discharge pressure of 25 mTorr, neither Cl_2 and BCl_3 gases exhibit any electronegative behavior.” The results show there is a nonlinear energy dependence of electron density, even in argon. It was further suggested, for every transfer reaction, its cross section is extremely energy sensitive, and this leads to a nonlinearity of the energy dependence of electron density. So for a

BCl_3 discharge, the electron densities as a function of power and pressure are of lower magnitudes and do not quite follow the same trend as electropositive Ar. It is suggested that instead, an additional loss mechanism via electron attachment reduces the electron density. Furthermore, for a BCl_3 discharge, electron density was found to be proportional to absorbed power and independent of discharge pressure above 40 mTorr. The electron temperatures recorded were from the low-energy tail of the EEDF via classical Langmuir theory, however there was no mention of negative ion peaks in the EEDF, characteristic of electronegative plasmas, in the study. For pure BCl_3, the electron temperature remained relatively constant as a function of power (20-130 W at 15 mTorr), and decreased nonlinearly as a function of pressure (10-125 mTorr at 150 W).

Howard used a Langmuir probe to find the positive ion density and electron temperature in BCl_3/N_2 discharges [31]. Electron temperature was only reported for very few concentrations of BCl_3/N_2. Although his thesis focused on the etching of copper, this work was interested in finding reasons why the addition of N_2 to BCl_3 enhanced the etch rate whereas Ar did not. The Langmuir probe results showed that there is little difference between the ion densities for BCl_3/N_2 and BCl_3/Ar plasmas. Howard's observations using OES and application of actinometry showed that the addition of N_2 to BCl_3 increased the concentration of Cl. One conclusion from Howard was that the etching characteristics cannot be attributed to a difference in ion bombardment, but instead the addition of N_2 to BCl_3 was a "chemical effect" on Cl

production. Recently, B. Pathak has determined that energy transfer from N_2 metastables is most likely responsible for the increased chlorine production [1].

2.2.2 Langmuir Probe Studies focused on SF_6 Plasmas

Langmuir probe experimentation for pure SF_6 plasmas exist in the literature [34-36], however the most recent probe experiments on SF_6 plasmas were focused on chemistries also involving noble gases [37-40]. Langmuir probe results involving small amounts of SF_6 added to potassium plasmas using a Q-machine have also been studied [41, 42].

The two studies in a Q-machine are included in this review to show previous experimentation on the attachment of electrons in SF_6 plasmas by the use of a Langmuir probe [41, 42]. The electron temperatures and chamber pressure in these studies were extremely low, as compared to ICP and RIE systems; however these results are pertinent to show the formation of negative ions in low temperature plasmas. Kim and Merlino state that, "Q machines are ideal negative ion sources due to the low electron temperature, $kT_e \approx 0.2$ eV, resulting from thermal ionization" [41]. Both studies primarily focused on density measurements with a small amount of SF_6 added to a low-temperature potassium plasma. The results are simple estimates of electron to negative ion density by Sato and electron to positive ion density by Kim and Merlino. Sato noted that probe measurements were difficult, and instead reverted to the study of propagation of ion waves to help estimate the densities. In both cases, plasmas containing very low electron densities in comparison to the positive and negative ion density were found. Both papers assumed the predominant negative ion

was SF_6^- due to the low energy of electrons in the plasma. SF_6 has a negative ion resonant capture peak at zero or near zero energies, and is very efficient in attaching low energy electrons [43].

For the literature focusing on chemistries involving noble gases and SF_6, the experimentation with Ar is the most abundant. Tuszewski and White studied this discharge in an ICP system for pressures between 2 and 10 mTorr and RF power between 100 and 900 W [40]. This experiment couples probe measurements via the Hiden analytical ESP Langmuir probe with a mass and energy analyzer by Balzers. The mass spectra of positive ion species were acquired by shutting off the ionizer of the mass analyzer. SF_3^+ was observed as the dominant positive ion for most SF_6/Ar discharges, with SF_5^+ and SF_2^+ the next in line depending on power and pressure. The negative ion species were, "not identified because it is difficult to attract them in a mass analyzer without altering the plasma chemistry." However, SF_3^- was chosen as an intermediate mass between F^- and SF_6^- (this rough approximation was not experimentally confirmed by the authors). The EEDFs, "appear roughly Maxwellian for electron energies less than 10 eV, and suggest some depletion of electrons with larger energies." The probe measurements report an electron temperature of ~3.0-3.5 eV, with negative ion to electron density ratio between 2 and 10. Electron density was on the order of 10^{10} cm^{-3}, with reported maximum positive ion densities of $3x10^{11}$ cm^{-3}.

Shindo et al. compared Langmuir probe data to measurements of phase velocity of ion acoustic waves (fast mode) in a double plasma (D.P.) device operated

at a neutral gas pressure, discharge voltage, and discharge current of 0.3 mTorr, 50 V and 60 mA, respectively [37, 38]. Shindo et al. state that, "A double plasma is a quiescent plasma generated by dc discharges between hot filaments and chamber wall, and has normally two plasma regions divided with a separation grid in order to operate two plasma regions separately." These studies focused on small additions of SF_6 to Ar (0 to 0.1 sccm of SF_6 added to 8 sccm of Ar). Shindo et al. also used a QMS system with entrance orifice located in the plasma bulk to estimate positive and negative ion species. No QMS sampling technique was given other than normalization of spectrum intensities to Ar^+ and F^- for the positive and negative ions, respectively, and that the location of the entrance orifice was in the bulk plasma. Dominant positive ions were Ar^+, SF_3^+, and SF_5^+, while negative ions were F^-, SF_5^-, and SF_6^-. Again, QMS of negative ions should only be considered as rough approximations due to difficulty in attraction without altering plasma chemistry. The classical Langmuir probe procedure was used to determine electron temperature and density, however these estimates can lead to incorrect results when there are negative ions in the plasma [13, 44]. The electron temperature was reported to increase as SF_6 was added to Ar, from approximately 0.3 to 0.6 eV. Both positive ion and electron density was reported to decrease as 0.1 sccm of SF_6 was added to 8 sccm of Ar, with an increase in negative ion density. Thus, the ratio of negative ions to positive ions (α) increases at SF_6 is added to Ar, and reached values above 0.9. The ion acoustic wave comparison shows that this method is in good agreement until the ratio is above 0.6. It was concluded that the probe method, which uses the reduction rate of the ion

and electron saturation current, is useful for measuring the negative ion density in reactive gas plasmas in the case of $\alpha < 0.6$. Their data showed that this value was reached when 0.3 sccm of SF_6 is added to 8 sccm Ar. Studies at the KU PRL typically exceed this flow rate and α ratio, thus a simplistic view of saturation currents is not applicable.

Stamate and Ohe investigated SF_6/Ar plasmas and an Ar plasma in a dc discharge, multipolar magnetic-confined plasma [39]. Maxwellian distributions were assumed for all charge carriers, and they reported a negative ion to electron density ratio larger than 700 in an SF_6/Ar plasma. For the cases studied in SF_6/Ar, the electron temperature was between 1.44 and 2.23 eV, with electron densities between 8.13×10^5 and 3.34×10^6 cm^{-3}.

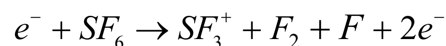
Kimura and Ohe investigated ICP discharges in Xe/SF_6 plasmas by use of a Langmuir probe [45]. The pressure was maintained at 2.5 mTorr, and the injected power was studied from 40-100 W. From examination of the EEDFs (or EDFs since negative ions were detected), a sharp peak was noticed around 0.4 eV when SF_6 was added to Xe. The authors attributed negative ions as a probable cause of this peak and included negative ion estimations from two methods by Amemiya, one using a ratio of currents and mass, while the other used radial motion theory [44, 46]. For the method using the ratio of currents and mass, the assumed dominant negative ion was F^-, primarily due to its high dissociation rate comparable to SF_6 and high electron density measurements. The negative ion to electron density ratio trends from both methods agree, however the radial motion theory predicted higher values of negative

ion density. The authors concluded that this ratio decreased gradually with injected power, and may be independent of SF_6 content higher than 20%. As SF_6 was added to Xe, the results showed an electron temperature increase of approximately 1 eV, and the electron density nearly halved when 40% SF_6 was added to Xe (i.e. possible electron attachment heating). The authors suggested a possible independency of electron temperature on SF_6 gas concentrations higher than 40% SF_6. The electron density was on the order of 5×10^{10} cm^{-3}, and the negative ion density was reported to be approximately 5 times higher than the electron density.

Riccardi et al. measured air and SF_6 RF discharges at relatively low pressures (0.05-0.1 mbar) and a power of 50 W by use of a Langmuir probe [36]. Through examination of the EEDF they note a near Druyvesteyn distribution for air, and an approximately Maxwellian distribution for SF_6. They state, "The evidence of negative ions comes directly from the inspection of the different Langmuir probe characteristics. Indeed in almost all operating conditions there is a large mismatch between the ion and electron densities (extracted as discussed in the previous section), which is larger in the SF_6 discharges compared to the air ones." Interestingly enough, they detected no presence of negative ions in the low energy regime of their EEDF. The following values reported in the literature were not separated for the two gases studied, air and SF_6. Thus, combined ranges of electron density, for both gases, was reported as 10^7 to 10^9 cm^{-3}, and found to be nearly proportional to RF power. Electron temperature was found to be nearly independent of RF power, and again, both gases were reported together with ranges of 5 to 10 eV.

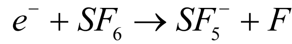
Picard presented mass spectrometry and Langmuir probe results with SF_6 in a capactively-coupled RF discharge [35]. One experiment in a SF_6/Ar plasma using a Langmuir probe was also included. The main species of an SF_6 plasma have been identified; neutral molecules (SF_6, SF_4, and F_2) via mass spectrometry at 70 eV, positive ions (SF_3^+, SF_5^+) via mass spectrometry with the orifice probe at floating potential and an extraction potential ~10-20 V, negative ions (SF_3^-, SF_5^-) via positive bias on an electrostatic lens placed behind sampling probe, and electrons via Langmuir probe detection. Again, QMS of negative ions should only be considered as rough approximations. A classical Langmuir approach was used in determining plasma parameters; the negative ion density was not measured, but an assumption that the charge carriers are in equal density yielded estimations. For SF_6 plasmas at a constant power of 25 W and variable pressure, the results showed relatively constant positive and negative ion densities and a slight decrease in electron density as pressure was increased from 20 to 100 Torr. For this same experiment and same pressure range, the electron temperature slightly increases as pressure increases. Above 100 Torr, the electron temperature rapidly increases with a corresponding rapid decrease in electron density. "This is attributed to the fact that electron attachment consumes the low energy electrons and thus shifts the mean energy of the resulting electrons towards higher energies." It was further concluded that atomic fluorine was created via dissociative ionization,

$$e^- + SF_6 \rightarrow SF_5^+ + F + 2e^-$$



$$e^- + SF_6 \rightarrow SF_3^+ + F_2 + F + 2e^-$$

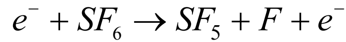
dissociative electron attachment,



$$e^- + SF_6 \rightarrow SF_5^- + F$$

$$e^- + SF_6 \rightarrow SF_3^- + F_2 + F$$

and electron impact dissociation,



$$e^- + SF_6 \rightarrow SF_5 + F + e^-$$

Kono et al. studied charged particle densities with SF_6 in a capactively-coupled RF discharge [34]. Estimations of electron density were determined using a microwave cavity technique, while negative ions were detected by measuring the density of photo-detached electrons produced by pulsed laser irradiation of the plasma. At 10 W, the photodetachment studies at 100, 200, and 400 mTorr suggested that F^- is the predominant negative ion in the discharge. However, the authors concluded that F^- and SF_6^- are not the predominant negative ions in the discharge, whereby stating that SF_5^- is a more likely candidate based on photodetachment cross sectional “estimations”. The positive ion density was obtained by Langmuir probe measurements and application of classical Langmuir probe theory; with assumptions that T_i = 300K and the mass is that of the predominant ion SF_5^+, determined by Picard [35]. The results show a constant increase in electron density with increasing power. However, it was concluded that for a constant RF power, the electron density is nearly constant in the low pressure range (≤ 100 mTorr) and it decreases with increasing pressure approximately proportional to the inverse of pressure in the high pressure range (≥ 200 mTorr). At higher presesures, the authors strongly suggest that

the dominant electron loss process is electron attachment to SF_6 as opposed to electron transport to the wall. The positive ion to electron density ratio was estimated to be a few hundred at low pressures and increased to a few thousand at higher pressures. The authors suggest that this trend in ratio extends to negative ions, since the positive and negative ion densities should be approximately the same with such low electron densities. The electron density was on the order of 10^9 cm^{-3}, while the negative ion densities were approximately 100 times higher.

2.2.3 Electron Collisions in Plasmas containing BCl_3

BCl_3 is commonly used to etch a variety of substrates, and in selective etching plasmas as a donor of Cl and Cl_2. Electronegative plasmas, like BCl_3, SF_6, Cl_2, and O_2 prefer electron acceptance; their negatively charged species are typically energetically favored. The resulting negatively charged species are also more stable than the transient metastable negative ions that are initially formed by electron capture [43]. BCl_3 has weak electron affinity, in comparison to Cl_2 and SF_6 [5, 47]. Specifically for BCl_3, the negatively charged, pyramidal ion BCl_3^- is stabilized by 0.33 eV (estimated electron affinity) to its neutral, planar BCl_3 molecule [48]. The BCl_3^- ion was found to be formed with a peak cross section at 0 eV in a narrow energy range of 0-0.1 eV [49, 50]. (See Chapter 3 for the theory of electron-molecule interactions).

The ionization potential of each particular species in the plasma is an indication of reactivity, but more importantly it is the energy required to remove an electron from an isolated atom or molecule. Schwabedissen et al. shows a simple inverse trend of electron density to ionization potential for the electropositive rare

gases in increasing ionization potential order: xenon, krypton, argon, neon, and a 96% He/Ar mixture [51]. Thus, the easier a gas is to ionize (lower ionization potential), the more free electrons will result for a given set of constant plasma conditions (i.e. pressure or source power).

There are several techniques to find the ionization energy, however they all typically agree within an electron volt. In increasing order, rough approximations to the number of electron volts required for ionization are: Cl_2 (11.49), BCl_3 (11.62), BCl and BCl_2 (12.0), and finally Cl (12.97) [52]. These values are significantly lower than most noble gases, and N_2, so it should theoretically be easier to form positive ions with the resulting free electrons in gases like BCl_3 and Cl_2. However, when dealing with cold, *electronegative* plasmas as seen in RIE and ICP discharges, the resulting free electrons are easily scavenged by the parent gas molecules and fragments (radicals or other products with electron affinity) from the reactions occurring from dissociation, dissociative ionization, or dissociative electron attachment. Thus, solely using electron density measurements will not accurately predict any trends in ionization or dissociation.

The electron temperature in typical processing plasmas is lower than 10 eV [53], and previous experimentation at the KU PRL with electronegative plasmas has never exceeded this value [1]. The dissociative reactions, with or without fragment excitation, and ion-pair formation are very sensitive to the number of superthermal electrons [53]. These superthermal electrons exist in low quantity, and are found in the high energy tail of an EEDF. Therefore, these reaction pathways occur more

frequently at higher electron temperatures (and average electron energy) and will typically result in more dissociation, ionization, and ion-pair formation.

A plasma is a quasi-neutral state, the free electrons have to go somewhere; they are affected by the electric field, so they may collide with the chamber housing, electrode, or different species in the plasma. Depending on the energy level of the resulting electrons, a certain number of reactions may occur. It has been proposed that they are attaching in various amounts to form negative ions [1, 13, 29, 43, 44, 54], and this may even be the predominant loss mechanism at high pressures in SF_6 plasmas [34, 35]. There are several processes to form these negative ions; the most understood is via electron attachment due to electron affinity, while the dissociative electron attachment reactions are the least understood.

Gottscho and Gaebe studied BCl_3 discharges between 100 to 300 mTorr with excitation frequencies between 50 and 750 kHz [49]. Their results show that the predominant negative ion is BCl_3^-, and detected some presence of Cl^- species. At their low frequency discharges Gottscho and Gaebe pointed out that much of the power was dissipated by ion conduction processes, so it was unlikely that either molecular dissociation or excitation occurred to much extent by energetic electron impact [49, 50]. Their results would be consistent with mass spectrometric observations of long lived BCl_3^{-*} [43, 55, 56], and with the results with Petrović et al. that the electron attachment rate constants they measured in their experiments are from the formation of BCl_3^- (since they investigated values of mean electron energy less than ~1 eV) [43,

57]. Petrović et al. also suggested that for dissociative electron attachment producing either Cl^- or Cl_2^- from BCl_3 is above ~1 eV [43, 57].

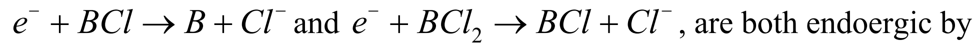
In a low frequency Cl_2 discharge, the dominant negative ion is Cl^-, which is primarily generated from dissociative attachment, $e^- + Cl_2 \rightarrow Cl + Cl^-$ [29, 49, 58]. Franz points out that, "this reaction is exothermic by 1.132 eV (difference between the electron affinity of Cl and the dissociation energy of Cl_2), and there was no energy threshold for this attachment" [29]. The electronegativity of atomic Cl is well documented in the literature and arrives at a value of 3.61 eV. The NIST database collects a myriad of values for the electron affinity of Cl_2, and the majority conclude a value of ~2.5 eV [52]. The bond dissociation energy of Cl-Cl is ~2.5 eV [59, 60].

The bond dissociation energies of BCl_2-Cl and BCl-Cl_2 are 4.61 eV and 5.65 eV respectively [43, 61, 62]. For dissociation via an electron collision resulting in neutrals, these are the approximate minimum energies are required to break apart their bonds. For dissociative electron attachment to BCl_3 resulting in a Cl^- negative ion, $e^- + BCl_3 \rightarrow BCl_2 + Cl^-$, in similar fashion to Franz using bond dissociation energy and electronegativity of Cl, one finds that this reaction is endoergic by ~1 eV. Likewise, for the dissociative electron attachment, $e^- + BCl_3 \rightarrow BCl + Cl_2^-$, one finds that this reaction is endoergic by 3.15 eV.

The electron affinity of BCl and BCl_2 are not as well documented, however BCl_2 has been reported as 0.6 eV [52]. The bond energy of B-Cl is well documented

at 4.72 eV and previously calculated at 5.51 eV from heats of formation [63].

Therefore, one finds that the dissociative electron attachment reactions,



$e^- + BCl \rightarrow B + Cl^-$ and $e^- + BCl_2 \rightarrow BCl + Cl^-$, are both endoergic by

approximately ~1.1 eV. Table 2-2 presents the energies and threshold wavelengths from Christophorou and Olthoff for the dissociation and ionization of BCl_3 as calculated by Lee et al. [43, 62].

Table 2-2 Energies and threshold wavelengths for the dissociation and ionization of BCl_3 as calculated by Lee et al. [43, 62].

Process	Energy (eV)	Wavelength (nm)
Dissociation		
$BCl_2 + Cl$	4.61	
$BCl + Cl_2$	5.65	
$BCl + 2Cl$	8.16	
$BCl^*\ (A) + Cl_2$	10.21	121.4
$BCl^*\ (A) + 2Cl$	12.72	97.5
$BCl_2 + Cl^*\ (4P'\ ^3P^0)$	16.31	76.0
$B + 3Cl$	13.77	
$B^*\ (3s\ ^2S) + 3Cl$	18.73	66.2
$B^*\ (2p^2\ ^2D) + 3Cl$	19.70	62.9
Ionization		
$BCl_3^+\ (\tilde{X}\ ^2A_2') + e$	11.64	106.5
$BCl_3^{+*}\ (\tilde{A}\ ^2E'') + e$	12.19	101.7
$BCl_2^+ + Cl$	12.30	
$BCl_3^+\ (\tilde{B}\ ^2E') + e$	12.66	97.9
$BCl_3^{+*}\ (\tilde{C}\ ^2A_2'') + e$	14.22	87.2
$BCl_3^{+*}\ (\tilde{D}\ ^2E') + e$	15.32	80.9
$BCl_3^{+*}\ (\tilde{E}\ ^2A_1') + e$	17.74	69.9
$BCl^+ + 2Cl + e$	18.37	

Using the above information, one finds that for dissociative electron attachment to BCl_3, BCl_2, and BCl resulting in Cl^-, all are endoergic by at least ~1 eV,

while the same reactions resulting in Cl_2^- are slightly higher (≥ 3.15 eV). For BCl_3 discharges, Cumali Tav points out that for Cl_2^- formation, “Stockdale et al. observed these ions at electron energies higher than 1 eV, where the Cl_2^- signal was less intense than the Cl^- signal” [50, 64].

The total electron attachment cross section of BCl_3 has been studied by electron beam and electron swarm methods. Buchel’nikova reported a very low threshold energy, 0.14 eV, attributed to the production of the Cl^- ion in the dissociation reaction: $e^- + BCl_3 \rightarrow BCl_2 + Cl^-$ using the electron beam method [43, 65]. Extrapolating an electron attachment rate constant, Tav et al. stated that Buchel’nikova’s results were “…clearly not compatible with any of the other measurements especially close to thermal energy.” Petrovic, Stockdale, and Tav et al. all show similar electron attachment rate trends as a function of electron energy, as compared to the results from Buchel’nikova [50, 57, 64, 65]. Figure 2-7 is a comparison of data by Christophorou and Olthoff, corresponding to total electron attachment cross section as a function of electron energy taken by Buchel’nikova and Tav et al. [43, 50, 65]. A better approximation of energy threshold for the reaction, $e^- + BCl_3 \rightarrow BCl_2 + Cl^-$, is ~1 eV [50, 57]. Electron impact studies on the relative cross section for the production of Cl^- verifies the maximum cross section near 1 eV [43]. At higher energies, ≥ 9 eV, the production of Cl^- observed by Marriott and Craggs, may be due to the ion-pair process, $e^- + BCl_3 \rightarrow BCl_2^+ + Cl^- + e^-$ [43, 66].

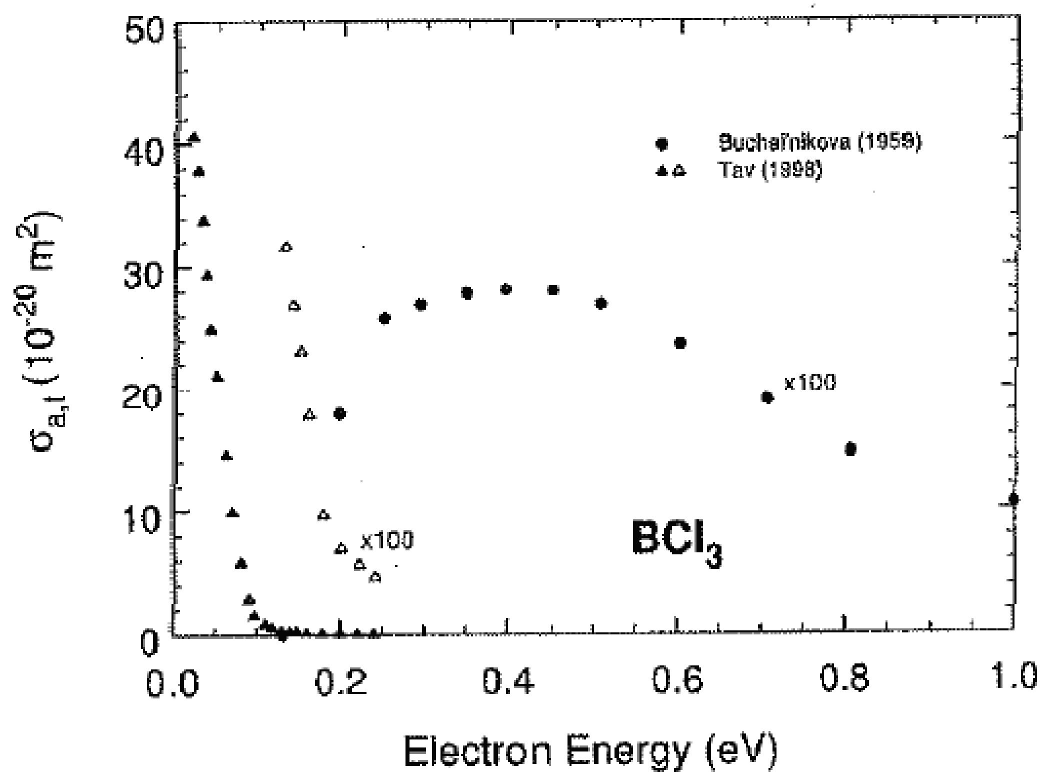


Figure 2-7 Total electron attachment cross section as a function of electron energy for BCl_3 (Note that the open triangles and closed circles are multiplied by 100 to facilitate comparison). Electron beam data was from Buchel'nikova, while electron swarm data was from Tav et al. [43, 50, 65].

Table 2-3a Electron affinity and negative ion states of BCl_3 and vertical detachment energy of BCl_3^- [43].

Value / Energy position (eV)	Method of determination	Comment/ Assignment	Ref.
Electron affinity			
0.33 ± 0.2	Measurement[a]	Adiabatic	[342]
0.27 to 0.42[b]	Calculation	Adiabatic	[336]
> 0.0	Swarm measurements	Formation of BCl_3^-	[368]
> 0.0	Beam measurements	Formation of BCl_3^-	[343, 344]
Negative ion states			
~ 0.9	Dissociative attachment producing Cl^-		[344]
1.1 ± 0.1	Dissociative attachment producing Cl^-		[339]
< 1.0	Electron transmission experiment/Calculation	a_2''	[343, 337]
0.25[c]	Calculation	B_2	[369]
0.41–0.79[b]	Calculation	Vertical attachment energy	[370]
0.00–1.30	Calculation		[371]
~ 1.8	Calculation[d]	B_2	[370]
~ 2.6	Threshold-electron excitation[e]		[339]
2.86	Electron transmission experiment/Calculation	a_1'	[343, 337]
2.5	Calculation[f]	A_1	[369]
5.16	Electron transmission *experiment/Calculation*	e'	[343, 337]
5.5	Calculation[f]	A_1; B_1	[369]
~ 6.5	Dissociative attachment producing Cl^-		[344]
~ 7.6	Threshold-electron excitation[e]		[339]
~ 7.6	Electron transmission *experiment/Calculation*	Core-excited shape resonance[g]	[343, 337]

[a]Determined using collisions of Cs atoms with BCl_3.
[b]The range of values corresponds to the results of various types of calculation.
[c]The position of this B_2 symmetry shape resonance moves from ~ 2.0 eV in the static exchange calculation to 0.25 eV with the inclusion of polarization effects [369].
[d]Static exchange approximation calculation.
[e]SF_6^- scavenger technique.
[f]Polarized-SCF calculations.
[g]Observed in electron transmission and in dissociative electron attachment experiments.

Table 2-3b (continued) Electron affinity and negative ion states of BCl_3 and vertical detachment energy of BCl_3^- [43].

Value / Energy position (eV)	Method of determination	Comment/ Assignment	Ref.
~ 7.8	Dissociative attachment producing Cl^-		[344]
8.7	SF_6^- scavenger technique		[339]
9.05	Electron transmission experiment/Calculation	Core-excited shape[g] resonance	[337, 343]
9.7	Threshold-electron excitation[e]		[339]
8.5	Calculation[d]	A_1, B_1	[369]
Vertical detachment energy			
1.77	Optogalvanic experiments		[372]
1.73–1.99[b]	Calculation		[336]

[a] Determined using collisions of Cs atoms with BCl_3.
[b] The range of values corresponds to the results of various types of calculation.
[c] The position of this B_2 symmetry shape resonance moves from ~ 2.0 eV in the static exchange calculation to 0.25 eV with the inclusion of polarization effects [369].
[d] Static exchange approximation calculation.
[e] SF_6^- scavenger technique.
[f] Polarized-SCF calculations.
[g] Observed in electron transmission and in dissociative electron attachment experiments.

Tables 2-3a and 2-3b present the electron affinity and negative ion states of BCl_3 and vertical detachment energy of BCl_3^- [43].With all of these negative ion states, the determination of the actual negative ion species that exist in BCl_3 plasmas without photodetachment studies is difficult. Fortunately, Fledderman and Hebner studied the laser induced photodetachment of BCl_3 and Cl_2 plasmas coupled with microwave density measurements to investigate negative ions in a GEC reference cell operated in the inductively coupled mode with coil excited at 13.56 MHz [32]. Their results strongly suggest that the negative ion, Cl^-, was the only negative ion detected

in significant quantities in BCl_3 discharges and that dissociative electron attachment to BCl_3 can be an important Cl^- formation mechanism in BCl_3 discharges ($e^- + BCl_3 \rightarrow BCl_2 + Cl^-$). The reaction pathway for the formation of Cl^- is quite complex, due to several other dissociative electron attachment reactions occurring with byproducts of dissociation of BCl_3 ($e^- + BCl_2 \rightarrow BCl + Cl^-$, $e^- + BCl \rightarrow B + Cl^-$, $e^- + Cl_2 \rightarrow Cl + Cl^-$), electron attachment to Cl, ($e^- + Cl \rightarrow Cl^-$), or surface recombination of Cl radicals dissociated from BCl_3 into Cl_2 and subsequent dissociative electron attachment ($2Cl \xrightarrow{Surface} Cl_2 \xrightarrow{Desorption} Cl_2 + e^- \xrightarrow{Gas\ Phase} Cl + Cl^-$) [32].

In summary, BCl_3^- is formed in the narrow energy range of 0-0.1 eV and is an unlikely candidate for the discharges at KU PRL. For the dissociative electron attachment reactions to occur with BCl_x molecules, all are endoergic at relatively low energy thresholds. All of these reactions may occur, but a very likely candidate is direct dissociative electron attachment to BCl_3 ($e^- + BCl_3 \rightarrow BCl_2 + Cl^-$). The most abundant negative ion in BCl_3 ICP sources, Cl^-, is a product of that reaction. The dissociation reactions of BCl_3 have energy thresholds of 4.61 eV and 5.65 eV, which will result in Cl and Cl_2 species respectively ($e^- + BCl_3 \rightarrow BCl_2 + Cl + e^-$ and $e^- + BCl_3 \rightarrow BCl_2 + Cl_2 + e^-$). To create reactive etching species from the parent BCl_3 molecule, and only with a single electron collision, the electrons must be at energy levels at or greater than 4.61 eV. For the specific molecule, Cl_2, energy is

created in the dissociative attachment, while energy is required in the dissociation reaction and will occur in plasma with electrons at or above energy levels corresponding to 2.5 eV. All of the ionization thresholds in BCl_3 discharges are above 11 eV. From section 2.2.1, the literature points to predominant positive ions BCl_3^+ and BCl_2^+ and the energy thresholds for ionization are approximately 11.62 and 12.0 eV, respectively.

2.2.4 Electron Collisions in Plasmas containing SF_6

Sulfur hexafluoride is a man-made, hypervalent molecule used in several applied areas due to its properties in gaseous form. The high-dielectric strength of SF_6 makes it primarily used in the electrical industry as a gaseous dielectric medium for high-voltage circuit breakers, switchgear, or any application used to isolate electrical equipment. Semiconductor manufacturing has taken interest in this gas for several reasons; it is used in plasma etching of silicon and silicon dioxide as well as SiC. It is also used in the selective etching of GaAs over aluminum containing III-V materials.

The ionization potential of SF_6 has been recorded as low as 15.29 eV [67], and the energetic sequence of the various orbitals are still not entirely understood [43]. The various techniques and experimentations to calculate the ionization energies of the orbitals has been presented by Christophorou and Olthoff, but for the most part, the threshold ionization energy for the formation of SF_5^+ is around 15.7 eV [43]. This value is more than 3 eV above the ionization potential of BCl_3 and Cl_2.

The positive ion, SF_6^+, is unstable. Christophorou and Olthoff state that, "Because the lowest ionic state of SF_6 is antibonding, the ionization process even at

threshold is dissociative and results in the formation of the fragments SF_5^+ and F. No SF_6^+ ion has been observed in the preponderance of investigations, and its abundance is estimated to be less than 10^{-4} compared to that of SF_5^+." Therefore, the primary ionization is the dissociative ionization reaction, $e^- + SF_6 \rightarrow SF_5^+ + F + 2e^-$; which results in a neutral fluorine atom, with electron affinity 3.4012 eV [43, 68]. This atom can readily form a negative ion due to fluorine having the highest electronegativity of all the elements, however in comparision to Cl, the electron affinity is slightly less due to the smaller size of the fluorine atom.

The bond dissociation energy of SF_5-F has been reported between 3.38 and 4.1 eV which is lower than BCl_2-Cl and BCl-Cl_2 [43]. The energy threshold for the electron-impact dissociation of $SF_6 + e^- \rightarrow SF_5 + F + e^-$ has been calculated at 9.6 eV [43, 69]. The electron affinity of SF_6 has been a topic of debate until recently, and there are over 20 reported values prior to 1983, as seen in the NIST database [52, 70]. The two most recent values, are widely accepted, and are the presently recommended value, 1.06 eV, which is higher than that of BCl_3 (0.33 eV) [43]. "Finally, it should be noted that no photodetachment cross sections appear to have been published for the other negative ions produced by dissociative electron attachment to SF_6, except for F^-", from Christophorou and Olthoff [43]. These cross sections are valuable to measure the negative ion densities in photodetachment studies for various types of gas discharges [43].

Table 2-4a Negative ion states of SF_6 [43].

Energy position (eV)	Type of study	Symmetry/ Orbital	Reference
~0.0	Many electron attachment studies		
0.38	SF_5^- from SF_6		[424, 504–506]
0.5 ± 0.1	SF_5^- from SF_6		[507]
~0.1	Excitation function of ν_1	A_{1g}	[489]
~0.1	Vibrational excitation by electron impact		[488]
~0.0	Multiple scattering calculation	a_{1g}	[508]
2.0	F_2^- from SF_6		[424]
2.2	F_2^- from SF_6		[509]
2.4	F_2^- from SF_6		[510][a]
2.6	F^- from SF_6		[424]
2.8	F^- from SF_6		[510]
2.8	F^- from SF_6		[509]
~2.9	F^- from SF_6		[511]
2.3	Total electron scattering cross section	a_{1g}	[512]
2.5	Total electron scattering cross section	A_{1g}	[513]
2.5	Total electron scattering cross section	a_{1g}	[514]
2.52 ± 0.15	Trochoidal derivative spectrum	a_{1g}	[515]
2.56 ± 0.15	Total electron scattering cross section	a_{1g}	[515]
2.7	Angular dependence of vibrationally elastic electron scattering	a_{1g}	[516]
2.1	Multiple scattering calculation	a_{1g}	[508]
3.30	Multichannel calculation with close-coupling	A_{1g}	[517]
4.4	F_2^- from SF_6		[424]
4.8	F_2^- from SF_6		[510]
4.8	F_2^- from SF_6		[509]
5.0	SF_4^- from SF_6		[509]
5.1	F^- from SF_6		[424]
5.2	F^- from SF_6		[510]
5.3	F^- from SF_6		[509]
5.4	SF_4^- from SF_6		[424]
5.4	SF_4^- from SF_6		[510]
~5.4[b]	F^-, F_2^-, and SF_4^- from SF_6		[511]
5.7 ± 0.1	F^- from SF_6		[507]
6.0 ± 0.1	SF_4^- from SF_6		[507]
6.7	Total electron scattering cross section	t_{1g}	[512]

[a] The values of Lehmann [510] given in this table have been deduced from his figures and were reduced by 0.6 eV as discussed in the text.
[b] Main resonance.

Table 2-4b (continued) Negative ion states of SF_6 [43].

Energy position (eV)	Type of study	Symmetry/ Orbital	Ref.
7.0	Total electron scattering cross section	t_{1u}	[514]
7	Angular dependence of vibrationally elastic electron scattering	t_{1u}	[516]
7	Total electron scattering cross section	t_{1u}	[513]
7.01 ± 0.16	Trochoidal derivative spectrum	t_{1u}	[515]
7.05 ± 0.10	Total electron scattering cross section	t_{1u}	[515]
7.2	Elastic electron scattering cross section	t_{1u}	[518]
7.2	Multiple scattering calculation	t_{1u}	[508]
8.8	F^- from SF_6		[424]
8.9	F^- from SF_6		[510]
9.3 ± 0.1	F^- from SF_6		[507]
9.4	F^- from SF_6		[509]
9.4	SF_3^- from SF_6		[424]
8.7; 9.1	Multiple scattering calculation	T_{1u}	[519]
9.85	Multichannel calculation with close-coupling	T_{1u}	[517]
11.2	F_2^- from SF_6		[424]
11.2	SF_3^- from SF_6		[510]
11.3	SF_3^- from SF_6		[509]
11.3	F^- from SF_6		[424]
11.5	F^- from SF_6		[510]
11.6	F^- from SF_6		[509]
11.6	F_2^- from SF_6		[509]
11.7	F_2^- from SF_6		[424]
11.8 ± 0.1	F^- from SF_6		[507]
12.0	SF_2^- from SF_6		[424]
12.3	SF_2^- from SF_6		[509]
13.0	SF_2^- from SF_6		[510]
11.87 ± 0.10	Total electron scattering cross section	t_{2g}	[515]
11.88 ± 0.07	Trochoidal derivative spectrum	t_{2g}	[515]
11.9	Total electron scattering cross section	t_{2g}	[514]
11.9	Total electron scattering cross section	t_{2g}	[512]
12	Total electron scattering cross section	t_{2g}	[513]
12	Elastic electron scattering cross section	t_{2g}	[518]
12	Elastic and vibrationally inelastic electron-impact excitation		[480]
11	Multiple scattering calculation	T_{1u}	[520]
11.0; 11.8; 13.7	Multiple scattering calculation	T_{2g}	[519]
12.7	Multiple scattering calculation	t_{2g}	[508]
13.10	Multichannel calculation with close coupling	T_{2g}	[517]

Dissociative electron attachment reactions also take place in SF_6 plasmas; the confirmation of this has been proven by electron attachment, electron scattering, and calculation experiments. Several experiments on the negative ion states of SF_6 have been extensively studied by Christophorou and Olthoff [43], and show the existence of SF_n^- (n=2,3,4,5), F^-, and F_2^-. Copies of tables of negative ion states of SF_6 by Christophorou and Olthoff are presented in Tables 2-4a and 2-4b [43]. At 0 eV, there is widespread evidence of electron attachment to SF_6 forming SF_6^-, and this evidence shows that SF_6 attaches thermal and near thermal (~0-0.1 eV) electrons with a very large cross section forming SF_6^- [43]. This resonance at 0 eV, has also been attributed to long-lived negative ionic state SF_6^{-*} at near-zero energies [71]. A higher negative ion state was found around 0, 0.38, and 0.5 eV, corresponding to SF_5^- [43]. However as Olthloff states, "it should be noted that at room temperature, the contribution of SF_5^- to the total electron attachment cross section below 0.1 eV is small compared to SF_6^- production." One resonance of a diatomic fluorine negative ion, F_2^-, from SF_6 is attributed to the 2.0 to 2.4 eV range, while a monotomic fluorine resonance is attributed to 2.6 to ~2.9 eV [43]. From the latter value, 2.9 eV until 4.4 eV, there are several negative ion states, however total electron scattering cross section studies do not clearly associate a state with the negative ion type [43]. At about 5.4 eV, Fenzlaff et al. associates this energy level with F^-, F_2^-, and SF_4^- from SF_6, and several studies confirm the existence of these negative ions within about 1 eV [43, 72]. At higher energy values, it is unclear which position correlates to a negative ion state. Christophorou and Olthoff state, "It is interesting to note that although electron

attachment studies and theory indicate a resonance near 9 eV, none of the electron scattering investigations show any evidence of it" [43]. At 9 eV, the negative ion formation could be F^- or SF_3^- from SF_6, however this energy level is not well understood [43]. Christophorou and Olthoff recommend a final negative ion state at 11.9 eV, and studies suggest that this energy level corresponds to F^-, F_2^-, SF_2^-, and/or SF_3^- [43]. By combining all of the previous studies, one can see that SF_6 is highly electronegative plasma.

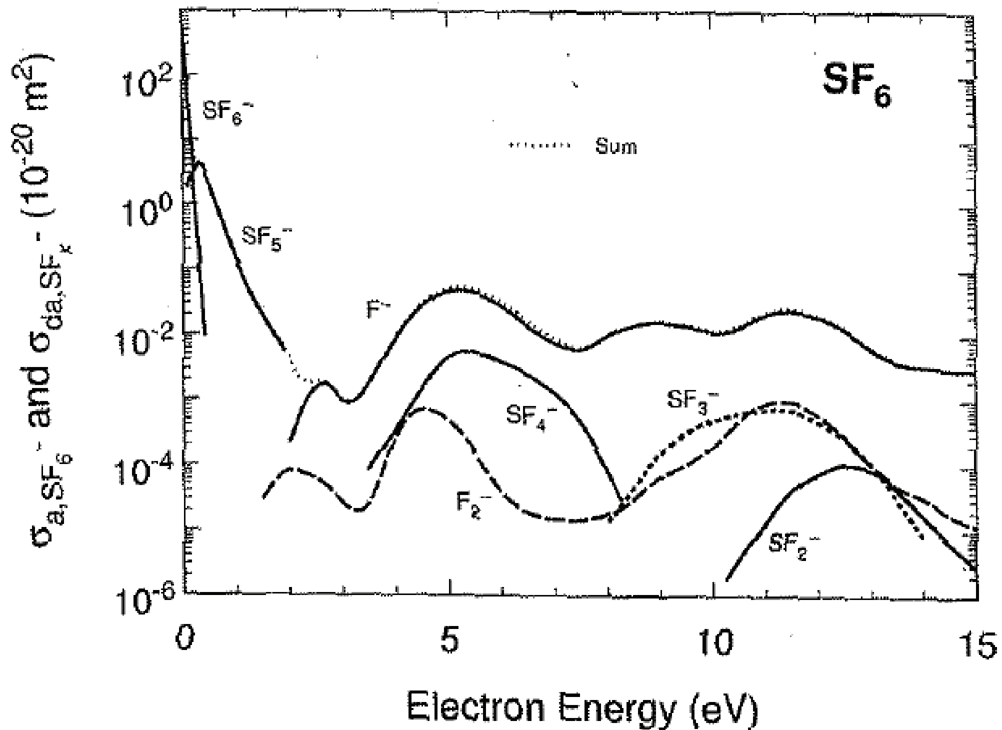


Figure 2-8 Recommended or suggested cross sections for negative ions (SF_6^-, SF_5^-, SF_4^-, SF_3^-, SF_2^-, F_2^-, and F^-) by electron attachment or dissociative electron attachment with parent species, SF_6 [43].

Figure 2-8 is a presentation of recommended or suggested cross sections for the various negative ions as determined from studying several cross section experimentation for SF_6 from Christophorou and Olthoff [43]. As a summary of work from Christophorou and Olthoff [43], the parent negative ion, SF_6^-, is formed at extremely low electron energies, below 0.2 eV. The fragment negative ions are formed via a number of negative ion resonances located between 0 and ~15 eV. SF_5^- occurs at energies below 2 eV with maxima at 0.0 and 0.38 eV. SF_4^- may occur at a broad resonance between 4 and 8 eV, whereby two different products may be formed, 2F and F_2, and their cross section maxima are 6.0 and 5.4 eV, respectively. SF_3^- occurs over a slightly larger range of 8 to 14 eV, with a maximum around 11 eV. SF_2^- forms primarily between 10 and 15 eV with a maximum near 12.5 eV. F_2^- is produced between 1 and 14 eV, with cross section maxima near 2.2, 4.7, and 11.5 eV. “The F^- ion is the predominant fragment negative ion produced by dissociative electron attachment to SF_6 at ambient temperature at electron energies above ~ 3 eV.” This ion may be formed between ~2 and >15 eV with cross sectional data exhibiting maxima near 2.8, 5.2, 9.1, and 11.5 eV. From section 2.2.2, the literature points to predominant positive ions, SF_5^+ and SF_3^+. Since SF_6^+ is unstable, and the primary ionization process is dissociative ($e^- + SF_6 \rightarrow SF_5^+ + F + 2e^-$) the threshold ionization is around 15.7 eV. The bond dissociation energy of SF_5-F has been reported between 3.38 and 4.1 eV, which is the approximate energy threshold (with only one electron collision) to form radical F species within a SF_6 plasma.

2.2.5 Literature Review Summary: Estimating Ion Mass

From section 1.3, a Langmuir probe can give estimations of plasma density, electron density, positive ion density, negative ion density, electron temperature, and average electron energy. The mass of each species must be known when determining densities. For electrons, this is a well known value. However, even in plasmas containing a diatomic molecule it is not well known or easy to attain the average mass of the positively or negatively charged ions.

From the literature review, tables summarizing the predominant ion species in BCl_3 and SF_6 plasmas will now be presented. Only the trends from each experiment are shown, from highest to lowest values. The mass spectrometric intensity from direct ion sampling of positive ions in BCl_3 and SF_6 discharges is presented in Table 2-5. To further support these studies, the partial electron-impact ionization cross sections from threshold to 35 eV are presented in Table 2-6.

Table 2-5 Estimation of positive ion mass in BCl_3 and SF_6 containing plasmas from QMS intensity.

Mass Spectrometry Intensity of Positive Ions	**Authors – Gas Composition**
$BCl_2^+ > BCl^+ > B^+$	Overzet and Luo [73] – BCl_3
$SF_3^+ > SF_5^+ > SF_2^+$	Tuszewski and White [40] – SF_6/Ar
$Ar^+ > SF_3^+ > SF_5^+$	Shindo et al. [38] – SF_6/Ar
$SF_3^+ > SF_5^+ > SF_2^+ > SF_4^+ > SOF_3^+ > SF^+$	Picard et al. [35] – SF_6

Table 2-6 Estimation of positive ion mass in BCl_3 and SF_6 plasmas from partial electron-impact ionization cross sectional data from threshold to 35 eV.

Partial electron-impact ionization cross sections	**Authors – Gas Composition**
$BCl_2^+ > BCl_3^+ > BCl^+ > Cl^+$	Jiao et al. [74] – BCl_3
$SF_5^+ > SF_3^+ > SF_4^+ > SF_2^+$	Rejoub et al. [75] – SF_6

From QMS and partial electron-impact ionization cross section studies, one can see that the most abundant positive ions in BCl_3 plasmas are BCl_2^+ and BCl_3^+. From similar studies, one finds that the most abundant positive ions in SF_6 plasmas are SF_3^+ and SF_5^+.

From the literature review, tables summarizing the predominant negative ion species are now presented. Again, only the trends from each experiment are shown, from highest to lowest values. Since mass spectrometry of negative ion species is difficult due to recombination in the sampling orifice and alteration of plasma chemistry when attracting these ions, better approximations using laser induced photodetachment coupled with microwave density measurements are presented in Table 2-7 for both BCl_3 and SF_6 plasmas. To support this evidence, electron attachment and dissociative electron attachment cross sections from 0-15 eV of BCl_3 and SF_6 are also presented in Table 2-8 and 2-9, respectively.

Table 2-7 Estimation of negative ion mass in BCl_3 and SF_6 plasmas using laser induced photodetachment coupled with microwave density measurements.

Relative Intensities	**Authors – Gas Composition**
Cl^- (only ion detected in significant quantity)	Fleddermann and Hebner [32] – BCl_3
F^- > SF_5^- and SF_6^-	Kono et al. [34] – SF_6

Table 2-8 Estimation of negative ion mass using BCl_3 electron attachment and dissociative electron attachment cross sections in decreasing order of cross section maximum over 0-15 eV energy range (unscaled energy range) [43].

Negative Ion	**Energy Range and in decreasing order of cross section maximum value**
BCl_3^-	0-0.2 eV
Cl^-	0.7-----------3 eV
Cl_2^-	$\geq$ 3.15 eV

Table 2-9 Estimation of negative ion mass using SF_6 electron attachment and dissociative electron attachment cross sections in decreasing order of cross section maximum over 0-15 eV energy range (unscaled energy range) [43].

Negative Ion	**Energy range and in decreasing order of cross section maximum value**
SF_6^-	0-0.2 eV
SF_5^-	0----------2 eV
F^-	2--15 eV
F_2^-	1--14 eV
SF_4^-	4---------------------8 eV
SF_3^-	8----------------------14 eV

From laser induced photodetachment coupled with microwave density measurements, one can see that the most abundant negative ions in BCl_3 and SF_6 plasmas are Cl^- and F^-, respectively. From the electron attachment cross sectional data, both parent BCl_3 and SF_6 molecules capture near thermal energy electrons to form the parent negative ions, BCl_3^- and SF_6^-. From the dissociative electron attachment cross sectional data, the fragment negative ions occur over broader and higher energy ranges. If the discharge primarily contains a distribution of electrons $\geq$ 0.2-10 eV (typical of Maxwellian and Druyvesteyn distributions), the most abundant negative ions should be that of Cl^- and Cl_2^- for BCl_3 plasmas, and F^- and F_2^- for SF_6 plasmas. Specifically, for SF_6 plasmas, the dissociative electron attachment resulting in F^- is approximately an order of magnitude larger than any of the other fragments over the entire 0-15 eV energy range. This may very well be why Kono et al. observed an abundance of F^- in their studies.

2.3 Objectives

2.3.1 Plasma Properties and Characterization

Langmuir probe studies in ICP and CCP discharges have primarily focused on noble and inert gases by applying classical Langmuir probe theory and assuming a Maxwellian distribution of electrons. The bridge between using a Langmuir probe in electropositive to electronegative plasmas has rarely been crossed; primarily due to the corrosive nature of electronegative plasmas and the formation of negative ions. To cross this bridge, application of classical Langmuir theory seems inapplicable; most

electronegative discharges are non-Maxwellian and examination of the energy distribution functions are required to gain further insight.

There are only a few Langmuir probe studies for plasmas comprised of pure BCl_3 and pure SF_6, yet none exist in a mixed chemistry of these two gases. BCl_3/SF_6 plasmas have been previously characterized using microwave infrometery, mass spectrometry, and optical spectroscopy. Prediction of electron attachment heating when SF_6 is added to BCl_3 was previously concluded by K.J. Nordheden and Y.S. Lee [5, 23].

The main objective of this research is to measure electron density and temperature of BCl_3/SF_6 plasmas by use of a Langmuir probe. This will help to confirm the hypothesis that the increase in etch rate of GaAs when SF_6 is added to BCl_3 is due to electron attachment heating. Secondary objectives are to further characterize this plasma by estimating positive and negative ion densities, in an attempt to model the plasma with subsequent explanations of root causes to the changes in the EDFs.

Chapter 3

Theory, Apparatus and Procedures

The experimental theory, apparatus, probe instrumentation, data acquisition technique, and analysis procedures are presented in this chapter. A brief plasma physics review will be given first with a subsequent Langmuir probe theory section. Following the experimental theory, the description of the experimental apparatus comprised of the plasma reactor and vacuum system are included along with a probe description used in the experimental work. The final section details the acquisition technique and analysis procedures that were used to sample the plasma with a Langmuir probe. This chapter includes thesis appendices from prior researchers at KU PRL for frequently used material involving fundamental theory, background, apparatus details, and procedures.

3.1 Experimental Theory

3.1.1 Plasma Physics Review

A review of relevant plasma physics is given in Appendix A.

3.1.2 Electron-Molecule Interactions

A brief description of the fundamental interactions between electrons and ground-state molecules is given in Appendix B. The principle direct and indirect collisions of low-energy electrons with molecules are included in Appendix B.1. One

particular indirect electron collision process, dissociative electron attachment, has an important role in this thesis, and greater detail is given in Appendix B.2. The temporary negative ions that can be formed as an intermittent stage for indirect collision processes are further explained in Appendix B.3.

3.1.3 Reactive Ion Etching Theory

The theory of plasma etching in a Reactive Ion Etching system and the formation of sheaths in this plasma chamber are presented in Appendix C.1. Further explanation on DC bias on the lower powered electrode and potentials in the chamber are explained in Appendix C.2.

As explained in Appendix C, the electrons in the etching plasma will collide with the neutral molecules and atoms causing ionization and dissociation reactions, giving rise to the formation of ions and highly reactive materials [76]. These ions and neutrals in turn may react with other species in the plasma or the substrate and help in the etching process. GaAs can be etched in chlorine based plasmas, whereas it cannot be etched in fluorine based plasmas. This work focuses on a mixture of BCl_3 and SF_6 which was used to selectively etch GaAs over AlAs [5]. In a BCl_3/SF_6 plasma, there are several possible reactions, which are again, given in generic form in Appendix B.1.

To expand upon these equations, Table 3-1 lists some of the many possible reactions in BCl_3/SF_6 plasmas that will occur in RIE systems. This is not a complete list of equations due to the vast amount of products and reactants, however it does include many of the reactions listed by Picard et al., Christophorou and Olthoff, and

Fledderman and Hebner [32, 35, 43]. Contribution for this table was also provided by R. Alapati [76].

Table 3-1a Reactions in BCl_3/SF_6 plasmas [32, 35, 43, 76]. (Long lived metastable refers to a transient, vibrationally excited negative ion that is in the ground electronic state.)

Dissociation into neutrals	$SF_n + e^- \rightarrow SF_{n-1} + F + e^-$ (n=3,4,5,6) $SF_6 + e^- \rightarrow SF_4 + 2F + e^-$ $SF_6 + e^- \rightarrow SF_4 + F_2 + e^-$ $SF_6 + e^- \rightarrow SF_3 + 3F + e^-$ $SF_6 + e^- \rightarrow SF_3 + F + F_2 + e^-$ $SF_6 + e^- \rightarrow SF_2 + 4F + e^-$ $SF_6 + e^- \rightarrow SF_4 + 2F + F_2 + e^-$ $SF_6 + e^- \rightarrow SF_4 + 2F_2 + e^-$ $BCl_n + e^- \rightarrow BCl_{n-1} + Cl + e^-$ (n=1,2,3) $BCl_3 + e^- \rightarrow BCl + 2Cl + e^-$ $BCl_3 + e^- \rightarrow BCl + Cl_2 + e^-$ $BCl_2 + e^- \rightarrow B + 2Cl + e^-$ $BCl_2 + e^- \rightarrow B + Cl_2 + e^-$
Ionization with or without parent fragmentation (Dissociative Ionization)	$SF_6 + e^- \rightarrow SF_5^+ + F + 2e^-$ $SF_6 + e^- \rightarrow SF_4^+ + F_2 + 2e^-$ $SF_6 + e^- \rightarrow SF_4^+ + 2F + 2e^-$ $SF_6 + e^- \rightarrow SF_3^+ + F_2 + F + 2e^-$ $SF_6 + e^- \rightarrow SF_3^+ + 3F + 2e^-$ $SF_4 + e^- \rightarrow SF_3^+ + F + 2e^-$ $BCl_3 + e^- \rightarrow BCl_3^+ + 2e^-$ $BCl_3 + e^- \rightarrow BCl_2^+ + Cl + 2e^-$ $BCl_3 + e^- \rightarrow BCl^+ + 2Cl + 2e^-$ $BCl_3 + e^- \rightarrow BCl^+ + Cl_2 + 2e^-$ $F_2 + e^- \rightarrow F_2^+ + 2e^-$ $Cl_2 + e^- \rightarrow Cl^+ + Cl + 2e^-$
Recombination	$SF_n + F \rightarrow SF_{n+1}$ (n = 2,3,4,5) $F^+ + e^- \rightarrow F$ $BCl_n + Cl \rightarrow BCl_{n+1}$ (n = 0,1,2) $Cl^+ + e^- \rightarrow Cl$ $BCl_n + F \rightarrow BCl_nF$ (n=1,2)
Electron Attachment: Parent negative ion formation	$SF_6 + e^- \rightarrow SF_6^{-*}$ (long lived metastable) $SF_6 + e^- \rightarrow SF_6^{-*} \rightarrow SF_6^- +$ energy $BCl_3 + e^- \rightarrow BCl_3^{-*}$ (long lived metastable) $BCl_3 + e^- \rightarrow BCl_3^{-*} \rightarrow BCl_3^- +$ energy $F + e^- \rightarrow F^-$ $Cl_2 + e^- \rightarrow Cl_2^-$

Table 3-1b (continued) Reactions in BCl_3/SF_6 plasmas [32, 35, 43, 76]. (Long lived metastable refers to a transient, vibrationally excited negative ion that is in the ground electronic state.)

Dissociative Electron Attachment	$SF_6 + e^- \rightarrow SF_6^{-*}$ (long lived metastable) $\rightarrow SF_5 + F^-$ $SF_6 + e^- \rightarrow SF_5^- + F$ $SF_6 + e^- \rightarrow SF_4^- + 2F$ $SF_6 + e^- \rightarrow SF_4^- + 2F$ $SF_6 + e^- \rightarrow SF_4^- + F_2$ $SF_6 + e^- \rightarrow SF_4 + F_2^-$ $SF_6 + e^- \rightarrow SF_4 + F + F^-$ $SF_6 + e^- \rightarrow SF_3 + 2F + F^-$ $SF_6 + e^- \rightarrow SF_2 + 3F + F^-$ $SF_6 + e^- \rightarrow SF_4 + F + F^-$ $BCl_3 + e^- \rightarrow BCl_3^{-*}$ (long lived metastable) $\rightarrow BCl_2 + Cl^-$ $BCl_3 + e^- \rightarrow BCl_2 + Cl^-$ $BCl_3 + e^- \rightarrow BCl_3^{-*}$ (long lived metastable) $\rightarrow BCl + Cl_2^-$ $F_2 + e^- \rightarrow F + F^-$ $Cl_2 + e^- \rightarrow Cl + Cl^-$
Excitation and Emission	$F_2 + e^- \rightarrow F_2^* + e^-$ $F_2^* \rightarrow F_2 + h\nu$ $F + e^- \rightarrow F^* + e^-$ $F^* \rightarrow F + h\nu$
Electron Detachment	$F^- + e^- \rightarrow F + 2e^-$ SF_6^{-*} (long lived metastable) $\rightarrow SF_6 + e^-$
Ion-pair formation	$SF_6 + e^- \rightarrow SF_5^+ + F^- + e^-$ $BCl_3 + e^- \rightarrow BCl_2^+ + Cl^- + e^-$

3.1.4 Preliminary Langmuir Probe Theory

Appendix D.1 includes an ideal case of Langmuir probe behavior and gives further detail to this section.

A Langmuir probe is a tool used to measure plasma characteristics by inserting some type of metal into plasmas and sweeping voltages for an I-V (current

vs. voltage) trace curve. During this sweep, the charged particles in the plasma are collected in different amounts depending on the probe bias voltage. For RF driven power sources, where the plasma source varies with time, a filtering method that is either passive or active must be included to suppress at least the primary RF frequency. Secondary and tertiary frequencies can also be suppressed, to prevent further inevitable high frequency oscillations that are created by the RF plasma driven power source.

Due to varying chamber configurations, the probe must be inserted into the 'bulk' plasma, which is not always the center of a chamber. This ensures that the probe avoids regions of electron or ion deprivation (sheaths). The areas to avoid are: near the walls of the plasma chamber, where the electron flux is greater, and near the powered electrode, where the positive ion flux is greatest. Fortunately, these regions can be easily avoided due to the plasma potential. A Langmuir probe can easily measure this potential with respect to ground throughout the chamber and determine the highest value. At this position, it is furthest away from the sheaths formed on the powered electrode and chamber walls.

For further use of a Langmuir probe, a voltage source bias can be used to 'sweep' voltages below a potential where the electron flux does not mask the positive ion saturation current. This region of an I-V trace curve is comprised of positive ions, if the probe is biased negatively enough that all the electrons and negatively charged ions are repelled from its surface. OML (Orbital-Motion-Limited) theory, or similar theories like ABR (Allen, Boyd, and Reynolds) or BRL (Bernstein and Rabinowitz,

and further refined by Laframboise) can then be applied to the I-V trace to determine positive ion saturation current and positive ion density (if the mass of the ions is known).

In a similar fashion, a Langmuir probe can also sweep voltages above a potential where the ion flux does not mask the electron and negative ion saturation current. In this region, the probe surface collects all of the electrons and negative ions. A potential barrier will repel all of the positive ions from the collecting surface. The area of most interest is the transition region which is in-between the positively and negatively charge species saturation regions. In this region, consisting of the floating potential (voltage where the positively and negatively charged species are equal and the net current is zero), all charged species are collected in a transient fashion. Langmuir probe theory can then be applied to eliminate the contribution of current by the positively charged species in this transient region. Further analysis techniques can use the remainder of the probe sweep to form the EDF. This uses the energies of electrons that overcome each potential barrier during the sweep. Furthermore, since the EDF is comprised of negative ions as well as electrons, special consideration must be employed to determine their contribution.

In Appendix D.2, OML theory is explained with equations pertinent to the determination of the positive ion density. This theory is most applicable in low density plasmas ($<1x10^{11}$ cm^{-3}), much like the majority of plasmas studied in RIE systems at the KU PRL. Appendix D.3 covers the formation of an EEDF with equations to determine electron density and average electron temperature from this

distribution function. For Maxwellian distributions it is well known that the electron temperature, kT_e, (or characteristic electron temperature for this particular distribution) is $\frac{2}{3}\langle\varepsilon\rangle$, where $\langle\varepsilon\rangle$ is the average electron energy (See Appendix D.3 for calculation and further explanation). Electron temperature in this work is reported as kT_e, and is first calculated as $\langle\varepsilon\rangle$ from the EDF (and approximate EEDFs), then simply multiplied by $\frac{2}{3}\langle\varepsilon\rangle$. This is not to say there is an assumed distribution of electrons (e.g. Maxwellian), but rather that these values are reported in this work to directly compare the electron temperature in this work to others.

3.1.5 Practical Considerations in an RF Driven Processing Plasma

Appendix D.4 includes the practical considerations for an RF driven processing plasma. Included in Appendix D.5 is further detail of the impacts of a time varying, RF plasma source.

3.1.6 Langmuir Probe Theory in Electronegative Plasmas

Special consideration must be used when dealing with electronegative plasmas due to charged particles of different mass and type. These plasmas consist of positive ions, electrons, negative ions, and charged metastables. Amemiya experimentally observed a Langmuir probe response to an electronegative iodine plasma [13]. His observations are extremely relevant since this thesis focuses on electronegative BCl_3, SF_6, and a combination of these chemistries. Appendix D.6 includes Amemiya's observations of the second derivative, and how to distinguish between the contributions of all of the ions, electrons, and metastable negative ions.

To apply the Druyvesteyn formula [77] to negative ions in electronegative plasmas, Amemiya replaces the electron mass with the negative ion mass [44]. This is obviously convoluted when there is more than one type of negative ion. Currently, the KU PRL does not have means to directly sample ions, which is why the literature review in Chapter 2 of this thesis suggests the most likely negative ion species.

3.2 Apparatus

This section presents the apparatus used in the experimental work of this thesis. These experiments consist of data collection software linked with a sourcemeter to bias a Langmuir probe inserted into to a PlasmaTherm 790 RIE Series chamber. Other equipment includes an oscilloscope to monitor RF frequencies, a turbomolecular and mechanical pump to evacuate the chamber, as well as electronic devices to monitor and operate the machinery. Figure 3-1 is provided for visualization of an overview of the entire system.

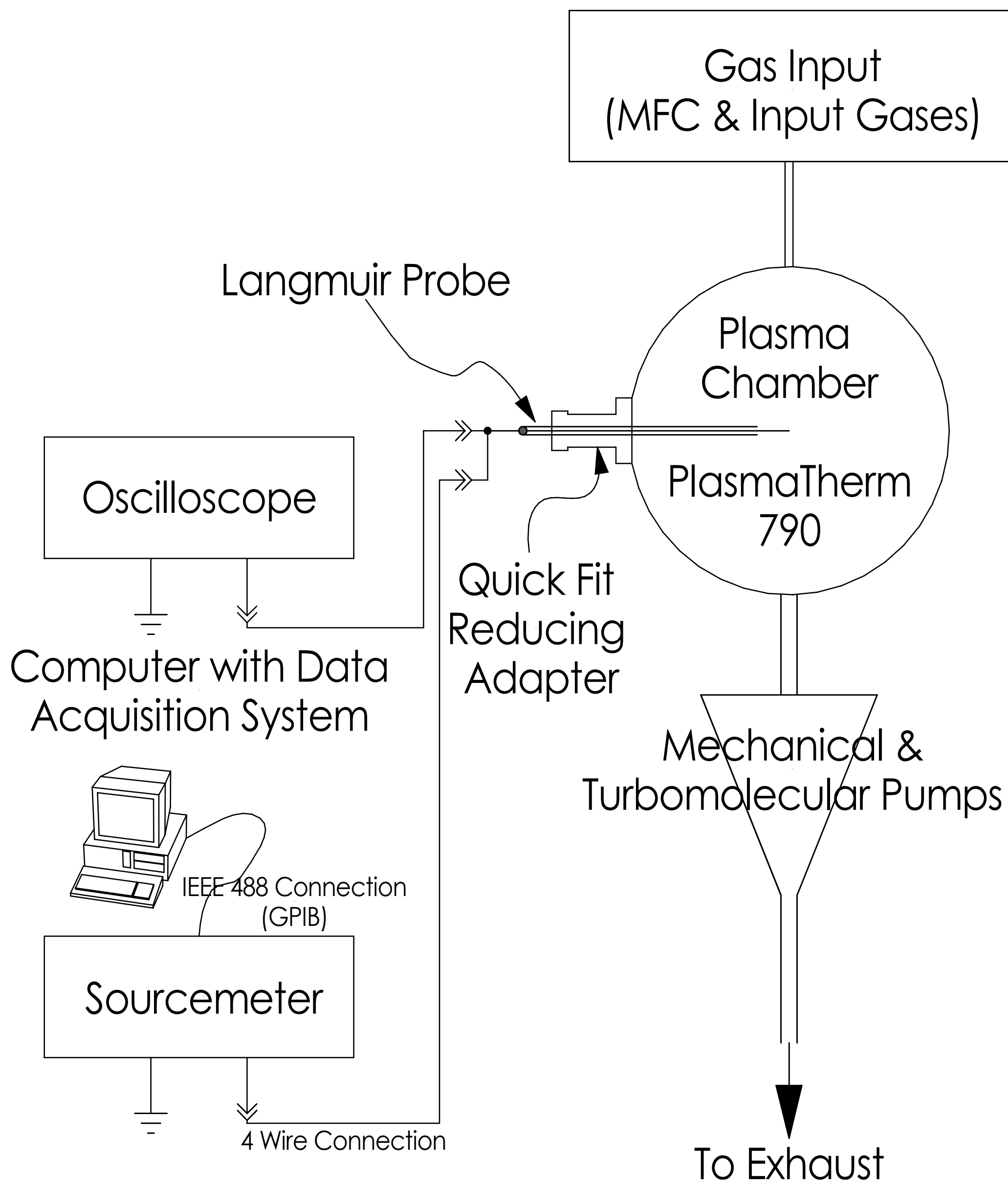


Figure 3-1 Schematic of experimental apparatus used in Langmuir probe studies [1].

The collected data sets can be analyzed to determine plasma characteristics under varying parameters (chamber pressure, driven power, DC bias, composition of

inlet gas). These settings will be included in the results section of Chapter 4, and variations will be noted with each section.

3.2.1 Plasma Reactor and Vacuum System

The PlasmaTherm 790 RIE Series plasma reactor system is presented in Appendix E.1. The Langmuir probe was inserted into one of the three viewing ports using a quick fit reducing adapter (See Figure 3-1). Due to the adapter having two quick connects, it was not perfectly centered. The height of the probe can therefore be changed to position it into the 'bulk plasma' (See Section 3.1.3 for purpose). The bottom sheath thickness on the powered electrode changed based on input parameters (and was assumed to also change for the top sheath near the showerhead, but could not be visually confirmed), however it was found that at maximum height, the probe was in a good position to maximize V_p (and thus avoid sheaths altogether). This height was 3.0 cm above the bottom, powered electrode, and 4.5 cm below the top, gas showerhead. The Langmuir probe was also centered radially within 1" (dependent on probe tip length). A base pressure of $5 x 10^{-6}$ Torr was achievable without a Langmuir probe and all view ports intact, however due to the nature of a quick fit reducing adapter on the chamber, and epoxy sealing of the Langmuir probe, a base pressure of $8.0\text{-}9.5 x 10^{-6}$ Torr was considered acceptable.

3.2.2 Langmuir Probe Description

A description of the Langmuir probe used in the experiments is included in Figure E-2. For all experimental work in this thesis, the probe tip consisted of a cylindrical platinum wire with 0.25 mm radius and 0.8 cm length. These dimensions

were a compromise so that sufficient current was drawn to the probe without depleting the plasma. The target radius was approximately twice that of the Debye length (See Appendix A), and this value will change based primarily on electron density and electron temperature.

3.2.3 Data Acquisition System

The data acquisition system consists of an x86 computer running Microsoft Windows 2000 with an Agilent 82350B IEEE-488 (GPIB, HPIB, etc) control board installed, a custom control program written in Microsft Visual Basic 6.0 by B. Pathak [1], a Keithley 2400 sourcemeter, and an Agilent 6000 series oscilloscope. The control program and associated hardware are used as a means to automate data acquisition via the sourcemeter by taking both voltage and current measurements, and record and organize data runs. The control program also includes probe tip cleaning automation between experiments. The monitoring of noise and checks for sufficient attenuation of the RF portion of the signal was periodically performed by the user using the Agilent 6000 series oscilloscope.

The Keithley 2400 sourcemeter can measure DC voltages, currents, and resistance and also provides both DC voltage and current sources. Using the acquisition system, the sourcemeter scans through a series of voltages provided by the control system, taking measurements at each voltage after a specified delay, and then reports the collected current measurements for each voltage via the control system for storage and processing.

The control program was written by B. Pathak in Microsoft Visual Basic 6.0, and combines the three major functions pertinent to the Langmuir probe operation: data storage and organization, probe cleaning, and sweep control for data acquisition [1].

3.3 Procedures

3.3.1 Data Acquisition Technique

The data acquisition technique is given in Appendix F.1, and also includes experimental protocol.

3.3.2 Analysis Procedures

After acquiring an I-V trace curve from the plasma, mathematical modeling may now be employed to understand the plasma characteristics. A series of MathCAD templates were developed for this specific purpose. These initial templates are in the Appendices of B. Pathak's thesis [1]. The initial templates focused on methods that seem inapplicable to electronegative plasmas (e.g. log-slope theory for determination of electron temperature), and they will not be listed here. The final form of the MathCAD worksheet is presented in Appendix G. This worksheet accomplishes ten tasks:

1) Display the various stages of the analysis graphically so that they can be examined for unusual behavior.
2) Smooth the original data using a LOESS filtering/curve fitting method.
3) Find an accurate V_f and V_p.

4) Create an approximate EDF and compare to Maxwellian or Druyvesteyn distributions.
5) Determine the contribution of negative ions to eliminate their impact on the EDF to create an approximate EEDF and estimate their density, N_{ni}.
6) Find kT_e and N_e by calculating them directly from the approximate EEDF.
7) Apply OML Theory, and curve fit the positive ion portion of the curve for estimations of positive ion density, N_{pi}.
8) Remove the contribution of the positive ions from the total current.
9) Re-evaluate the EDF and approximate EEDF and determine the impact of removing the contribution of positive ions from the total current to values of kT_e (or $\langle\varepsilon\rangle$), or N_e.
10) Provide a method to easily export the values of kT_e (or $\langle\varepsilon\rangle$), N_e, and any of the stages of analysis back into Excel so summary charts can be created.

For all electronegative plasmas, the EDF showed an immense depletion in low energy electrons near thermal energy (~0.1 eV). A local minimum in the EDF was determined (0-2 eV depending on process inputs like chamber pressure, power, or composition) to distinguish the regions between negative ions and electron of the EDFs. The approximate EEDF was formed for regions (of electrons) above this local minimum. If a linear distribution (this is a rough approximation) of electrons is assumed from 0 eV to the local minimum, the contribution of electrons to electron density in this region was found to be minimal (≤5% as compared to completely

ignoring them). Therefore an approximate EEDF was formed, which was comprised entirely of the electrons above the local minimum and the assumed distribution of electrons below the local minimum is 0. (Sometimes the local minimum was even found to be below the x-axis, so in some cases the number of electrons in this region is very near 0).

The LOESS polynomial smoothing technique was implemented for several reasons [78, 79]. Since the EDFs rely on derivatives of the original data, any small noise perturbations are magnified. This noise was surprisingly high in BCl_3 and SF_6 plasmas and required some type of post-acquisition filtering technique. This technique is a curve fitting method that takes small sections of the curve and fits a low degree polynomial allowing good resolution. Finally, because of the curve fitting nature of LOESS, it allows for finer detail than that of a Gaussian smooth, where the data would smear out when the smoothing window was increased.

Chapter 4

Experimental Results and Discussion

This chapter begins with Langmuir probe power and pressure studies of both pure BCl_3 and pure SF_6 plasmas. Those studies will help determine the behavior of mixing the gases for a final study of BCl_3/SF_6 plasmas with gas composition as a variable at constant RF power and chamber pressure. For all experimental work in this thesis the total inlet gas flow rate was kept constant at 20 sccm.

4.1 BCl_3 Pressure and Power Study

For electropositive gases, it is well known that electron density increases as a function of power and pressure [1, 8, 10, 51, 80, 81]. An adequate model for an electropositive discharge has been presented [82]. This model is based on the assumption that plasma density is proportional to gas density; the concentrations of all the gas species, including ionized species, rise with an increase in chamber pressure. Therefore there are more electrons to dissipate the same power which leads to a decrease in the electron temperature [83]. The electron temperature is determined by the equilibrium between ionization in the bulk plasma and the losses at the surface, and is inversely dependent on the logarithm of discharge pressure, since the dominating loss mechanism is diffusion [29, 83].

For electropositive plasmas, ionization is balanced by ambipolar diffusion, whereas in strongly electronegative discharges it is also balanced by electron

attachment [29]. The trend of increasing electron density as a function of power also holds for electronegative plasmas [29, 32, 34, 36, 45, 84], however the magnitudes of electron density are drastically lower in comparison to electropositive plasmas. By reasoning of ionization potentials, and how electronegative gases typically have lower ionization potentials than electropositive gases, a loss mechanism of electron attachment must exist in electronegative plasmas to cause lower magnitudes of electron densities [29, 34-36, 40-43, 45]. For reference, the recommended values for ionization threshold energy for He, Ar, BCl_3 and SF_6 are 24.59 eV, 15.76 eV, 11.62 eV and 15.32 eV, respectively [52].

This loss mechanism can be explained by the fact that electronegative gases will consume low energy electrons to form negative ions. For these plasmas, the two effects of electron attachment and diffusion will compete and govern the net electron density in the plasma. Furthermore, in electronegative discharges, both processes of generation and annihilation of electrons scale somewhat linearly with pressure to maintain a relatively constant electron temperature [29].

Similar Langmuir probe studies of power and pressure in pure BCl_3 were performed at the KU PRL by B. Pathak and K. Nordheden, however their work was conducted at 15 mTorr and 50 W [1]. Because Y.S. Lee's and K. Nordheden's work in BCl_3/SF_6 plasmas focused on 50 mTorr and 150 W, the experiments in this work are centered on that pressure and power [5, 22].

4.1.1 BCl_3 Pressure Study

For this first experiment, the chamber power was maintained at 150 W to study the plasma properties of a pure BCl_3 discharge with variable pressure. This discharge does not behave like electropositive gases, nor does it follow classical gas kinetics with increasing pressure. Furthermore, upon inspection of the Energy Distribution Functions (EDFs), the electron portion of the curve does not follow a purely Maxwellian or Druyvesteyn distribution. This is why inspection of the EDFs is crucial in determining plasma properties such as electron temperature. Most techniques to analyze probe data assume one particular type of energy distribution of electrons and often will give erroneous results; especially when the presence of low energy electrons is reduced via electron attachment.

For this work, the electron density and temperature is obtained from the EDFs. In an attempt to model the charge carriers, OML theory is applied to model the density of positive ions and by quasi-neutrality the resulting negative ions. It is then compared to that of Amemiya's theory for electronegative plasmas, so that one can understand the nature and trends of the negative charge carriers [13, 44].

For precise evaluations for the density of the charge carriers both OML and Amemiya theory require the mass of the ions. Since the literature does not adequately quantify ions for the pure or mixed chemistries investigated and the KU PRL does not have a means to directly sample the ions to determine the mass of the charge carriers, this paper only investigates trends and ranges of ion densities from both theories. The

literature review can then be coupled with ion density ranges to guide an approximation.

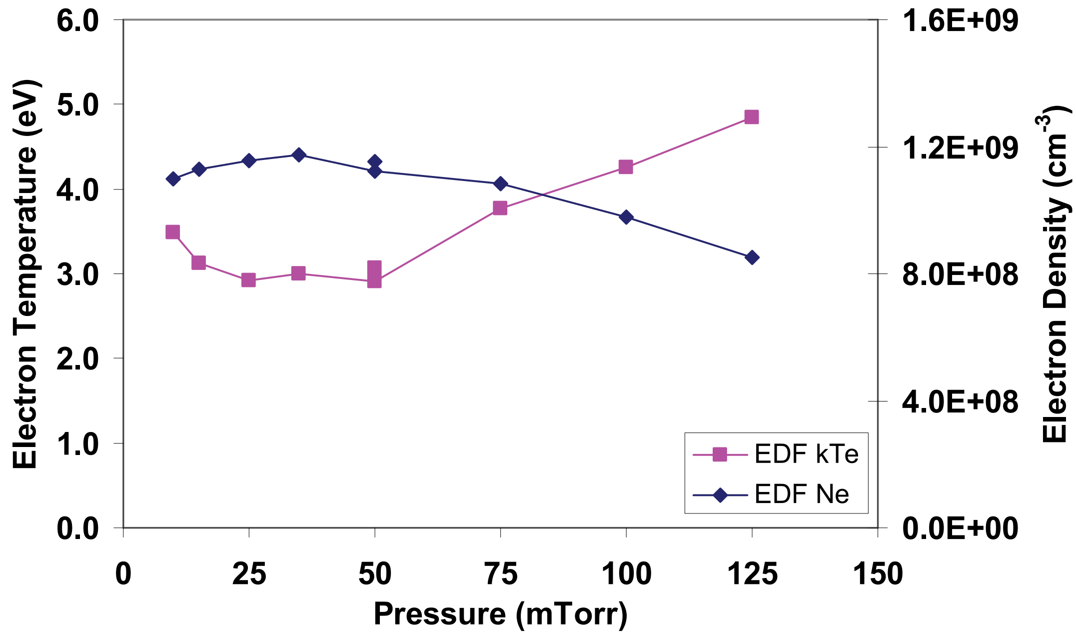


Figure 4-1 Electron temperature and density as a function of chamber pressure for pure BCl_3 plasmas at constant 150 W power.

Electron temperature and electron density results for this pressure study at 150 W are presented in Figure 4-1. As a whole, in BCl_3 plasmas the electron density appears to be relatively independent of pressure; however there are two distinct trends. At low pressures, the BCl_3 plasma does indeed behave electropositively, since the electron density increases and electron temperature decreases with increasing pressure. Above 25 mTorr, these two trends switch and obvious electronegativity occurs by means of a decreasing trend in electron density. Furthermore, by studying the EDF, a negative ion peak was not found prior to 25 mTorr; this agrees with previous work with BCl_3 plasmas that there is an obvious transition from an

electropositive to electronegative plasma at 25 mTorr [1, 29]. Y. S. Lee studied the effects of pressure on electron density in a 80%/20% BCl_3/SF_6 plasma at 150 W using microwave interferometry and also noticed a transition around 25 mTorr, as well as the same trend in electron density [5].

Two other studies also find that the electron density in electronegative BCl_3 is relatively independent of pressure [29, 32]. Schwabedissen et al. mentions that there is no clear dependence of electron density on pressure for O_2, another weakly electro-negative gas [51]. This is in contrast to their studies of rare gases, in which they found that there is a near linear increase in electron density as a function of increasing pressure.

For a BCl_3 plasma studied at constant 300 W in an ICP, Fleddermann and Hebner found the negative ion density and electron density both constant and independent of pressure in the range of 5 to 40 mTorr [32]. Pathak states, "BCl_3 is likely to also exhibit increased electronegativity at higher powers" [1]. Therefore, in the study by Fleddermann and Hebner which was at much higher power than in this study, they were most likely well above the electropositive to electronegative transition region.

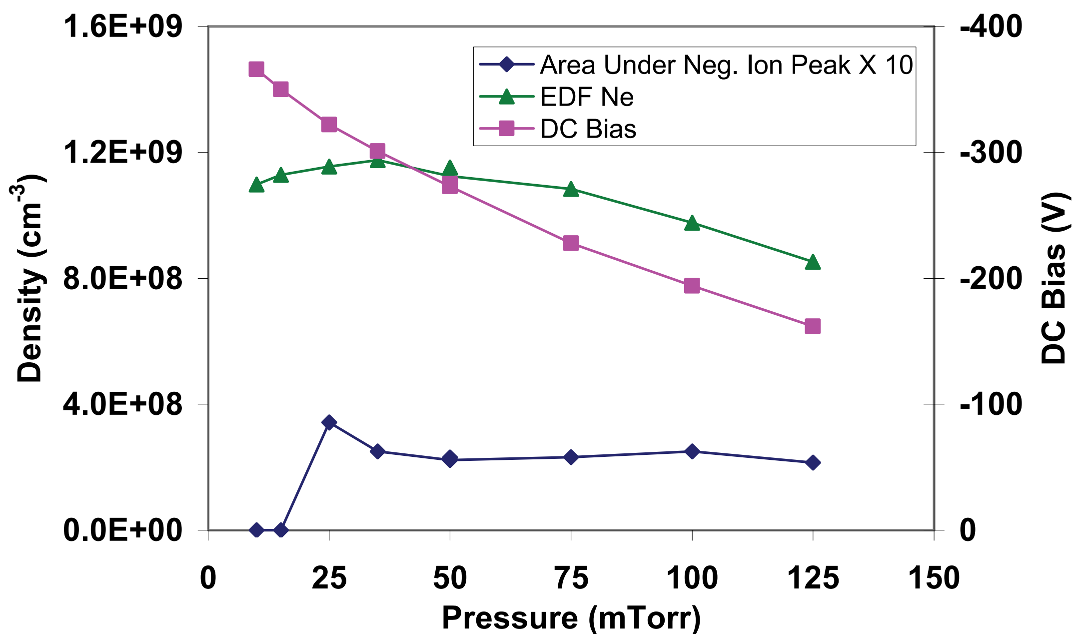


Figure 4-2 Area under the EDF negative ion peak, electron density, and DC bias as a function of chamber pressure for pure BCl_3 plasmas at constant 150 W power.

Figure 4-2 shows electron density, DC bias, and the integrated area under the negative ion peak in the EDF as a function of pressure in pure BCl_3 plasmas at 150 W. A similar trend in DC bias and electron density is apparent at pressures above 25 mTorr. The two factors that dictate DC bias are mobility and density of electrons within plasma. At higher pressures the neutral gas density increases, thus the mean free path of an electron decreases and more collisions will occur to decrease mobility. This decrease in electron density is also explained by the negative ion formation at 25 mTorr and above, where the electron density is depleted by attaching to electronegative BCl_3.

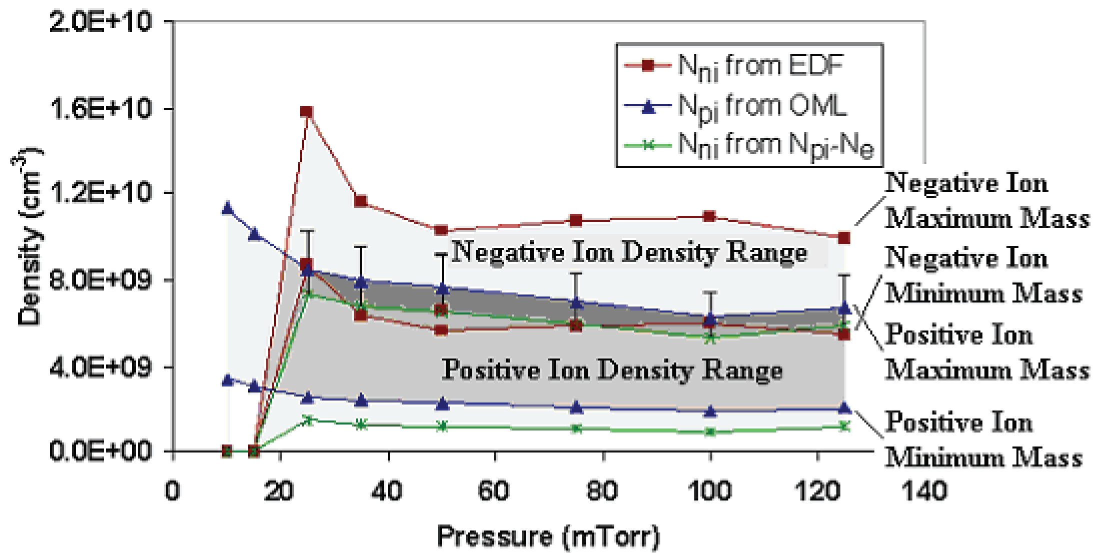


Figure 4-3 Positive and negative ion densities as a function of chamber pressure for pure BCl_3 plasmas at constant 150 W power.

Figure 4-3 is a comparison of ion density measurements from OML and Amemiya's theory for the pressure study of pure BCl_3 plasmas at 150 W. Positive ion density (N_{pi}) measurements are determined from OML theory. Negative ion density (N_{ni}) measurements are obtained by use of the EDF and Amemiya's theory and then compared to that of OML theory assuming quasi-neutrality (N_{ni} from N_{pi}-N_e). The ions used in calculation for upper and lower bounds for N_{pi} are BCl_3^+ and B^+, respectively. These are associated with the heaviest and lightest probable positively charged species (molecule or radical). In the same manner, the upper and lower bounds of N_{ni} are BCl_3^- and Cl^-, respectively.

OML Theory is notorious for under-predicting densities, so much so that they can err by a factor of 2 or more in the value of density in partially ionized plasmas, and it is quite difficult to give a value of density better than 20% [12]. The error bars

are for this uncertainty, and are +40%. Furthermore, due to a positive value of floating potential measured by the Langmuir probe for all cases in this thesis, and quasi-neutrality of plasmas, the positive ion density should be larger than the combined electron and negative ion density. This further necessitates a need for error bars; Amemiya's theory for several cases was predicting a higher negative ion density than the positive ion density predicted by OML.

Quite simply put, for a BCl_3 discharge at 150 W, Figure 4-3 shows the positive and negative ion density is decreasing as a function of pressure. The literature may now guide a better approximation of ion densities.

Of the possible positive charge carriers, BCl_2^+ and BCl_3^+ are the most abundant in pure BCl_3 plasmas. These charge carriers have a low ionization threshold [22, 43], and from 11 to 19 eV, BCl_2^+ was found to be produced from the fragmentation of the excited states of BCl_3^+ [85]. From threshold to 60 eV, BCl_2^+ was found to be the most abundant positive ion using electron-impact ionization [74]. The population of electrons greater than 20 eV is virtually non-existent for all capacitively coupled plasma studies at the KU PRL. Overzet and Luo observed, in order of decreasing magnitude, the positive ions BCl_2^+, BCl^+, and B^+ with mass spectrometry. Their results were taken on the grounded electrode, and due to the difference in chamber pressure (200 mTorr) and RF source power (10 W average power at 1 kHz) their results can only be used as general estimations for ion mass [73]. From the literature, to guide a better approximation of positive ion density, the actual values are

closer to the upper bounds on Figure 4-3, by use of the heaviest ion masses BCl_2^+ and BCl_3^+.

Of the possible negative ion charge carriers, Cl^- is the predominant negative ion. This follows the work of Fleddermann and Hebner (in ICP), by which studies using laser photodetachment confirmed that Cl^- is the only negative ion species of significant density in BCl_3 plasmas [32]. The mass spectrometry results from Overzet and Luo also confirm Cl^- was the predominant negative ion using BCl_3 and BCl_3/Ar chemistries [73]. These results were again, taken on the grounded electrode, at different pressure, power, and frequency than this study. Thus, their results can only be used as general estimations to estimate ion mass. Furthermore, when sampling negative ions with mass spectrometry, plasma chemistry can be altered and recombination in the sampling orifice have added more uncertainty [40]. This is evidenced by the other lower (using relative intensity) signal detections of: $BOCl_2^-$, BCl_4^-, $B_2Cl_4^-$, and $B_2Cl_5^-$ from Overzet and Luo in a BCl_3 discharge using mass spectrometry [73]. The negative ion density in this study should be closest to the lower bound of Figure 4-3 by use of the most probable, lightest negative ion mass, Cl^-

The electron attachment reaction resulting in dissociation, $BCl_3 + e^- \rightarrow BCl_2 + Cl^-$, has been reported with a low energy threshold of ~1 eV [50]. The electron attachment rate constant of BCl_3 has been reported with peak at 0 eV with rapid decay for higher energy levels, therefore BCl_3^- will only be present in plasma discharges with low energy electrons [50, 57]. BCl_3 initially captures electrons forming a transient metastable negative ion, BCl_3^{-*}, and must be

collisionally stabilized (to remove excess energy) to form BCl_3^-. This can partially explain the absence of detection of this negative ion [32, 73], and reasons why the results from this work with comparison of negative ion densities (OML and Amemiya theory coupled with quasineutrality) estimates a negative ion mass closer to that of Cl^-. The low electron affinity of BCl_3 (~0.33 eV), as compared to dissociated species with much higher electron affinity like Cl, can further help explain the absence of detection for this negative ion.

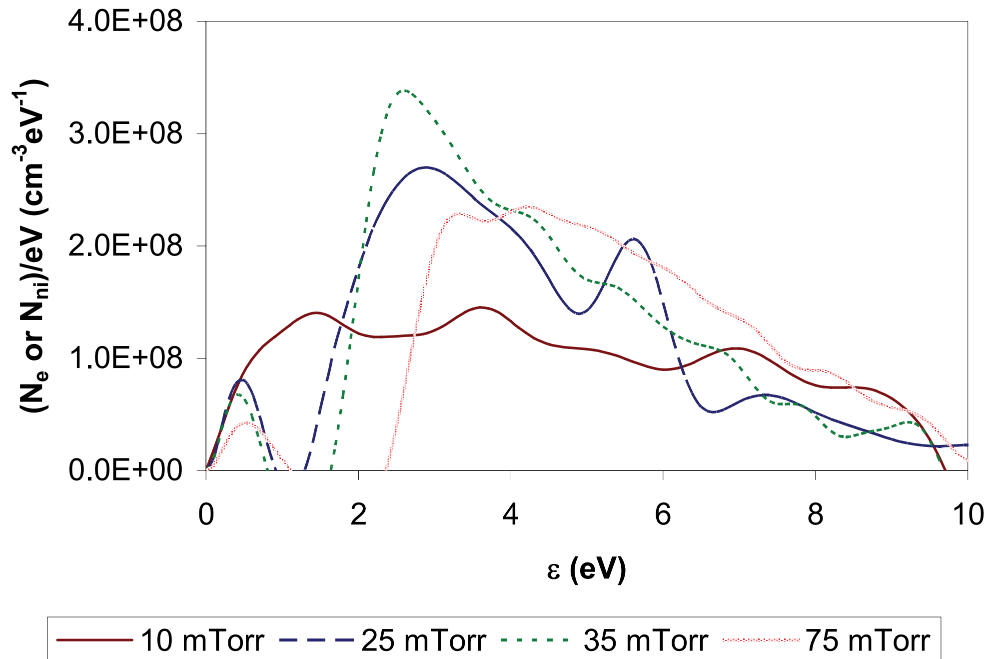


Figure 4-4 Energy Distribution Function in pure BCl_3 plasmas at constant 150 W power for chamber pressure at 10, 25, 35, and 75 mTorr.

The EDFs give a much clearer picture to the electron energy levels. Figure 4-4 is a presentation of energy distribution functions from 0 to 10 eV for the BCl_3 pressure study at 150 W. Clearly, above 25 mTorr, the low energy electrons have

disappeared from the plasma, and a negative ion peak near 0 eV exists. Again, this further proves that the plasma is transitioning from electropositive to electronegative by reasoning of low energy electrons (~0-2 eV) attaching to form negative ions. By reasoning of the particular depletion of electrons at 1 eV in the EDF, Petrović et al. and Tav et al. may be perfectly correct in stating that for dissociative electron attachment to BCl_3 to occur, an energy threshold of ~1 eV is required, even though the negative ions were not directly identified [43, 50, 57]. Interestingly, the EDFs also show an *increase* in number of electrons between ~2 to 6 eV for this electropositive to electronegative transition. Due to the overall decrease in electron density, fewer electrons are available to dissipate the same power which leads to an *increase* in the electron temperature. This is a complete reverse trend of the model of electropositive plasmas [82, 83]. Electron loss to electron attachment may even be the dominating loss mechanism in electronegative plasmas as proposed by Franz [29]. Finally, if long lived BCl_3^{-*} [55, 56] is being formed in the plasma, the I-V trace has no means to measure their quantity, and they are not directly measured in the negative ion peak observed in the EDF [13, 44]. They appear as secondary electron emission, above the plasma potential [13, 44], and may have a role in the transition of BCl_3 plasma from electropositive to electronegative.

4.1.2 BCl_3 Power Study

For this experiment, the chamber pressure was maintained at 50 mTorr to study the plasma properties of a pure BCl_3 discharge with variable power. Typical electronegativity was observed, and again, classical gas kinetics did not apply with

increasing power. The densities of the charge carriers were also modeled using OML and Amemiya's theory. Figure 4-5 shows the electron temperature and electron density as a function of power for BCl_3 at 50 mTorr.

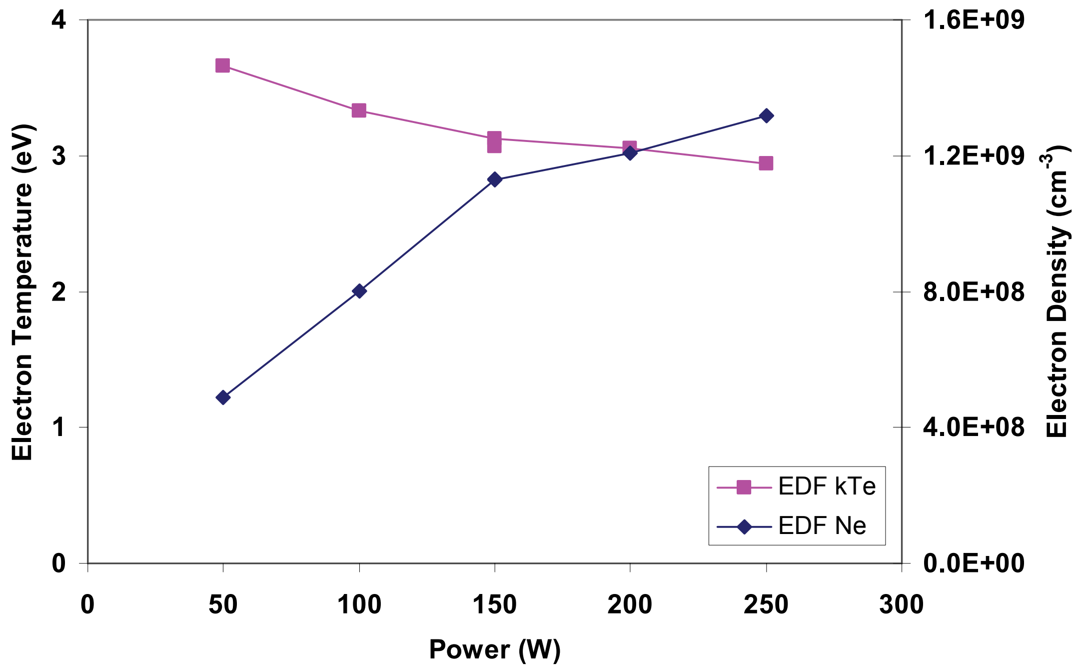


Figure 4-5 Electron temperature and density as a function of power for pure BCl_3 plasmas at constant chamber pressure of 50 mTorr.

As mentioned earlier, electron density increases as a function of power for both electropositive and electronegative plasmas, but their magnitudes are different due to the presence of negative ions. For electron temperature, in electronegative plasmas, it was found that it remains relatively constant as a function of power [1, 29]. Both trends agree with previous findings.

At higher powers, the electron density starts to saturate. This effect has been seen in other gases and is typically due to an increase in collisions (from an increase

in density). However, for this electronegative plasma, the concentration of negative ions continues to increase as a function of power. Figure 4-6 shows this trend of increasing negative ion density, and thus electrons are attaching to the chlorinated species in the plasma and providing an additional loss mechanism.

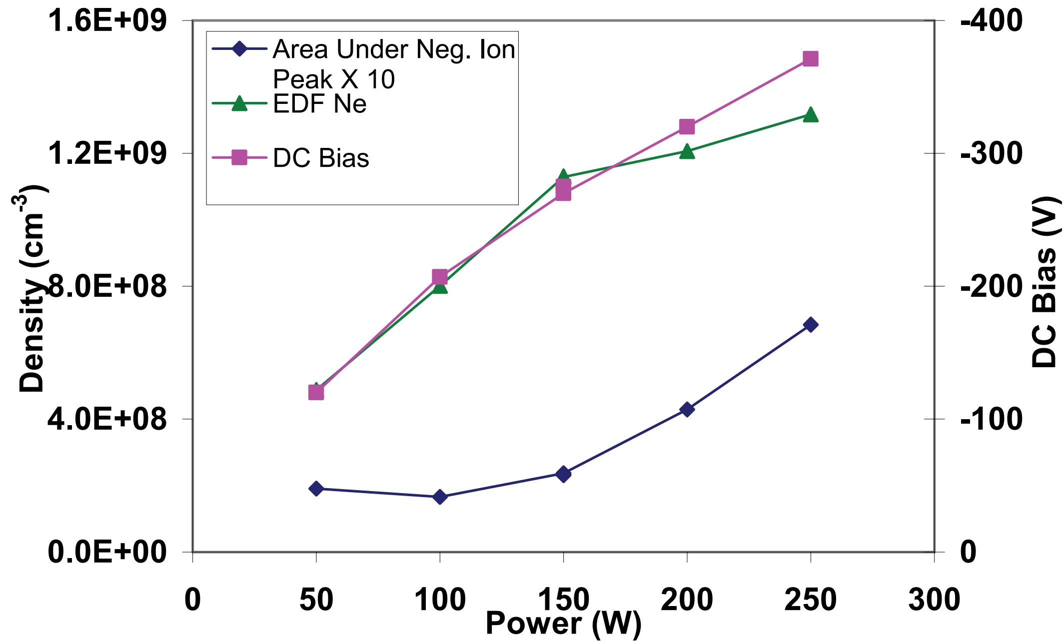


Figure 4-6 Area under the EDF negative ion peak, electron density, and DC bias as a function of power for pure BCl_3 plasmas at constant chamber pressure of 50 mTorr.

Figure 4-6 shows electron density, DC bias, and the integrated area under the negative ion peak in the EDF as a function of power for constant chamber pressure of 50 mTorr. From the previous section, at this pressure, the BCl_3 plasma exhibits electronegativity due to the chamber pressure being above the transitional pressure of 25 mTorr. For CCP discharges, an increase in DC bias occurs with increasing RF power. This relationship is developed from the accumulation of electrons on the

powered electrode. The similar trend in DC bias and electron density is again, due to the dependence of relative mobility and density of electrons in the plasma.

Figure 4-7 is a comparison of positive ion density measurements determined from OML theory, the corresponding negative ion density measurements via subtraction of the electron density from OML theory and assuming quasi-neutrality, and comparison to negative ion density measurements using the EDF. The upper and lower bounds for both N_{pi} and N_{ni} use the same ions as in the previous section for the BCl_3 pressure study. By the reasoning in the previous section, the positive ion density is closer to that of the upper bound by use of the heaviest ion masses BCl_2^+ and BCl_3^+ [22, 43, 73, 74, 85]. The negative ion density is closest to the lower bound by use of the lightest ion mass, Cl^- [32, 73].

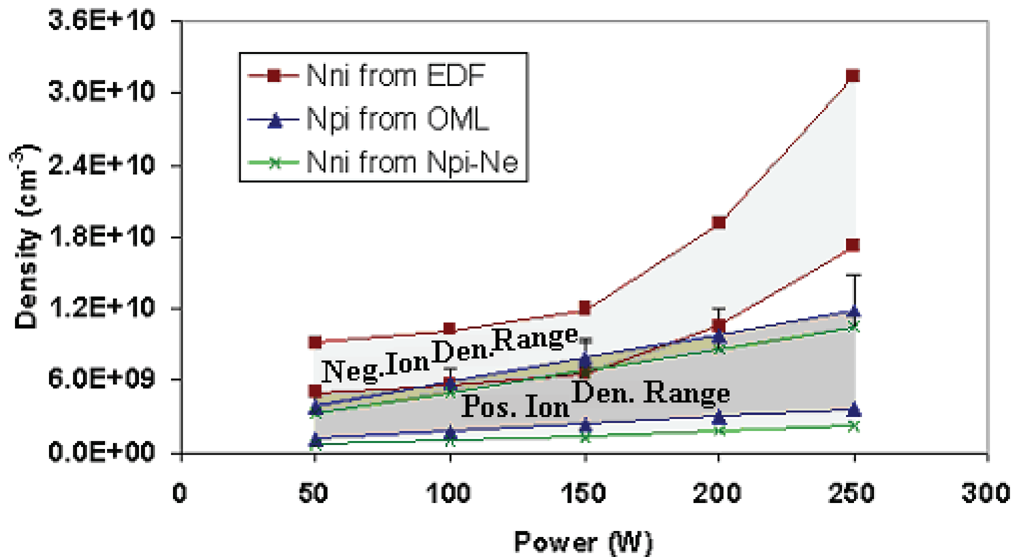


Figure 4-7 Positive and negative ion densities as a function of power for pure BCl_3 plasmas at constant chamber pressure of 50 mTorr.

For a BCl_3 discharge at 50 mTorr, OML Theory shows that the positive ion density is increasing as a function of power. Both techniques to estimate the negative ion density agree and show a trend of increasing negative ion density as a function of power. It is also noted, that the negative ion density by Amemiya's theory predicts a higher negative ion density than positive ion density, however the atomic mass of Cl^- is the lowest feasible mass and the resulting negative ion density can not be mathematically lower than the values presented.

4.2 SF_6 Power and Pressure Study

Using the same experimental apparatus as the work in this thesis, Alapati previously investigated SiC etching in SF_6/He plasmas. His results from microwave interferometry of a pure SF_6 plasma show a relatively linear increase in electron density as power is increased [76]. Another similar study at the KU PRL by Jaiprakash using a parallel plate plasma reactor at KU PRL shows the same trend in low frequency plasmas and dual frequency plasmas (100 kHz and 12.2 MHz) [86]. The trends in this study are quite similar to the previous BCl_3 power study. As a function of power, electron density increases, and due to somewhat linear scaling of processes of generation and annihilation of electrons, a relatively constant electron temperature is found.

4.2.1 SF_6 Power Study

For this experiment, the chamber pressure was maintained at 50 mTorr to study the plasma properties of pure SF_6 with variable power. In Figure 4-8, the results of electron temperature and density as a function of power for pure SF_6 plasma are presented.

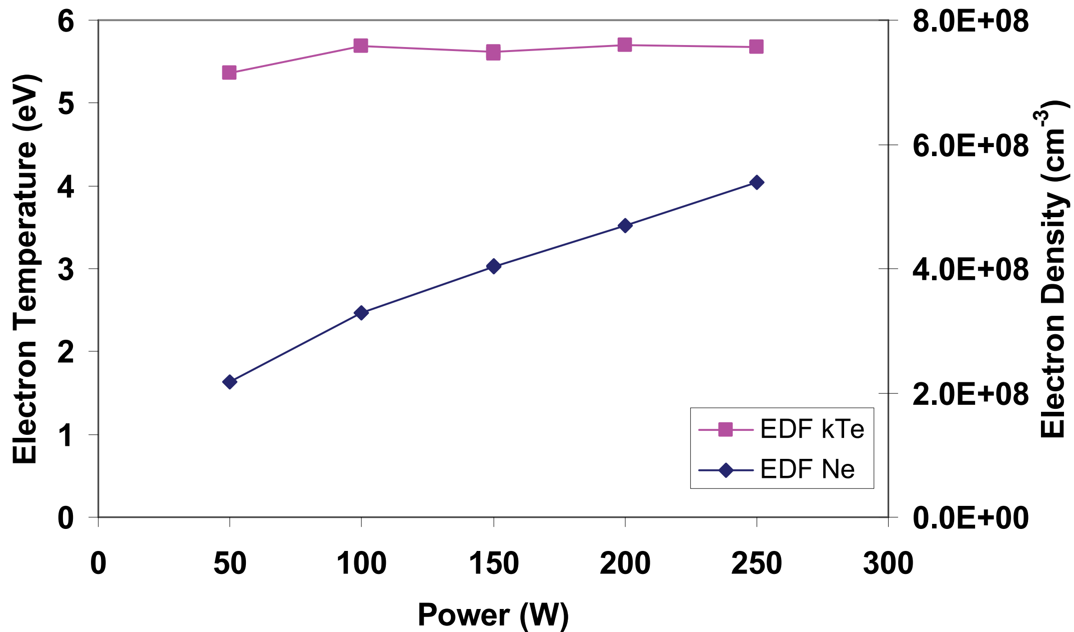


Figure 4-8 Electron temperature and density as a function of power for pure SF_6 plasmas at constant chamber pressure of 50 mTorr.

From the experimental data, for pure SF_6 plasmas at 50 mTorr, the electron density increases as a function of power and the electron temperature remains relatively constant. These two trends agree well with previous findings [29, 76, 86].

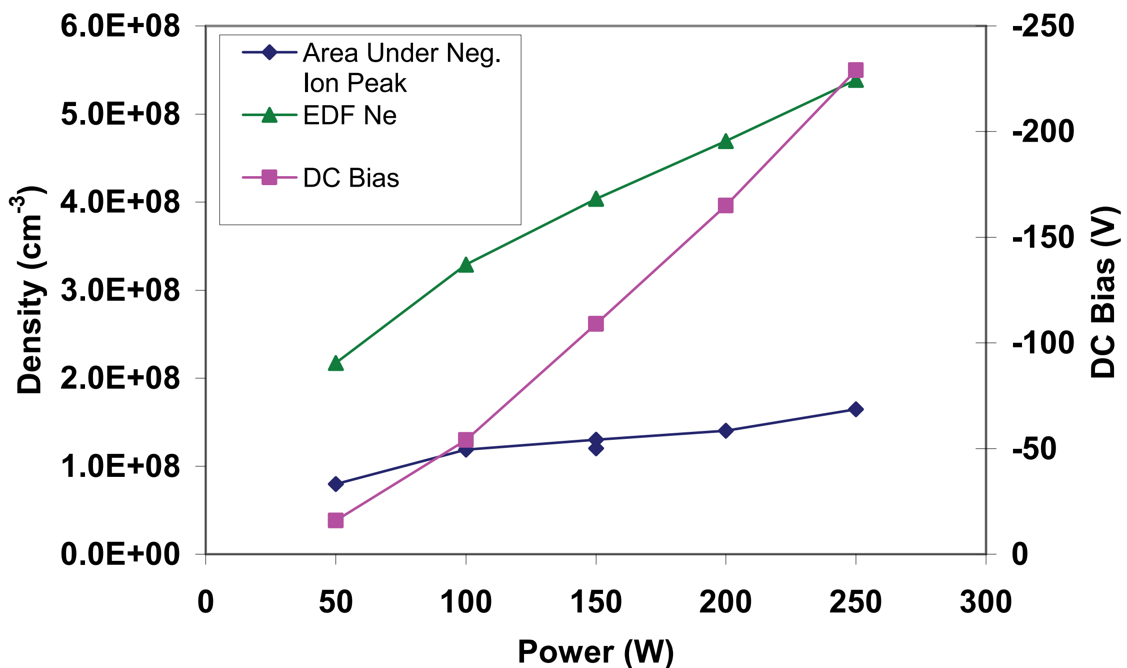


Figure 4-9 Area under the EDF negative ion peak, electron density, and DC bias as a function of power for pure SF_6 plasmas at constant chamber pressure of 50 mTorr.

The electron density, DC bias, and the integrated area under the negative ion peak in the EDF as a function of power at constant chamber pressure of 50 mTorr are presented in Figure 4-9. The DC bias is again, increasing as power increases due to accumulation of electrons on the powered electrode and is dependent on electron density and mobility. The area under the EDF negative ion peak is increasing as a function of power. Assuming a relatively constant negative ion mass for the power range investigated, this would mean an increase in negative ion density as power is increased. Similar to the BCl_3 study, the electron density is saturating at higher powers, and the increase in collisions and formation of negative ions explains this loss in electron density.

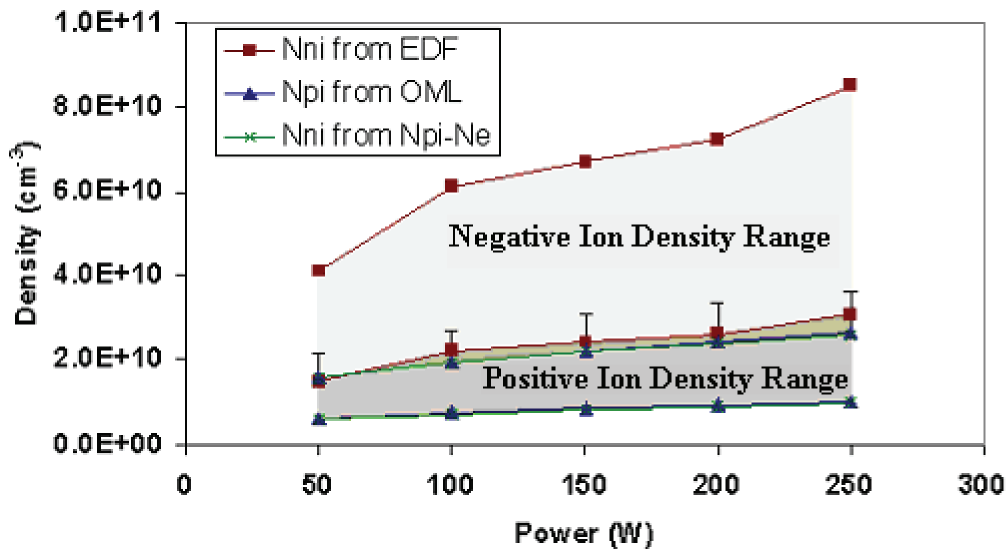


Figure 4-10 Positive and negative ion densities as a function of power for pure SF_6 plasmas at constant chamber pressure of 50 mTorr.

Figure 4-10 is a comparison of positive ion density measurements, determined from OML theory, the corresponding negative ion density measurement via subtraction of the electron density from OML theory and assuming quasi-neutrality, and comparison to negative ion density measurements determined from the EDF. The ions used in calculation of upper and lower bounds for N_{pi} are SF_5^+ and F^+, respectively. These are associated with the heaviest and lightest probable positively charged species (molecule or radical). In the same manner, the upper and lower bounds of N_{ni} are SF_6^- and F^-, respectively. Again, OML theory is notorious for under-predicting densities, so much so that they can err by a factor of 2 or more in the value of density in partially ionized plasmas, and therefore it is quite difficult to give a value of density better than 20% [12]. The error bars are for this uncertainty, and are

+40%. It should be noted that the curve for N_{ni} from N_{pi}-N_e overlaps with the curve for N_{pi} from OML.

For the power studies, at 50 mTorr, both charge carrier density trends agree for SF_6 and BCl_3; they increase as a function of power. However, due to the higher electronegative behavior of SF_6, the electron density is of lower magnitude, approximately half that of BCl_3. As far as electron temperature, the relative independence on power is the same for both gases; however SF_6 is higher by approximately 2.5 eV from BCl_3. The literature may now guide a better approximation of ion densities.

Of the possible negative ion charge carriers, F^- is most likely the predominant negative ion. This follows the work of Christophorou and Olthoff, who state, "The F^- ion is the predominant fragment negative ion produced by dissociation electron attachment to SF_6 at ambient temperature at electron energies above ~ 3 eV" [43]. Furthermore, SF_6^- is formed at extremely low electron energies, below 0.2 eV, while SF_5^- occurs at energies below 2 eV [43]. By studying the EDFs, one does not find significant presence of electrons below 2 eV. For a better approximation of negative ion density, the values are closer to the lower bounds on Figure 4-10 by use of the most probable, lightest ion mass, F^-.

The predominant positive charge carriers are most likely SF_5^+ and SF_3^+. This follows the work of Christophorou and Olthoff, who examined four studies of partial ionization cross sections and state, "…that SF_5^+ is by far the most abundant positive ion fragment" [43]. Furthermore, these ions have the lowest threshold energy,

whereby the process of ionization of SF_6 is dissociative ruling out SF_6^+ entirely [43]. The other likely candidate, SF_3^+, was found to be in slightly higher abundance than SF_5^+ in mass spectrometry studies [35, 37, 40]. However, mass spectrometry studies are not often reliable for determining charged species unless direct ion sampling is used. From the literature, the positive ion density in Figure 4-10 is closer to that of the upper bound by use of the most probable, heavier ion masses SF_5^+ and SF_3^+.

By combining all the experimental results from the BCl_3 and SF_6 power studies at constant chamber pressure of 50 mTorr with the best approximations to negative and positive ion density, generic trends of these plasmas may be given. These experiments determine, of the power ranges studied, that SF_6 has twice (or greater) the positive and negative ion densities than BCl_3. As mentioned earlier, the electron density of BCl_3 is approximately twice that of SF_6 for this same power range. This being the case, strictly measuring electron density will not give any indication to ion densities in electronegative plasmas. It has now been experimentally shown that at 50 mTorr, and over a 50 to 250 W power range in an RIE system, that SF_6 plasmas are more electronegative than BCl_3 plasmas, thus more electrons attach to SF_6.

4.2.2 SF_6 Pressure Study

For this experiment, the chamber power was maintained at 150 W to study the plasma properties of a pure SF_6 with variable chamber pressure. The electron density and temperature for this pressure study at 150 W are presented in Figure 4-11. Again, classical gas kinetics did not apply, and electronegativity was observed. The results

show both electron density and temperature maintained a relatively constant value for the pressure range examined.

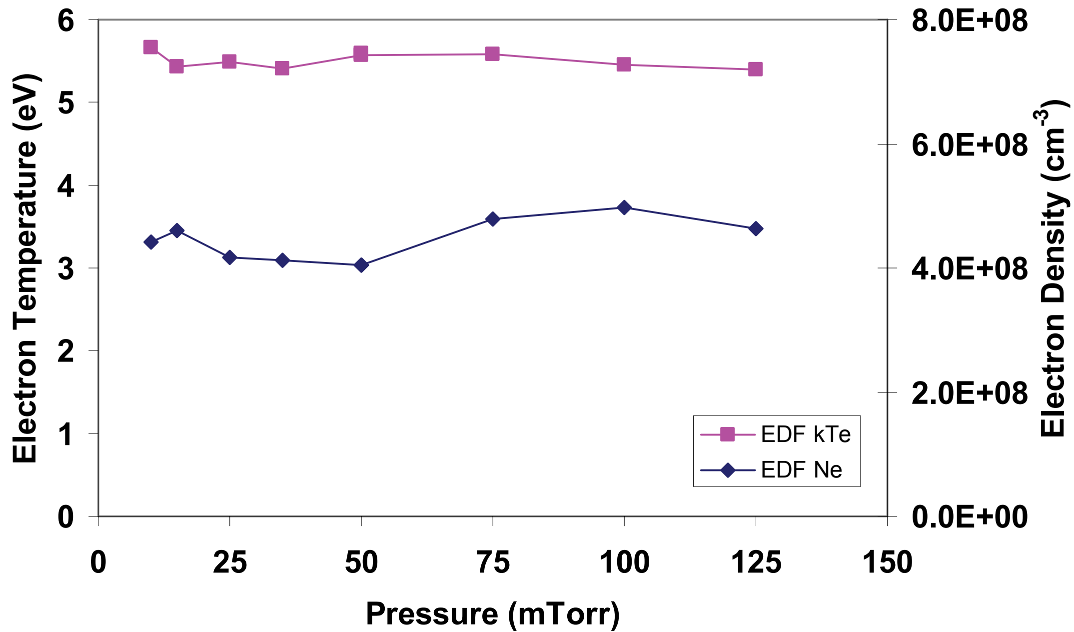


Figure 4-11 Electron temperature and density as a function of chamber pressure for pure SF_6 plasmas at constant 150 W power.

The effect of pressure in SF_6 plasmas was previously studied by Picard et al. in a capactively-coupled RF discharge at 25 W. In agreement with this thesis, their results show a relatively constant electron density and temperature as a function of pressure [35].

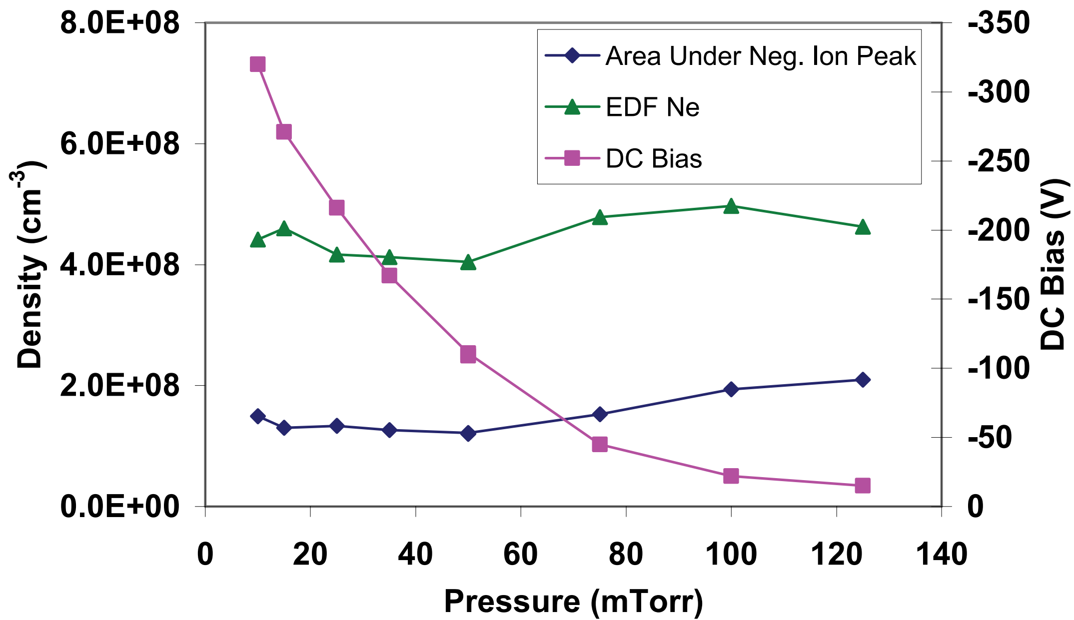


Figure 4-12 Area under the EDF negative ion peak, electron density, and DC bias as a function of chamber pressure for pure SF_6 plasmas at constant 150 W power.

Figure 4-12 shows the electron density, DC bias, and the integrated area under the negative ion peak in the EDF as a function of pressure. Both pressure studies of BCl_3 and SF_6 confirm a DC bias decrease as pressure is increased. DC bias depends on electron density and mobility. The mobility of electrons decreases as pressure is increased, which can explain the DC bias decrease. The electron density for this pressure study of SF_6 was approximately half that of BCl_3. Clearly, the higher electronegativity of SF_6 results in a lower electron density due to more electrons attaching than for BCl_3.

Figure 4-13 is a comparison of positive ion density measurements determined from OML theory, and the corresponding negative ion density measurements via subtraction of the electron density from OML theory and assuming quasi-neutrality,

and comparison to negative ion density measurements using the EDF. The upper and lower bounds for N_{pi} and N_{ni} use the same ions as in the previous section for the SF_6 power study. By the reasoning in the previous section, the positive ion density is closer to that of the upper bound by use of the most probable, heaviest ion masses SF_5^+ and SF_3^+. The negative ion density is closest to the lower bound by use of the most probable, lightest ion mass, F^-.

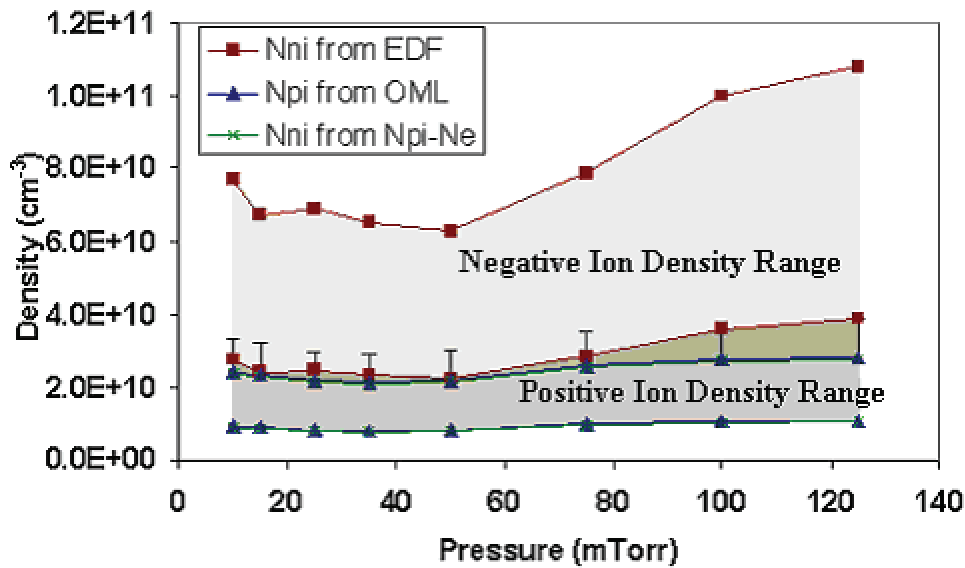


Figure 4-13 Positive and negative ion densities as a function of chamber pressure for pure SF_6 plasmas at constant 150 W power.

For a SF_6 discharge at 150 W, between 50 and 125 mTorr, the positive ion density is increasing as a function of increasing pressure. Both techniques to estimate the negative ion density agree quite well, and show a trend of increasing negative ion density as a function of pressure. It is again noted, that the negative ion density by Amemiya's theory predicts a higher negative ion density than positive ion density by

OML theory. Again, OML theory under predicts positive ion density, and necessitates error bars.

4.3 BCl_3/SF_6 Composition Study

For this final Langmuir probe experiment, chamber pressure and power were maintained at 50 mTorr and 150 W to study the plasma properties as a function of composition in BCl_3/SF_6 plasmas. Their work predicted that an electron temperature increase occurred when SF_6 was added to BCl_3 and was the primary motivation behind this experiment.

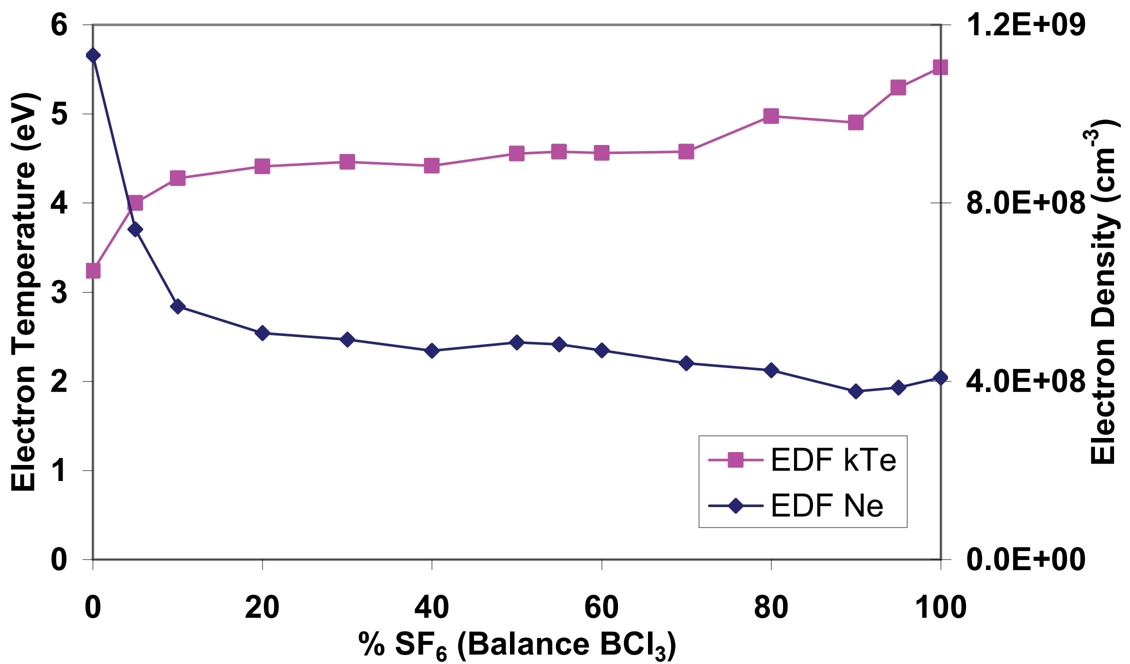
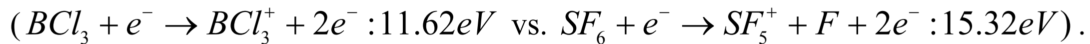


Figure 4-14 Electron temperature and density as a function of composition in SF_6 and BCl_3 plasmas at 50 mTorr and 150 W power.

Figure 4-14 presents the electron temperature and density measurements as a function of SF_6 composition in BCl_3/SF_6 plasmas at 50 mTorr and 150 W using a Langmuir probe. The electron density rapidly decreases in approximately half as 10% SF_6 is added to BCl_3, and then gradually decreases for higher concentrations of SF_6. The rapid electron density depletion from 0% to 10% SF_6 is a characteristic of electron attachment to species within the plasma. Y. S. Lee and K. Nordheden previously measured the electron density using microwave phase shift measurements and agrees in trend with this experiment [5]. Furthermore, the electron density depletion cannot be fully explained by the difference in ionization potential of SF_6 and BCl_3, which is about 3.7 eV higher than that of BCl_3



$$(BCl_3 + e^- \rightarrow BCl_3^+ + 2e^- : 11.62eV \text{ vs. } SF_6 + e^- \rightarrow SF_5^+ + F + 2e^- : 15.32eV) .$$

Remarkably, under similar conditions, K.J. Nordheden and Y.S. Lee noticed the OES Ar emission, increased as SF_6 was added to BCl_3 (at constant Ar inlet flow rate) [5, 23]. The increase in Ar OES emission can now be confirmed as an increase in electron temperature and a subsequent increase in the rate coefficient [5, 23].

Over the compositional range of 0 to 10% SF_6, the experimental results also show an electron temperature increase of about 1.1 eV (from ~3.2 eV to ~4.3 eV). This electron temperature rise, coupled with rapid electron density depletion, is characteristic of electron attachment heating, whereby low energy electrons attach to species within the plasma, increasing the average electron energy [24-28]. The fewer remaining electrons must sustain the same power dissipation, thus increasing their

average energy [23]. The electron temperature does not simply scale from their pure gas values (i.e. a non-linear transition) [24], as is easily seen from this experiment.

Dissociative reactions, which result in more etchant species, can require relatively higher energies than that of the bulk plasma electron temperature. Specifically for BCl_3, the lower energy thresholds for the dissociation reactions are:

$BCl_3 + e^- \rightarrow BCl_2 + Cl + e^- : 4.61 eV$ and $BCl_3 + e^- \rightarrow BCl + Cl_2 + e^- : 5.65 eV$

[61]. Recall that electron temperature is related to average electron energy by the relation, $kT_e = \frac{2}{3}\langle \varepsilon \rangle$. For this experiment, the average electron energy in pure BCl_3 is 4.86 eV, which is slightly above the first dissociation energy threshold. The average electron energy increases to 6.87 eV when the gas composition reaches 55% SF_6, which was found to have maximum etch rate of GaAs. As SF_6 is added to BCl_3, the average electron energy surpasses both of the lower dissociation energy thresholds. The increase in electron temperature (and average electron energy) explains the increase in etch rate of GaAs as SF_6 is added to BCl_3 by means of increasing the number of electrons available to dissociate BCl_3 into reactive species Cl and Cl_2, and increasing the number of superthermal electrons to ionize both parent and dissociated products into the reactive ion etching species, Cl^+ and Cl_2^+.

This plasma mixture has been studied by Y.S. Lee and K. Nordheden using mass spectrometry [5, 22]. Their work observed an increase in BClF and BCl_2F species in the plasma mixture as SF_6 is added to BCl_3. The formation of these species

would help to prevent the recombination of active etch species (i.e. Cl and Cl_2), and may partially contribute to the increase in etch rate as SF_6 is added to BCl_3.

Figure 4-15 shows electron density, DC bias, and the area under the negative ion peak in the EDF as a function of SF_6 composition. Again, DC bias depends on electron density and mobility, which is why they have a similar trend. It is well known that SF_6 is more electronegative than BCl_3. These results show an increase in area under the negative ion curve as SF_6 is added to BCl_3. A negative ion density increase associated with this peak cannot be fully explained by a change in negative ion mass and further shows that the plasma is transitioning to a more electronegative plasma.

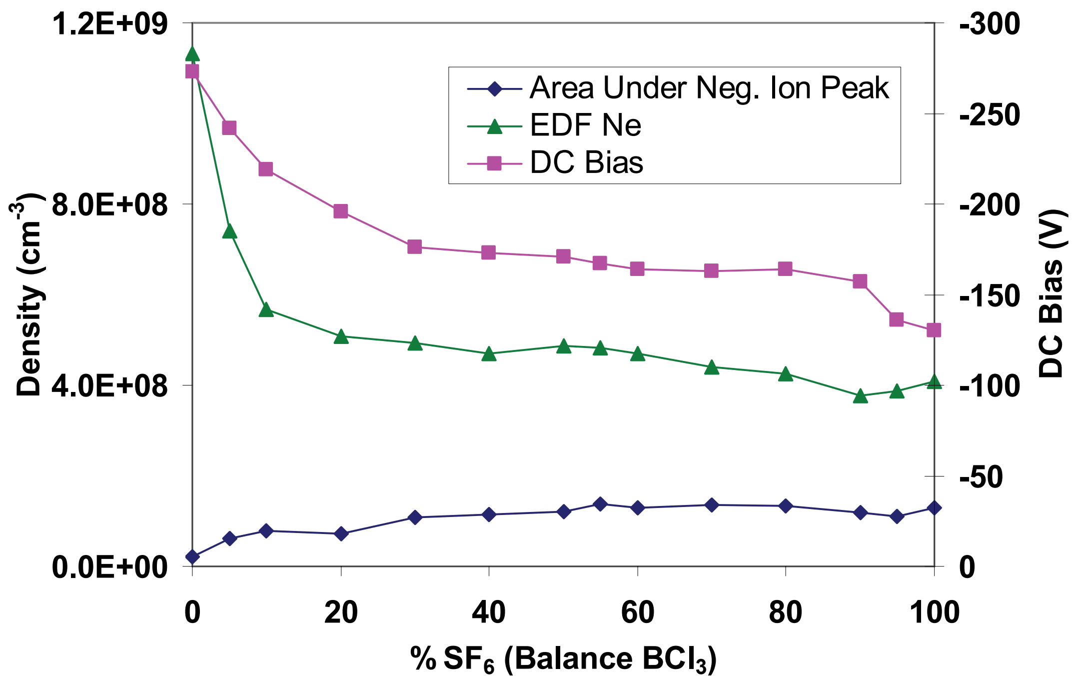


Figure 4-15 Area under the EDF negative ion peak, electron density, and DC bias as a function of composition in SF_6 and BCl_3 plasmas at 50 mTorr and 150 W power.

Figure 4-16 is a comparison of positive ion density measurements, determined from OML theory, the corresponding negative ion density measurements via subtraction of the electron density from OML theory and assuming quasi-neutrality, and comparison to negative ion density measurements using the EDF. Previous sections showed that these methods agree well, and that the assumed predominant ions were most likely correct. Again, there is a 40% error bar on the OML theory due to uncertainty and under prediction.

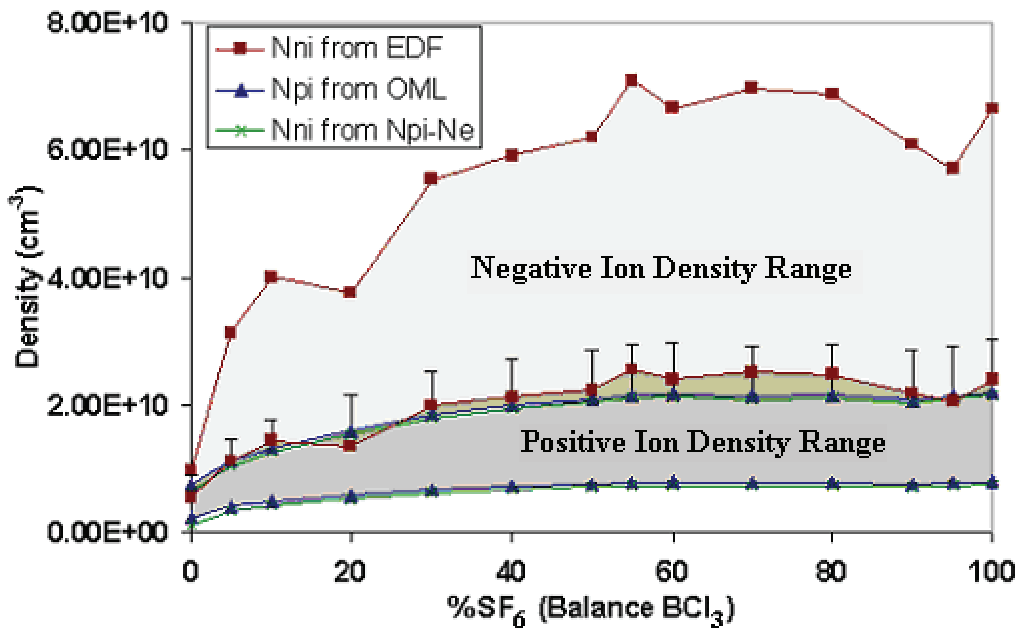


Figure 4-16 Positive and negative ion densities as a function of composition in SF_6 and BCl_3 plasmas at 50 mTorr and 150 W power.

For the mixed chemistries, SF_5^+ and SF_6^- are used as the heaviest ion masses, while F^- and F^+ are used as the lightest. This is not to say that chlorinated species do not exist in the mixed chemistry plasmas, it is precautionary to use the heaviest and lightest possible masses of ions (the chlorinated species would lie within this range).

According to the previous sections in this paper, one may now guide a better approximation of ion densities. From the literature, and due to the good agreement between OML and Amemiya Theory from the experimental results sections, the positive ion mass should most likely be a combination of SF_5^+, SF_3^+, BCl_3^+, and BCl_2^+. These are among the heaviest ion masses possible; therefore the positive ion density is closer to that of the upper bound of Figure 4-16.

Similarly, for a better approximation of negative ion density the literature and experimental results sections points to F^- and Cl^-, which are among the lightest of the possible negative ions. Therefore, the negative ion density is closer to that of the lower bound of Figure 4-16.

Both positive and negative ion density increase as SF_6 is added to BCl_3, and by mass estimation from the literature, both OML and Amemiya Theory agree for estimating negative ion density. The trend of increasing positive ion density means that through electron impact ionization, more parent molecules are being ionized. From the literature, the ionization threshold of SF_6 is higher than that of BCl_3. Therefore, by adding SF_6 to BCl_3, the increase in positive ion density must also be coupled with an increase in the number of superthermal electrons which raise the electron temperature and are responsible for the increase in dissociative ionization reactions [53]. Furthermore, mass spectrometry results at KU PRL for this mixture show an increase in Cl and Cl_2 neutral species as SF_6 is added to BCl_3 up to 70% SF_6.

As mentioned previously, the average electron energy increase is primarily responsible for the increase in etch rate of GaAs as SF_6 is added to BCl_3. This

elevation in electron temperature also increases the number of dissociation and ionization reactions, which was evidenced in QMS results from Y.S. Lee and in this thesis with the increase in positive ion density up to ~55% SF_6. Thus, this increase in electron temperature raises the number of reactive etch species and ion bombardment flux to increase the etch rate of GaAs. Furthermore, the species BClF and BCl_2F are increasing in concentration as (from 0 to 30%) SF_6 is added to BCl_3, which should prevent the recombination of reactive etching species and also contribute to the increase in the etch rate of GaAs. Interestingly, assuming constant electron temperature and density, the addition of SF_6 should lower the GaAs etch rate, since dissociated fluorine from SF_6 should compete with Ga sites, forming non-volatile GaF_3. This should slow down the etch rate as compared to a BCl_3 plasma at the same electron temperature and density. Other factors which would act to decrease the etch rate include the electron density depletion, and the decrease in percent BCl_3 as SF_6 is added. Comparatively, at 100% BCl_3, even though the number of parent gas species available (to potentially dissociate) is at maximum, the electron temperature is too low (~3.2 eV) to create abundant active etch species, Cl^+, Cl_2^+, Cl and Cl_2. In determining etch rates of GaAs, a relatively complex balance of all these factors will determine the overall etch rate trends [23].

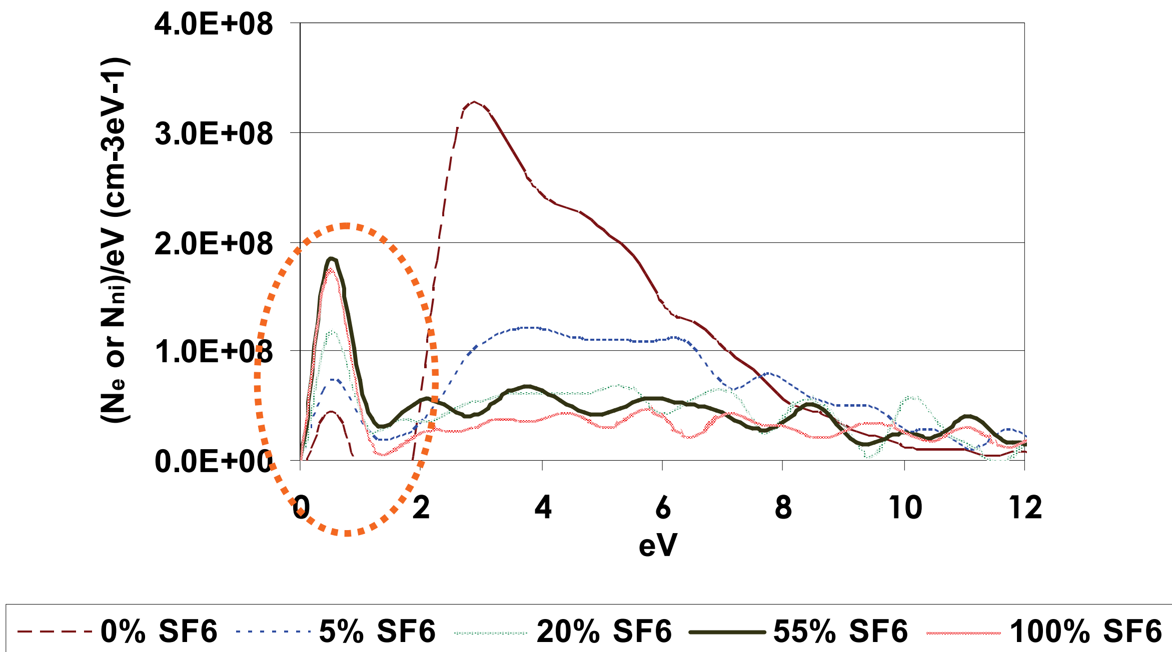


Figure 4-17 Energy Distribution Function in mixed chemistry SF_6 and BCl_3 plasmas at 50 mTorr and 150 W for 0%, 5%, 20%, 55% and 100% SF_6.

The EDFs for this mixed chemistry are now presented to give a clearer picture. Figure 4-17 is a presentation of energy distribution functions from 0 to 12 eV for the mixed chemistry BCl_3/SF_6. At low energies, the EDFs show a peak characteristic of Amemiya's theory associated with negative ions. The area under this peak increases as SF_6 is added to BCl_3 (up to ~55% SF_6) confirming that more negative ions are forming. By reasoning of quasi-neutrality the density of positive ions is also be increasing, thus more reactive ion etching species are be formed. This increase in positive ion density is also confirmed by OML theory. At slightly higher energy levels (above ~1 eV), the EDF is comprised entirely of electrons and the results show a depletion of electrons between 2 and ~8 eV as the plasma composition

of SF_6 increases. Dissociative electron attachment to SF_6 resulting in negative ions F^-, F_2^-, SF_3^-, SF_4^- has been attributed to electrons with energy levels in this region via studies on cross sectional data [43]. Of these negative ions, F^- is the most abundant and is formed via a dissociative electron attachment reaction, $e^- + SF_6 \rightarrow SF_5 + F^-$, with the largest cross section for negative ion formation from SF_6 above 2 eV. Depending on the bond energy calculation, it may also be slightly energetically favored. These dissociative electron attachment reactions are partly responsible for the depletion of electrons in this energy range (~2-8 eV) and increase in electron temperature as SF_6 is added to BCl_3. Parent negative ion formation from electrons near thermal energy (~0.1 eV) is also responsible for the depletion of electrons and increase in electron temperature as SF_6 is added to BCl_3 with the largest cross section for negative ion formation for these near thermal electrons.

The enhancement of GaAs etch rate as SF_6 is added to BCl_3 plasmas is primarily due to the rise in electron temperature (and average electron energy) which increases the dissociation of BCl_3 forming reactive etch species, and increases the ionization of molecules and radicals forming reactive ion etch species. This enhancement in electron temperature is from the attachment and dissociative attachment of electrons (from 0 to ~8 eV) by adding a more electronegative gas, SF_6, to BCl_3.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

This work confirms that the enhancement of GaAs etch rate as SF_6 is added to BCl_3 is primarily due to electron attachment heating. From 0 to 55% SF_6 where the maximum etch rate was found, the electron temperature increases by approximately 1.3 eV (from 3.2 eV to 4.5 eV) and the electron density decreases approximately 2 fold (from $1.1x10^9$ cm^{-3} to $4.8x10^8$ cm^{-3}). The EDFs show a scarce quantity of electrons near thermal energy (~0.1 eV) for the SF_6/BCl_3 plasmas, and as SF_6 is added to BCl_3, a depletion of low energy electrons between 2 and 8 eV occurs. In this study, plasma quasi-neutrality, positive ion density measurements, and negative ion density measurements indicate an overall low mass of negative ions and an overall high mass of positive ions for BCl_3, SF_6, and BCl_3/SF_6 plasmas.

The electrons near thermal energy are easily scavenged by both BCl_3 and SF_6 forming parent transient metastable negative ions; however collisonal stabilization or emission (to release excess energy before detachment) is required for these transient ions to form stable parent negative ions and this may be why these ions are not detected in abundance. As evidenced in the EDFs, both low energy electrons (~2-8 eV) and electrons near thermal energy (~0.1 eV) are responsible for the change in electron temperature and electron density. These respectively correspond to

dissociative electron attachment forming primarily F^- and Cl^-, and attachment forming parent negative ions SF_6^- and BCl_3^-. This means that attachment mechanisms are primarily responsible for both the rapid increase in electron temperature and rapid depletion of electron density (electron attachment heating).

Both dissociation and dissociative electron attachment occur in the 2 to 8 eV energy range, while the threshold for dissociation of BCl_3 and SF_6 occurs at the mid to high side of this energy range. Dissociative electron attachment consumes the electrons, while dissociation scatters the electrons. From the attachment mechanisms depleting electrons, the fewer remaining electrons must sustain the same power dissipation, and hence this increases their average energy. Furthermore, the F radicals that are dissociated from SF_6 react with BCl_2 and BCl radicals to form BClF and BCl_2F which reduces the recombination of Cl and Cl_2, and results in higher concentrations of reactive etch species in the chamber. This reduction in recombination can partially contributes to the increase the etch rate. The increase in etch rate by adding SF_6 to BCl_3 is also evidenced by a continual increase in positive ion density from 0 to ~55% SF_6. This increase is ~160% assuming constant positive ion mass, and ~190% by using the heaviest possible ion mass dependent on composition. The increase in positive ion density and electron temperature corresponds to a higher positive ion flux to the substrate, resulting in an increased etch rate as SF_6 is added to BCl_3. Both parent molecules will be ionized, however BCl_3 has a lower ionization threshold and will be more susceptible to this increase in electron temperature.

5.2 Recommendations

From the knowledge gained from the experiments presented in this study, the following recommendations are made for further understanding BCl_3/SF_6 plasmas for particular use in etching GaAs and other materials.

It has been concluded from these studies that the electron temperature increases due to low energy (0-8 eV) electron attachment mechanisms forming negative ions. However, the number of energetic electrons in the tail of the EDFs is still uncertain. This is due to noise from unfiltered harmonics and the corrosive nature of the electronegative plasmas studied. Since high resolution of the low energy regime of the EDF is required for mathematical calculations of negative ion density and electron temperature, the small span for LOESS polynomial smoothing technique in this work was determined specifically for that region. A multiscale polynomial filter for adaptive smoothing using a Savitzky-Golay filter [87] would probably be a better technique. Efforts are underway at the KU PRL to examine our data using this approach.

As mentioned previously, for accurate positive ion density measurements a mass of the respective ions is required. Since the KU PRL does not have means to directly sample positive ions, the only estimations to this mass was by extensive literature review. Further, direct positive ion sampling studies in RIE and CCP systems at similar conditions would give a better means to estimate the averaged mass of all of the positive ions, which would in turn make density predictions using

Langmuir probe measurements more accurate. Furthermore, the geometric mean of positive ion density from ABR and BRL theories has been shown by F. Chen to be closer to that of microwave density measurements in high density Ar discharges ($\geq 5 \times 10^{11}$ cm^{-3}) [7]. Applying these theories may improve the positive ion density measurements.

Similar issues arise for accurate negative ion density measurements. A study in CCP or RIE systems using laser photodetachment to estimate relative concentrations of negative ion species in BCl_3, SF_6, and BCl_3/SF_6 plasmas will most likely confirm the presence of the predominant negative ions, F^- and Cl^- (The predominance of Cl^- has been confirmed using laser photodetachment in ICP). However, other than F^-, more photodetachment cross sections need to be published for SF_6. This technique could also give better estimations to averaged negative ion mass which would in turn make negative ion density predictions using Langmuir probe measurements more accurate.

Using the techniques described in this work, investigations of different electronegative plasmas may be performed. This will help separate out the different mechanisms associated with each plasma chemistry, and perhaps allow for specific tailoring for desired electron temperature (or number of electrons within certain energy levels) and density of species in the plasma for various gas additives.

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Appendix A

Plasma Physics Review

This section is an excerpt from B. Pathak's thesis [1]. {Any changes are marked by these parentheses.}

Appendix A: Plasma Physics Review

{Plasma is energetically the fourth state of matter. Often viewed as a gas that is ionized, it can also be obtained when sufficient energy is provided to a liquid or solid to cause its vaporization and ionization.} It can be either fully ionized or partially ionized, but it must have a sufficient number of ionized particles (electrons, positive ions, or negative ions) to affect its macroscopic physical, electrical, and perhaps chemical properties. It then becomes conductive, begins to exhibit other electrical and physical properties, and its constituent particles interact collectively to create unique phenomena because of the interaction of the separated charged particles.

If one looks at a plasma in isolation, such as a plasma in outer space, or a volume of bulk plasma that is sufficiently far away from any other state of matter, several properties become clear. First, the sum of the charges of the negative and positive charge carriers is equal to zero when summed over a large volume (i.e., a large number of particles is observed). Second, while the net charge of the volume is zero, the particles inside it are actively attempting to recombine into stable molecular or atomic species via the electro-magnetic forces that are created because of the

charge separation. These forces cause the charge carriers to cease their purely random motion and to accelerate toward (or be repelled by) the electric fields created by the other charge carriers. Third, because of the lack of boundaries of an isolated plasma, charge carriers that enter the plasma replace those that escape it.

Any time a non-plasma object comes in contact with a plasma, the lighter, more quickly moving electrons collide with its surface more frequently than the heavier, positively or negatively charged ions. Because these interactions result in charge transfer, the object quickly acquires a negative charge relative to the plasma. If the object is electrically insulated (or non-grounded) this accumulated charge then repels increasingly energetic electrons until only the few electrons with a kinetic energy above a certain threshold can overcome the object's electric potential barrier. The more massive positive (or negative) ions do not move as quickly even when they are attracted to (or repelled by) the negatively charged object, and so are only termed to "drift" towards (or away from) it. Provided there are enough electrons in the plasma, the negative charge on the surface continues to accumulate, repelling negatively charged particles (ions and electrons) and attracting positively charged ones (ions) until the sum of the electron and negative ion flux is equal to that of the positive ions. The volume of influence of this electric field is termed the Debye sheath or the plasma sheath. (N.B: This is different from the Debye radius, which is the characteristic radius of influence of a charged particle within a plasma.)

{If an electric field is created in the plasma, the charged particles will respond to reduce the effect of the field. The lighter, more mobile, electrons will respond

fastest to reduce the electric field. The response of the charged particles to reduce the effect of the local electric fields is called Debye shielding, and the shielding gives the plasma its quasi-neutrality characteristic [88]. For a good compromise to draw sufficient current while not depleting the plasma near the probe, and keep the OML estimates of ion density reliable, the target probe radius should be approximately twice that of the debye radius [11].}

V_p (the plasma potential) is physically the average electric potential that exists on a scale smaller than that of the Debye radius (wavelength or length—λD) between the individual charged particles within a plasma. In this context, however, it also corresponds to the voltage at which the probe is at the same potential as the plasma. At this probe bias voltage, all the charge carriers (mostly electrons) that cross the probe tip's boundary—high and low energy alike—are captured by the probe. Because the probe must have a path to ground to achieve this voltage, the accumulated negative charge these carriers transfer to the probe drains off the probe to ground through the voltage source. This is equivalent to having a positive current being emitted by the probe.

Despite the quasi-neutrality of bulk plasmas, the small reduction of negatively charged particles (mostly electrons) around the edges of the plasma generates a positive V_p throughout the plasma. The typical capacitively coupled plasma (CCP) RIE chamber geometry and the circuit used to generate the plasma allows these electrons to escape in larger numbers than in other plasma systems. The typical CCP chamber, like the PlasmaTherm 790 used in the KU PRL, is composed of an

electrically grounded chamber housing and a powered electrode that is DC isolated from the chamber RF power source by a capacitor and is physically isolated from the chamber housing. A high power RF signal is sent through the electrode and induces an oscillating electric field between the electrode and the chamber housing. The few free electrons that are normally present in any gas respond to this oscillation by accelerating toward and away from the electrode. When these electrons inevitably collide with parent molecules in the source gas they sometimes knock other electrons out of the outermost molecular or atomic orbits ionizing the gas. The original and new free electrons continue to be affected by the electric field and an avalanche of ionization begins. A portion of this cloud of free electrons then collides with both the chamber housing and the electrode. The electrons that collide with the housing drain off because the chamber is grounded, while the electrons that collide with the electrode are trapped by the DC blocking capacitor and build up a negative charge. Since the only sources of electrons in the system are the outermost orbits of the parent molecules, the plasma becomes positively charged and thus V_p is noticeably positive. This phenomenon also explains why the electrode becomes negatively charged leading to a negative DC bias voltage with respect to ground. This DC bias attracts positive ions across the sheath and these ions bombard the substrate, reacting and consequently etching it.

One can quickly infer that if the difference between V_p and the electrodes changes, the sheath will have to change to compensate. This change can take on many forms but if the potential difference is large enough it generally changes the

dimension of the sheath. (Although the term sheath height, radius, or length is often used informally depending on the inducing electrode's geometry.) If the difference in potential is small, the compensation does not affect the sheath dimension, and instead the sheath itself adjusts internally. This adjustment forms the basis for Langmuir probe theory. However, because each plasma is a unique mixture of negative ions, positive ions, and electrons it will react similarly but not identically to minute perturbations, leading to the wide ranging experiments using Langmuir probe studies.

Appendix B

Electron-Molecule Interactions

The following section is an excerpt from Fundamental Electron Interactions with Plasma Processing Gases by Christophorou and Olthoff [43]. Modifications were performed for clarity and relevance to this thesis. {Any changes are marked by these parentheses.}

B.1 Electron-Molecule Interactions

There is a unique richness in the variety of reactions which occur when a low-energy {see below} electron encounters a molecule. The encounters themselves may be conveniently separated into two types: *direct* and *indirect*. By *direct* we mean nonresonant collisions occurring over a wide range of electron energies where the electron is scattered at a distance from the molecule and the electron-molecule collision time is very short ($\sim 10^{-16}$ s). By indirect collisions we mean resonant collisions, which occur only over limited energy rangeds when the electron energy is low and the duration of the collision is long—comparable to or longer than the time taken by the bound electrons of the target molecule to complete their orbits. In such intimate collisions, the electron enters the empty orbitals of the target molecule and is temporarily retained (captures) by the molecule forming characteristic resonances, the so-called negative ion resonances. Both types of collisions are discussed below.

{By low energy, Christopohoru and Olthoff mention “mostly less than 100eV”, and that this, “relatively low electron energy”, satisfies the majority of these collisions. The population of electrons in the PlasmaTherm 790 RIE is generally less than 20 eV, and the populations of electrons exceeding 20 eV are low [1].}

Interactions of low-energy electrons with Ground-State Molecules

As mentioned in the preceding paragraph, the collisions of low-energy electrons with atoms and molecules are of two types: *direct* and *indirect*. The principal *direct* elastic and inelastic electron scattering processes are:

$$e(\varepsilon) + AX \rightarrow AX + e(\varepsilon) \qquad \text{\{B-1\}}$$

(Direct elastic electron scattering)

$$\Rightarrow AX^{*} + e(\varepsilon') \qquad \text{\{B-2\}}$$

(Direct inelastic electron scattering)

$$\Rightarrow A + X + e(\varepsilon') \qquad \text{\{B-3\}}$$

(Dissociation into neutrals)

$$\Rightarrow A + X^{*} + e(\varepsilon') \qquad \text{\{B-4\}}$$

(Dissociative excitation)

$$\rightarrow AX^{+} + 2e \qquad \text{\{B-5\}}$$

(Molecular ionization)

$$\Rightarrow A + X^{+} + 2e \qquad \text{\{B-6\}}$$

(Dissociative ionization)

$$\Rightarrow A^{(*)} + X^{+} + 2e \qquad \{B\text{-}7\}$$

(Dissociative ionization with fragment excitation)

$$\rightarrow A^{+} + X^{-} + e\left(\varepsilon^{'}\right) \qquad \{B\text{-}8\}$$

(Ion-pair formation)

In the above reactions, e(ε) and e($\varepsilon^{/}$) represent, respectively, the incident electron with energy ε and the scattered electron with energy $\varepsilon^{/}$. The notation AX, AX^*, and AX^+ represents, respectively, ground-state, excited, and ionized molecules. Similarly, the notation A and X, X^*, X^+ and A^+, and X^- represents, respectively, ground-state fragments, excited fragments, positive ion fragments, and stable negative ion fragments. The asterisk denotes an excited species and the double arrow indicates multiple reaction pathways, which occur abundantly for polyatomic molecules. Reactions {B-5 to B-7} can also lead to multiple ionization of AX or X, generating multiply charged positive ions AX^{n+} or $X^{n+}(n \geq 2)$.

{Christophorou and Olthoff state, "The products of each such reactions are studied as a function of the incident electron energy ε, and at times also as a function of the scattering angle (θ). The probability of the various processes represented by the reaction channels {B-1 through B-8} in an electron-molecule collision is described by the corresponding cross section, σ(ε), for that reaction. The cross sections for each direct electron collision channels extend over a range of incident electron energies which depends on the plasma reaction process." Excluding elastic electron scattering (Equation B-1), "the cross section for each of the other processes has an energy

threshold which depends on the physical process itself.” Direct vibrational excitation is usually much lower than that of molecular dissociation and ionization, “while the cross section for elastic electron scattering is over a wide range of electron energies.”}

In contrast with the direct electron collision processes just discussed for which the corss sections are substantial over a wide range of electron energies, in the low-ernergy region (usually ≤ 20 eV), electrons can be selectively captured by the molecule AX to form transient (metastable) negative ions AX^{-*} {vibrationally excited, but in the ground electronic state}. These indirect, capturing collisions are resonant, and they occur over a narrow range of electron energies which are characteristic of the target molecule. The transient negative ions live for approximately 10^{-15} to 10^{-2} s. They decay by auto detachment leaving the neutral molecule AX with or without excess internal energy, or via the processes of dissociative electron attachment. They can also form a stable parent negative ion AX^{-} if the molecule AX has a positive electron affinity and the excess energy in AX^{-*} is removed. These indirect electron-collision processes can be represented as

$$e(\varepsilon) + AX \rightarrow AX^{-*} \rightarrow AX + e(\varepsilon) \qquad \{B\text{-}9\}$$

(Indirect elastic electron scattering)

$$\Rightarrow AX^{*} + e(\varepsilon') \qquad \{B\text{-}10\}$$

(Indirect inelastic electron scattering)

$$\Rightarrow A + X^{-} \qquad \{B\text{-}11\}$$

(Dissociative electron attachment)

$$\rightarrow AX^{-} + energy \qquad \{B\text{-}12\}$$

(Parent negative ion formation)

Resonance nondissociative electron attachment processes leading to the formation of AX^- {Equation B-12} occur over a narrow electron energy range that is less than a few eV. In fact, most known cases of parent negative-ion formation by electron impact in the field of the molecular ground state, the parent negative ions AX^- have a maximum probability of formation at ~0.0 eV (e.g, see the cross section for the formation of SF_6^- in Fig. {not shown, but it is a close-up of 0.0001 to 1 eV of Figure 2-8 of this thesis} of Ch. {2}). {Similarly, Tav et al. have attributed the rise in cross section below ~0.1 eV to the formation of BCl_3^- [50].} To form AX^-, the adiabatic EA(AX) {electron affinity of AX} must be positive and the transient negative ion must be stabilized. On the other hand, resonance dissociative electron attachment processes {Equation B-11} leading to X^- occur over a wider energy range (0 to ~20 eV) and do not require stabilization (the dissociation products take away the excess energy of AX^{-*}).

To further explain dissociative electron attachment reactions, the following section is included from Graupner and Field [89].

B.2 Dissociative Electron Attachment

In low temperature technological plasmas, the majority of free electrons have kinetic energies below the ionization thresholds of gas molecules present. These electrons can excite the gas molecules rotationally, vibrationally, and electronically, which may lead to molecular dissociation. Low energy electrons can also attach to gas phase molecules to form 'Temporary Negative Ions', which are unstable with respect to loss of the electron. Temporary negative ions formed may dissociate to give neutral and negatively charge fragments; this process, dissociative electron attachment, can be represented for a general molecule AB by

$$AB + e^- \rightarrow AB^{-*} \rightarrow A + B^- \qquad \{B\text{-}13\}$$

where AB^{-*} is the temporary negative ion. Temporary negative ions are generally formed at quite specific electron energies because the energy of the electron must be equal to the difference in energy between the initial state of the neutral molecule and the temporary negative ion state.

The following section is an excerpt from Tybislawski et al. and will clarify the role of temporary (transient) negative ions [90].

B.3 Temporary (Transient) Negative Ions

The collisionally induced generation of negative ions from gas-phase molecules was up to now extensively investigated with electrons as projectiles. Here,

several processes may occur, depending on the electron energy and the properties of the encountered molecule. If the electron energy is low (less than about 10 eV), a negative ion can only be produced via resonant electron capture associated with the formation of a temporary negative ion. The question whether the parent ion or stable negatively charge fragments of it are observed within a particular observation time depends on the decay rates of the competing reaction channels, including also the reemission of the captured electron. Attachment of free electrons leads in principle to a transient parent ion that is unstable towards the emission of the extra electron. If the electron energy is high enough (usually above 10 eV) the process of ion-pair formation becomes an alternative mechanism of negative (fragment) ion production, additionally creating a positive partner fragment wile the electron is, just like a catalyst, not used up in the process, therefore being capable to initiate further reactions after the collision. With increasing electron energy this non-resonant process becomes the dominant mechanism of negative ion production.

Appendix C

Reactive Ion Etching Theory

The following two sections are excerpts from J. Sia's thesis and Y.-S. Lee's thesis, respectively [5, 91]. Additional contribution in the first section was given from A. Agarwal, V. Berry, and R. Alapati.

C.1 Reactive Ion Etching Theory and Sheath Formation

Plasmas are conductive assemblies of charged particles and neutrals. The motion of the charged constituents of the plasma causes local electric fields and currents that generate magnetic fields. These fields in turn affect the motion of the charged particles themselves. The combined effect is dependent on plasma composition [83].

In the plasma chamber, the electrons move in response to the RF (13.56 MHz) voltage applied between the electrodes, which enhance their probability of having collisions. Because of the small size and small mass of the electrons, they have a high diffusivity and hence tend to move more swiftly than the other particles. As a result, the electrons are attracted towards the walls and the RF powered electrode. The RF powered electrode is coupled to ground through a capacitor, which does not allow the electrons to escape and a negative charge accumulates, resulting in a negative DC bias. This bias is developed almost immediately as the plasma is turned on. The walls of the chamber on the other hand, are grounded and allow the electrons to drain away so, no charge builds up on the walls. The negative DC bias on the RF powered

electrode repels the electrons and attracts the positive ions creating a small dark layer above it, which is depleted of charged particles. This layer is called the sheath layer. The potential difference across the sheath layer gives direction to the positive ions bombarding the substrate.

In reactive ion etching, there are essentially two mechanisms that are responsible for the etching process. One is purely chemical and the other involves physical bombardment of the surface by reactive ions. Sputtering (physical removal of chemical material by chemically unreactive species) also plays a minor role. The plasma produces highly reactive neutrals, which diffuse though the plasma and reach the substrate and chemically react with the surface to produce volatile products. These volatile products then diffuse back to the plasma and are pumped away from the system. The other mechanism involves positive reactive ions which are accelerated towards the substrate and interact with the surface both chemically and physically to remove material. At high DC bias, this mechanism produces highly anisotropic etches. The combination of chemical and physical etching results in a much better etch rate and etch profile than either mechanism on its own.

C.2 Potentials and DC Bias

Since the more massive ions have too much inertia to respond to instantaneous changes in the electric field (unlike the electrons), the plasma potential (V_p) with respect to the potential of either the powered (V_c) or the grounded electrode remains positive for the entire duration of the discharge. At RF frequencies, the sheath

essentially behaves like a capacitor, charging and discharging as the direction of the voltage changes periodically. The current density of positive ions across the sheath is uniform and is equal at both electrodes. The ratio of the area of the rf powered electrode to the area of all grounded surfaces in contact with the plasma is a key parameter in determining how the applied voltage is distributed among the plasma sheaths. The dc potential difference (V_p-V_c) increases as the ratio of the area between the rf and the grounded electrode decreases. A classic theory of plasma characteristics from Koenig and Maissel can be expressed as [92]:

$$\frac{V_p - V_c}{V_p} = \left(\frac{A_a}{A_c}\right)^4 \qquad \{C\text{-}1\}$$

where A_a and A_c are the grounded surface and the rf powered electrode areas, respectively. The sheath voltage near the smaller electrode is always larger than that near the larger electrode. Since the grounded electrode is typically connected to the reactor walls, it will create a time-averaged negative DC bias on the lower powered electrode. The difference between the plasma potential and the negative DC bias on the powered electrode determines the energy of ions bombarding the substrate surface.

Appendix D

Langmuir Probe Theory

With the exception of Appendix D.2, the following sections are excerpts from B. Pathak's Thesis [1]. Appendix D.2 is an excerpt from Lecture Notes on Principles of Plasma Processing by F. Chen and J. Chang [12]. {Any changes are marked by these parentheses.}

D.1 Ideal Langmuir Probe Behavior in a DC Plasma, Single Species

While Langmuir's original work and several other more recent monographs and articles [77, 83, 93-96] admirably explain the basic principles of electrostatic probes, a brief visualization of an ideal probe characteristic may help guide the reader.

The probe current comprises two competing currents—the positive charge carrier current (positive ion current, I_+) and the negative charge carrier current. In plasmas that ionize predominantly into positive ions and electrons, called electropositive plasmas, the negative charge carrier current is the electron current (I_e). In plasmas that have a sufficient number of negative ions so as to influence the plasma, termed electronegative plasmas, the negative charge carrier current is the sum of I_e and the negative ion current (I-). In this example, I- is taken to be zero. If one does not attempt to take sheath expansion into account, and if the thermal energy of the electrons is much greater than the thermal energy of the positive ions ($kT_e >> kT_+$), which is typically true,

$$I_+\left(V_b\right)=\begin{cases} I_{+sat}\exp\left(\frac{q_e\left(V_p-V_b\right)}{kT_+}\right) & \text{when } V_b \ge V_p \\ I_{+sat} & \text{when } V_b < V_p \end{cases} \qquad \{D\text{-}1\}$$

where $I_{+sat}=0.6\cdot q_e\cdot N_+\cdot A_{probe}\cdot\sqrt{\frac{kT_e}{m_+}}$, the Bohm Current, and

$$I_e\left(V_b\right)=\begin{cases} I_{esat}\exp\left(\frac{q_e\left(V_b-V_p\right)}{kT_e}\right) & \text{when } V_b \le V_p \\ I_{esat} & \text{when } V_b > V_p \end{cases} \qquad \{D\text{-}2\}$$

where $I_{esat}=\frac{1}{4}q_e\cdot N_e\cdot A_{probe}\cdot\sqrt{\frac{8kT_e}{\pi\cdot m_e}}$, the random electron current. This results in the type of curve seen in Figure {D-1}. This oversimplifies the probe characteristic because the electric potential sheaths do not expand as they must in order to retard the positive ions and electrons in the regions slightly above and below V_p, nor do they continue expanding as the bias spreads away from V_p. Still, the transition region from V_f to V_p is similar to what one would expect in a well-behaved DC plasma with no collisions in the sheath (such as the plasmas found in fusion Q-machines) and the knee that one sees at V_p is one of the first indicators of a “good” I-V characteristic.

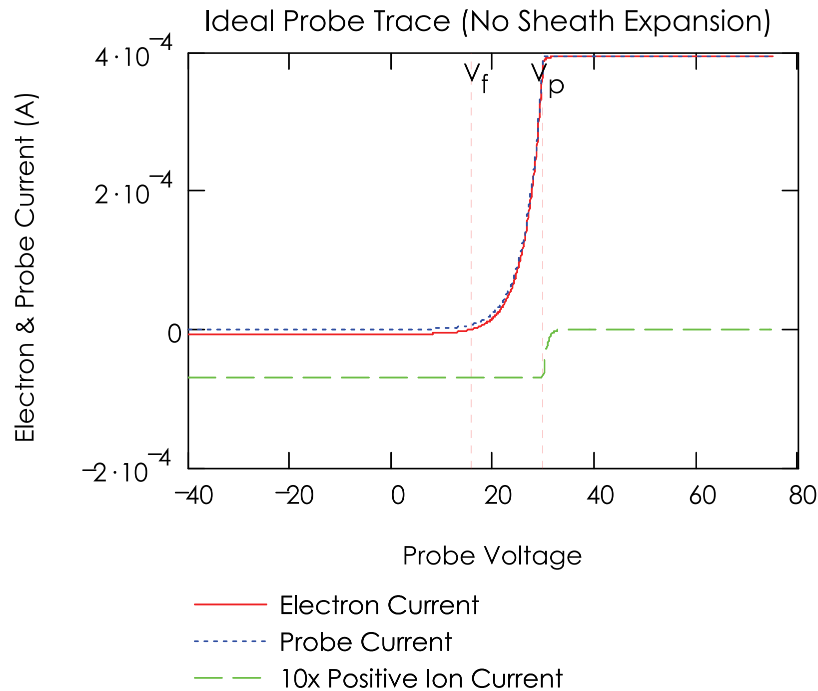


Figure {D-1} Ideal probe trace with V_f and V_p labeled. The positive ion mass is taken to be that of helium [1].

Such clean curves were indeed found by Langmuir, Druyvesteyn, Chen and others working in the realm of fully ionized plasmas, validating the original Langmuir probe theory. Unfortunately, to quote Francis Chen (a well respected electrostatic probe researcher) after he presented several examples of Q-machine I-V characteristics: “Such nice exponentials were never seen again!” This is emblematic of the realities of today’s plasmas, which are inevitably time varying and usually collisional.

D.2 OML Theory

As the negative bias on a probe is increased to draw I_i (positive ion current), the sheath on the cylindrical and spherical probes expands, and I_i does not saturate. Fortunately, the sheath fields fall off rapidly away from the probe so that exact solutions for $I_i(V_p)$ can be found. We consider cylindrical probes here because spherical ones are impractical to make, though the theory for them converges better. The simplest theory is the orbital-motion-limited (OML) theory of Langmuir.

Consider the ions coming to the attracting probe from infinity in one direction with velocity v_0 and various impact parameters *p*. The plasma potential *V* is 0 at ∞ and is negative everywhere, varying gently toward the negative probe potential V_p. Conservation of energy and angular momentum give

$$\begin{aligned} \tfrac{1}{2} m v_0^2 &= \tfrac{1}{2} m v_a^2 + eV_a \equiv -eV_0 \\ p v_0 &= a v_a \end{aligned} \qquad \text{\{D-3\}}$$

where eV < 0 and *a* is the distance of closest approach to the probe of radius R_p. Solving, we obtain

$$\begin{aligned} \tfrac{1}{2} m v_a^2 &= \tfrac{1}{2} m v_0^2 \left(1 + \frac{V_a}{V_0}\right) \\ p &= a\frac{v_a}{v_0} = a\left(1 + \frac{V_a}{V_0}\right)^{1/2} \end{aligned} \qquad \text{\{D-4\}}$$

If $a \leq R_p$, the ion is collected; thus, the *effective* probe radius is $p(R_p)$. For mononenergetic particles, the flux to a probe of length L is therefore

$$\Gamma = 2\pi R_p L \left(1 + {}^{V_a}\!/\!_{V_0}\right)^{1/2} \Gamma_r \qquad \text{\{D-5\}}$$

where Γ_r is the random flux of ions of that energy. Langmuir then extended this result to energy distributions which were Maxwellian at some large distance r = s from the probe, where *s* is the "sheath edge". The random flux Γ_r is then given by the usual formula

$$\Gamma_r = n\left(\frac{KT_i}{2\pi M}\right)^{1/2} \qquad \text{\{D-6\}}$$

with A_p defined as the probe area, integrating over all velocities yields the cumbersome expression

$$\Gamma = A_p \Gamma_r \left\{ \frac{s}{a} erf\left(\Phi^{1/2}\right) + e^{\chi}\left[1 - erf\,(\chi + \Phi)^{1/2}\right]\right\}, \qquad \text{\{D-7\}}$$

where $\chi \equiv -eV_p / KT_i, \Phi, \quad \Phi \equiv \left(\frac{a^2}{s^2 - a^2}\right)\chi, \quad a = R_p$

Fortunately, there are small factors. In the limit s >> a, when OML theory applies, if at all, we have $\Phi \ll \chi$, and for $T_i \rightarrow 0$, $1/\chi \ll 1$. Expanding in Taylor series, we find that the Ti dependences of χ and Γ_r cancel, and a finite limiting values of the OML current exists, independently of the value of T_i,

$$I \xrightarrow[T_i \rightarrow 0]{} A_p n e \frac{\sqrt{2}}{\pi}\left(\frac{eV_p}{M}\right)^{1/2} \qquad \text{\{D-8\}}$$

Thus, the OML current is proportional to $|V_p|^{1/2}$, and the I-V curve is a parabola, while the I^2-V curve is a straight line. This scaling is the result of conservation of energy and angular momentum. Because ions have large angular momentum at large distances, though they have small velocities, they tend to orbit the probe and miss it. The probe voltage draws them in. The value of T_i cancels out mathematically, but T_i has to be finite for this physical mechanism to work.

The OML result, though simple, is very restricted in applicability. Since the sheath radius s was taken to be infinite, the density has to be so low that the sheath is much larger than the probe. The potential variation V(r) has to be gentle enough that there does not exist an "absorption radius" inside of which the E-field is so strong that no ions can escape being collected. Except in very tenuous plasmas, a well developed sheath and an absorption radius exist, and OML theory is inapplicable. Nonetheless, the I^2-V dependence of I_{sat} is often observed and is mistakenly taken as evidence of orbital motion.

D.3 Electron Energy Distribution Function (EEDF)

Like any statistically characterized system, the free electrons in a CCP plasma are not all at the same energy. While the main force that initiates the electrons' motion is the RF oscillation, a myriad of forces including collisions with other species in the plasma influences each electron and therefore the electrons take on a variety of speeds and corresponding energy levels. The resulting distributions give insight into the kinetics of the plasma, the reactions that occur, and how the driving electrical

forces are converted to particle motion. Because this thesis focuses on the average electron energy, it will focus on the electron energy distribution function (EEDF) and not work with the electron velocity distribution function (EVDF) which can be derived from the EEDF.

An accurate EEDF is the definitive way to measure both the average electron energy and electron density of a plasma as described in Equations {D-9} and {D-10}.

$$N_e = \int_0^\infty EEDF(\varepsilon)\, d\varepsilon \qquad \{D\text{-}9\}$$

$$\langle \varepsilon \rangle = \bar{\varepsilon} = \frac{\int_0^\infty \varepsilon \cdot EEDF(\varepsilon)\, d\varepsilon}{\int_0^\infty EEDF(\varepsilon)\, d\varepsilon} \qquad \{D\text{-}10\}$$

where $\varepsilon = V_p - V_b$. Experimentally observed distributions vary tremendously and can be of any shape. For example, a nitrogen plasma EEDF has been observed to have a "hole" between 2 and 4 eV for certain pressures and powers in the GEC Reference Cell because the N≡N bond resonates at that energy [11, 97]. While initially suggested by Langmuir, Druyvesteyn [77] demonstrated that the second derivative of the electron current in the transition region of a Langmuir probe sweep was proportional to what is termed the electron energy probability function (EEPF) through the Druyvesteyn formula

$$EEPF(\varepsilon) = \frac{2\sqrt{2 \cdot m_e}}{q_e^3 \cdot A_p} \cdot \frac{d^2 I_e(\varepsilon)}{d\varepsilon^2} \qquad \{D\text{-}11\}$$

where m_e is the mass of an electron, q_e is the elementary charge, A_p is the area of the probe tip, and $\frac{d^2 I_e(\varepsilon)}{d\varepsilon^2}$ is the second derivative of the probe electron current in units of A/V^2. Further, he showed that the EEPF was related to the EEDF by the relation in Equation {D-12}:

$$EEDF(\varepsilon) = \sqrt{\varepsilon} \cdot EEPF(\varepsilon) \qquad \text{\{D-12\}}$$

Druyvesteyn's work provided the bridge between the probe characteristic and the EEDF for any non-concave (typically planar, cylindrical, or spherical) probe tip geometry. As a side note, the term EEPF can be a bit confusing and the reader should be aware that the EEPF is not a true probability distribution because its integral is not equal to one.

While the EEDF is a highly effective method for finding the average electron energy and electron density, it suffers from a number of drawbacks. First, because ε relies on knowing V_p, it can easily be skewed. Second, the EEPF relies on the second derivative of the electron current and taking the second derivative magnifies the noise in the transition region which already has a low signal to noise ratio because of the inherent thermal and RF noise and a signal that peaks at values on the order of 0.5-1.5 mA. Third, because $I_e(\varepsilon)$ is the electron current and not the raw probe characteristic, a correction for the positive ion current must be made to obtain accurate values of the EEDF at higher energy values. Nonetheless, even an approximate EEDF provides insights that cannot be gleaned from the other methods that will be described that avoid some of the EEDFs pitfalls.

D.4 Practical Considerations in a RF Driven Processing Plasma

Langmuir originally developed electrostatic probes in inert DC discharges or glows (i.e., with a steady electric field inducing the plasma, and in Ar, H_2, or He) [96]. Because of the static nature of those plasma sources, the electric potential of the plasma, the driving electrode, and the direction of electron flow did not vary with time. This allowed the difference between the plasma potential and the probe bias voltage to remain constant for each point on the characteristic curve. Further, because the gases were inert and non-reactive, there was relatively little chemical interaction between the plasma and the probe tip. (Although the reader should note that this does not mean that the two did not interact at all.) In modern processing plasmas, however, the plasma source is rarely static and the gases are always reactive—less so with the probe tip than with the substrate, but they still react. Specifically, the KU PRL PlasmaTherm 790 RIE receives power from a 13.56 MHz RF generator that connects to the biased electrode via two coaxial cables. These realities ensure that the plasma oscillates at 13.56 MHz, introduce the possibility of a non-sinusoidal driving function, and guarantee that the plasma species will quickly affect the electrical characteristics of the probe tip.

D.5 Time Varying, RF Plasma Source

If one simply ignored the existence of the RF oscillations and used a non-compensated probe to measure the I-V characteristic in an RF plasma, the RF interference would effectively obscure the target measurements. To quote Paranjpe et

al. [84], “Numerous papers have demonstrated the perturbing effects of [RF] interference on the single probe characteristic.” This comment rings true because even the simplest Helium and Argon plasmas do not behave nearly as well when they are created with an RF source because of the dynamic electric fields to which the plasma species are subjected. Unlike the Q-machine or other DC plasmas where the electric field used to ionize the parent gases is constant, the RF sources in a CCP accelerate electrons back and forth between the electrodes (or more accurately their accelerating sheaths) until the electrons collide with some particle—more than likely a parent molecule—dissociating, ionizing, exciting, or attaching to it. Meanwhile, the ions formed react to the changing field much more slowly, and are largely unaffected by the rapid changes in the electric field. Unfortunately, this still means that the electric potential between the DC probe bias and the plasma is rapidly changing in the all-important transition region. Even if one relies on the “average” DC value that the ammeter provides, because of the non-linearity of the I-V curve, the knee will effectively be obscured and the transition region deformed as seen in Figure {D-2}.

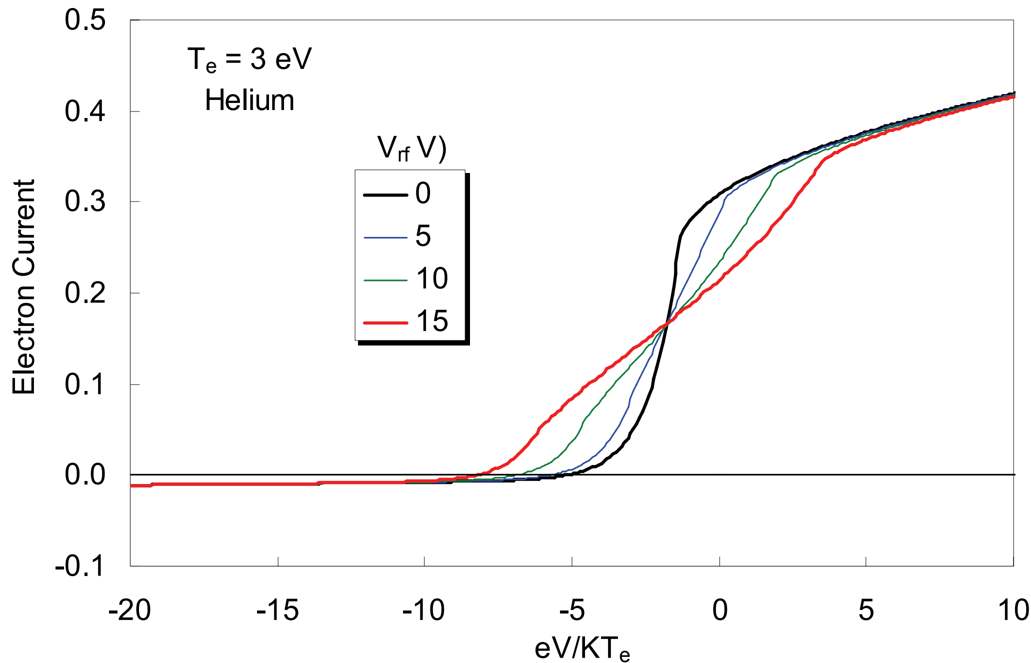


Figure {D-2} Illustration of various levels of RF distortion of the electron current [1, 12].

Unless one uses an extremely fast volt/current meter to attempt to capture the time resolved data, the probe must either suppress or mimic and ride the RF signal used to create the plasma. While each of these options have their own disadvantages ranging from an unknown response of sheath potential drop to a strongly nonlinear current response, various researchers have tried them all, and Annaratone et al, even compared the passive and active probe methods [98]. This remains an active area of research with recently issued patents [99]. Because of the nascent nature of Langmuir probe research in the KU PRL, we opted for the simplest method of the three—suppression and filtering. With this scheme it does not matter if the driving signal is non-sinusoidal or out of phase with the source. We focused on designs used by both Chen and Hopkins to passively filter the RF from the plasma signal [11, 100, 101].

D.6 Negative Ions and Charged Metastables in Electronegative Plasmas

Most {previously studied} plasmas are electropositive. This means that the ionized components of the plasma consist of electrons and positive ions. Historically, Langmuir probe theory assumed this, and only upon further investigation were negative ions included in the analysis. Further, if a plasma contains enough negative ions that they need to be taken into account because they affect the plasma's behavior, the plasma is termed electronegative. Unfortunately, the first attempts to fit a theory that would characterize these plasmas contained a mathematical inconsistency that propagated throughout the field through textbooks despite being corrected in an earlier journal article [102, 103].

Fortunately, H. Amemiya experimentally observed the Langmuir probe response to an electronegative plasma and identified both the current and features of the second derivative the negative ions and metastable negative species induce [13, 44]. Since our experiments use BCl_3 as a primary parent gas, and it results in an electronegative plasma, these particular features become extremely relevant when observing our Langmuir probe results. Figure {D-3} shows both the ideal and actual cases for negative ion current and its second derivative (i_-'' in the figure, I-" in this thesis). The local minimum seen in the actual second derivative results from a reconfiguration of the sheath around the Langmuir probe. It is the point at which the slow negative ions reach a critical ratio with the remaining fast electrons in the sheath

and change the response of the sheath from one dominated by electrons to one dominated by negative ions. This reconfiguration of the sheath momentarily slows down the increase in negative charge carrier current and creates the local minimum in the second derivative preceding the negative ion peak.

Amemiya also discusses the matter of negatively charged metastable species. Citing Wiesemann [104], he warns that these species result in a secondary electron emission spike similar to $-i_+''$ in Figure {D-3} just above V_p. When these metastables collide with the probe, they relax back to a lower energy state releasing energy in the form of electrons. These electrons are then rapidly recaptured by the probe, resulting in a spike in the second derivative. Amemiya also notes that this spike should be discriminated from the spike caused by negative ions that should appear just below V_p.

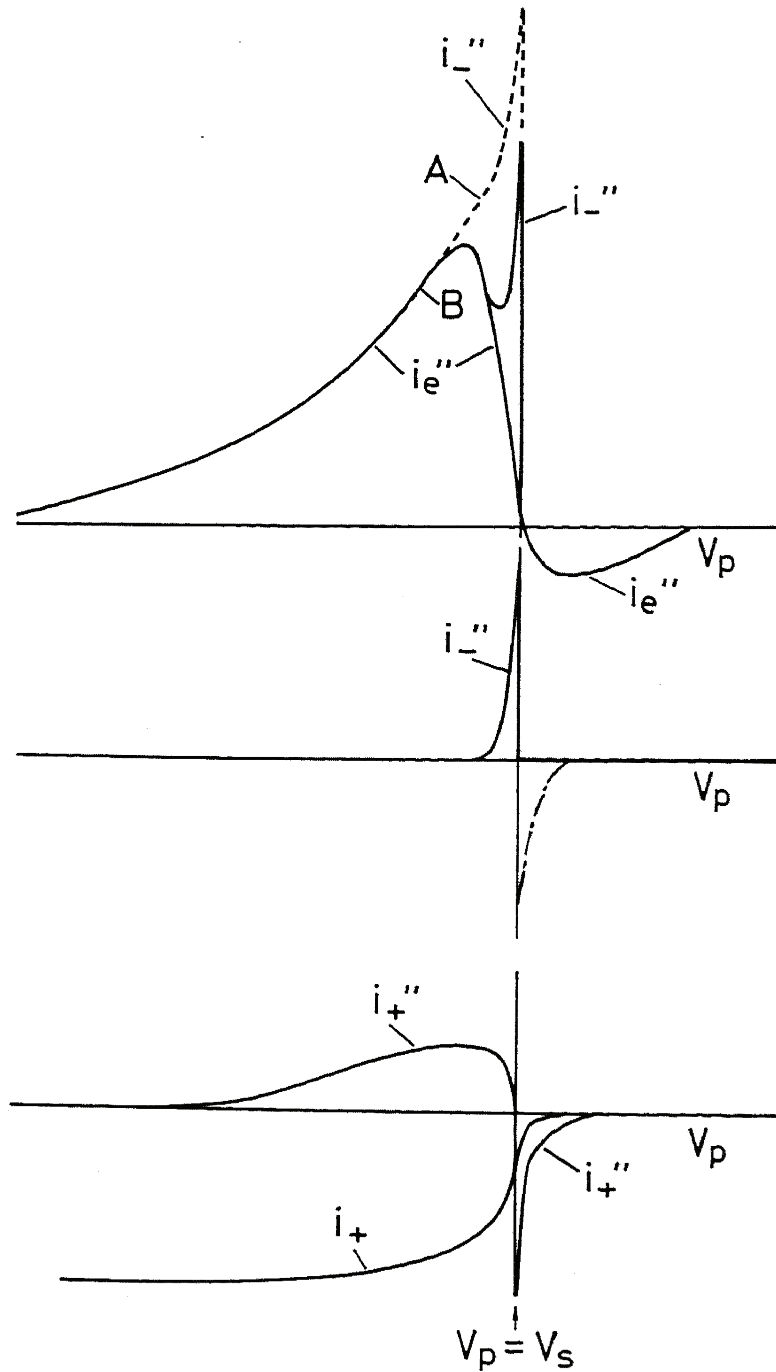


Figure {D-3} Schematic drawings of the positive ion current (i_+) and the second derivative of the electron, negative ion, and positive ion currents (i_e", i_-", i_+"). Dotted curve: ideal case; solid line: actual observation [13].

Appendix E

Experimental Apparatus

Section E.1 is an excerpt from J. Sia's thesis [91]. Section E.2 is an excerpt from B. Pathak's thesis [1].

E.1 Reactive Ion Etching Apparatus

The reactive ion etching system used to generate the plasma and etch samples was a Plasma Therm 790 series parallel plate system. A schematic of the equipment is shown in Figure E.1. The system generates the plasma at the standard frequency of 13.56 MHz and has the capability to control RF power, DC bias, flow rate of inlet gases, and pressure.

The chamber is 15" in diameter and 10" in height. The diameter of the RF powered electrode is 10". The system is comprised of parallel plate capacitively coupled electrodes separated by 3 inches. Samples as large as 8" can be loaded into the system manually by lifting the chamber lid. The lower electrode in the system, where the sample is placed, is powered and the chamber walls are grounded. The chamber is equipped with three Pyrex glass view ports to facilitate visual inspection of the plasma and can be used for plasma diagnostic tools. The gases enter the system from a showerhead in the chamber lid and are evacuated around the circumference of the powered electrode.

The lower RF powered electrode is temperature controlled by a water circulator system (Neslab RTE 111). The base pressure inside the system is

maintained at 10^{-6} Torr to avoid any contamination from the atmosphere. This low pressure is maintained by pumping the chamber through a 150 l/s Leybold turbo-molecular pump backed by a 32 cfm Leybold rotary vane mechanical pump.

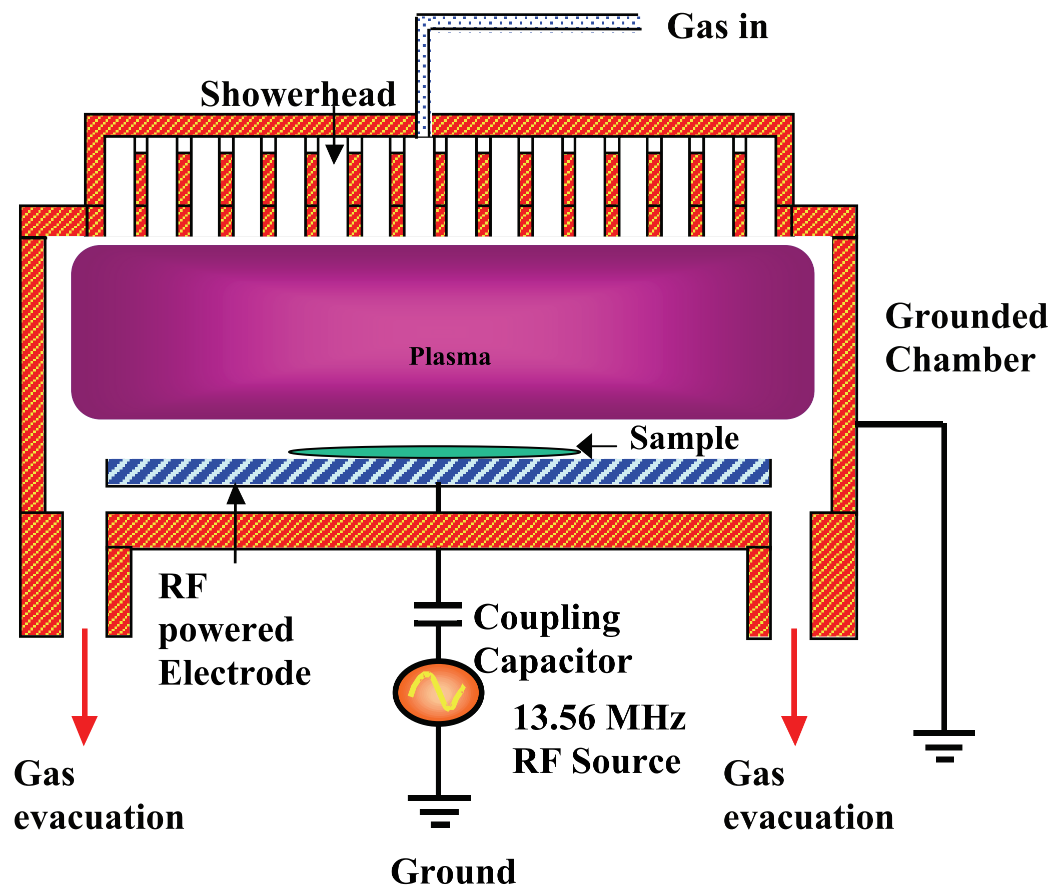


Figure {E-1} Schematic of the RIE chamber [91].

All the controls in the system are performed by control software operational on Microsoft windows. This software provides a graphical interface for the user to operate and adjust various parameters.

E.2 Langmuir Probe Description

In our design of a Langmuir probe, we use a wire for our probe tip giving us a cylindrical Langmuir probe. The wire protrudes from a quartz tube fitted with a ceramic plug on one end and an epoxy plug on the other to keep the probe vacuum tight. A passive RF filtering network connects the probe tip to a lead wire that is swept across a range of voltages by a sourcemeter that also measures the actual voltage applied to and current flowing through the probe (and consequently the plasma). Figure {E-2} exemplifies the KU PRL probe structure.

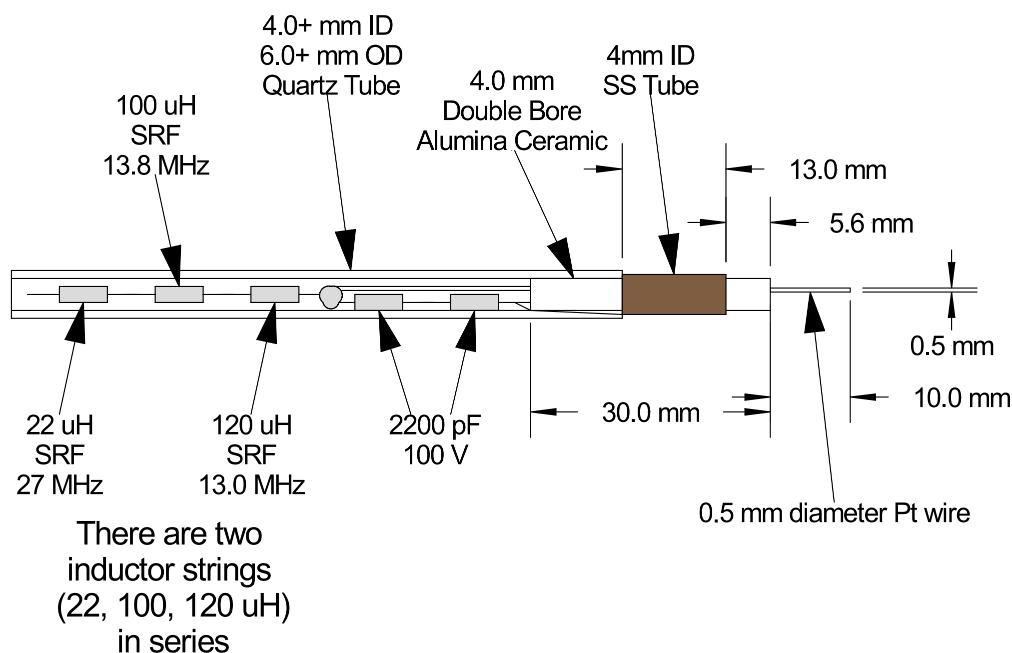


Figure {E-2} Illustration/Schematic of typical Langmuir probe construction. Based on previous designs by Chen et al. and Hopkins et al. [1, 11, 100, 101].

The compensation electrode for the majority of preliminary Langmuir probes consists of nickel tubing obtained from UTI Corporation (now Accellent Corporation). The tubing's inner diameter (ID) is 4 mm and its outside diameter (OD) is 4.5 mm. In preliminary models of the probe, the compensation electrode is 1 cm long, and has a hole drilled into it to facilitate attaching a nickel lead from the internal passive filter. In the later models of the probe, the compensation electrode consists of a 316 stainless steel tube obtained from Small Parts Corporation. Like the nickel tubing, the ID is 4 mm, and the OD is 4.5 mm. However, because of an improved

understanding of the target plasmas, and to counteract possible errors due to Debye length concerns, newer probes used a longer (1.3 cm) compensation electrode.

Probe body and housing

The probe housing consists of a 6 mm OD, slightly greater than 4 mm ID quartz tube obtained from the University of Kansas glass blower. As can be seen in the diagram, a 4 mm OD, 0.8 mm ID double bore alumina ceramic tube plugs one end of the tube (Alfa Aesar Stock #32550). The ceramic also acts as a support for the compensation electrode, isolates the electronics housed in the probe from the plasma, and isolates the cylindrical probe tip from everything but the plasma and the signal port of the RF filtering network.

Internal Probe Electronics

Electrostatic probe analysis in RF generated capacitively coupled plasmas (CCPs) requires that a passive or active filter suppress the RF signal used to generate the plasma. Only then can the probe measure the stationary DC current-voltage (I-V) pairs that make up a sweep. While the active method has the theoretical advantage of using the same RF driving signal as the plasma source to suppress it exactly, we have found that not only does the plasma act as a mixer, but other signals between 13.56 MHz and 27.12 MHz are present. Because of this, we chose to implement a passive filtering scheme.

The minimum passive filtering network consists of a blocking inductor (or RF choke) with a self-resonant frequency (SRF) that corresponds to the plasma frequency in series with the probe tip and a capacitor that smoothes the incoming RF signal that

rides the bias potential between the probe tip and the compensation electrode. In practice, because the filtering network should be placed as close to the probe tip as possible, all of the filtering capacitors and inductors must fit inside the quartz tube making up the probe body. No single inductor that can fit into the probe body can sufficiently attenuate the driving signal at the plasma frequency and its harmonics so a series of inductors commonly called a choke chain must be employed. Further, because the electron bombardment portion of the cleaning cycle subjects the probe tip to voltages that can reach up to 175 V above the plasma floating potential, a series of capacitors must replace the single capacitor. (Again, since no single capacitor that can withstand this voltage can fit into the probe body.)

Manufacturers rarely market inductors with a specific SRF and even inductors with the same ratings will have 1) different SRFs and 2) different impedances at that frequency because of manufacturing differences. Each inductor, therefore, must be tested before it is used in a passive filter. As alluded to previously, the spectral profile of the plasma does not have just one peak at 13.56 MHz. Preliminary tests using a probe with capacitors but no inductor choke chain indicated additional harmonics at both 27.12 MHz and 40.68 MHz. Because of this, additional RF chokes were used in two basic configurations. The first aims to broadly attenuate frequencies above 13.56 MHz while the second focuses on the fundamental and second harmonics.

Table {E-1} below details the inductors used in both configurations. Because the manufacturers list a minimum SRF, the inductors are each tested with a function generator and an oscilloscope to determine the actual SRF. These particular inductors

have been found to have an SRF either at the target frequency (either the fundamental plasma frequency or the secondary harmonic) or slightly below or above it. Ideally one chooses an SRF that is slightly above the target frequency to avoid ringing and other distortions in the filter network. The first (or broadband) configuration uses one or two 33 μH inductors and a mix of 100, 120, 150, and 180 μH inductors. The second (or tuned) configuration uses two or three Vishay Dale 180 μH inductors in series with two of the 33 μH inductors. Both methods yielded good suppression, but neither seems to work for all plasmas.

Table {E-1} Inductor characteristics used in the passive RF filters [1].

Manufacturer	Part Number	Value	Minimum SRF
JW Miller (Bourns)	8230-68-RC	100 μH	13 MHz
JW Miller (Bourns)	8230-70-RC	120 μH	12 MHz
JW Miller (Bourns)	8230-72-RC	150 μH	11 MHz
JW Miller (Bourns)	8230-56-RC	33 μH	24 MHz
Vishay Dale	IM02BH181K	180 μH	10 MHz

The capacitors used have fewer restrictions. While a larger capacitor smoothes out the RF signal more effectively, it also decreases the step response of any change in the electrode bias. Therefore, a judicious choice of capacitance is around 1000 pF. We used two Kemet 2200 pF, 100 V (Part #C420C222J1G5TA7200) capacitors in series to form the capacitive leg of the filtering network.

Appendix F

Data Acquisition Technique

This section is an excerpt from B. Pathak's thesis [1].

Appendix F: Data Acquisition Technique

While the experimental setup and protocol for each of the chemistries investigated was slightly different, a set of guiding principles directs all the experimental protocols. First, one must select the proper probe design. Second, based on each discharge's unique characteristics, one must determine the vertical placement of the probe within the chamber that will capture the region of interest. Third, the probe must be cleaned. And finally, several timing parameters must be selected to ensure that the sweep is a valid representation of what actually occurs in the plasma.

Determination of Plasma Region of Interest and Correct Probe Height

Because (at least) two sheaths form in an RF plasma, one at the powered electrode and one at the grounded electrode, and since a Langmuir probe obtains information about a plasma locally, interference from these sheaths and their presheath regions must be avoided. To further complicate things, the sheaths' heights change based on the difference in mass between the positive and negative charge carriers and the other layers in the plasma often vary based on the electron density. Consequently, each chemistry and pressure potentially requires adjustment of the probe height within the chamber.

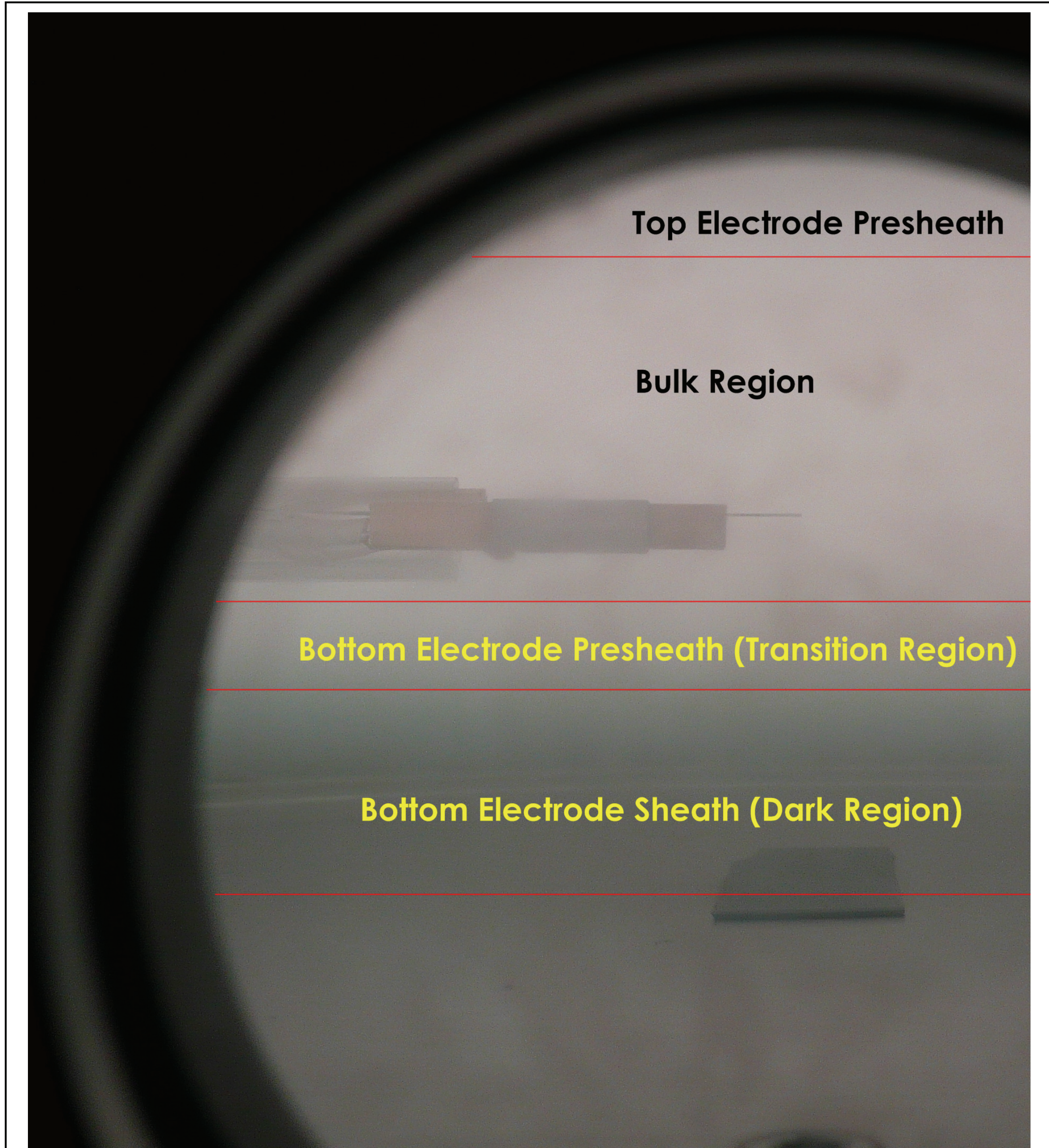


Figure {F-1} Labeled photograph of a probe *in situ* demonstrating the visual guides used to determine accurate vertical positioning [1].

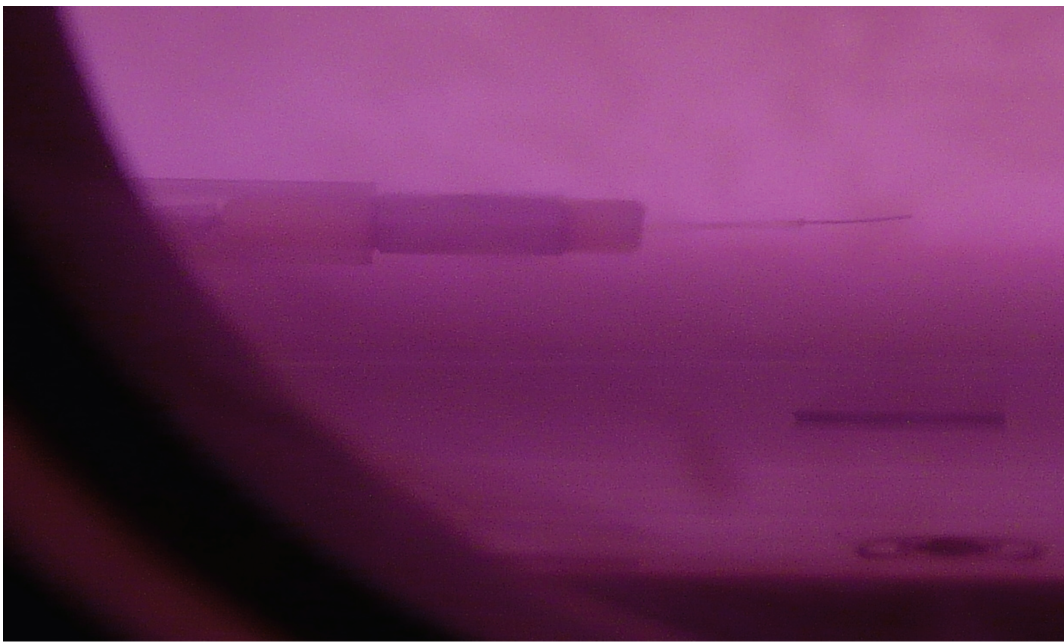


Figure {F-2} Photographs of a probe positioned to measure the presheath (Top, 100% N_2, 15 mTorr, 50 W) and the bottom of the bulk of the plasma (Bottom, He plasma, 50 mTorr, 100 W) [1].

For calibration, the main region of interest is the bulk of the plasma since it is well mixed and large enough to provide uniform plasma characteristics several (5–20 depending on the plasma) debye lengths above and below the probe. However, for plasmas that include N_2 and BCl_3 it is also worthwhile to examine the presheath region since this is the region that produces most of the ions that directly influence etching and if there are vertically varying effects one would expect significant variations in the EEDF and consequently kT_e and N_e in these regions (See {Figure F-2}).

Even for cleaning the probe, the proper height is important. Since the sheath height is larger in a He plasma than in a BCl_3 or N_2 plasma, one can adjust the probe to be in the bulk region for the target plasma and find that the probe is in the sheath for a He cleaning plasma, rendering the cleaning cycle useless.

Cleaning

In-situ cleaning of the probe consists of electron bombardment and optionally ion bombardment. If ion bombardment is used, then the cycle can be repeated as many times as needed. The cleaning is then followed by a cooling down time. During electron bombardment, the probe is biased to a highly positive voltage with respect to the plasma. The result is that the electrons in plasma are strongly drawn to the probe and the resulting collisions not only transfer charge but also momentum and create heat. Any impurities that have formed a surface layer on the probe are either knocked off or evaporate off of the tip. The probe glows a bright orange color during this

phase of the cleaning cycle. Electrons have a very small mass, however, and so the primary mode of cleaning is thermal. Ion cleaning complements this action. By biasing the probe strongly negative, the opposite effect occurs. The positive ions are strongly attracted to the probe, and though the probe does not glow orange-hot during this phase, the momentum transfer of the ions sputters away any remaining contaminants.

The probe tip was typically cleaned in a 50 mTorr, 100 W He plasma. If a He plasma was to be investigated, then an electron bombardment at 750 mW (around 100–130 V) would suffice to clean the probe. With N_2 and BCl_3, (and later SF_6) however, electron bombardment (as before) and ion bombardment (at –150 V) cycles were used because of the contaminant films that readily formed on the probe surface. Typically each electron and ion bombardment phase lasted two minutes as did the cool down after the clean was finished.

Probe Sweep and Plasma Settling Timing Parameters

The probe sweep duration and data point settling time were chosen as trade-off parameters. The A/D integration time on the sourcemeter was chosen as 0.1 PTAD (a unit determined by the frequency of the AC power source, in the US 1/60 Hz) or 1.667 ms. The settling time was chosen as 1 ms, and because the sourcemeter has as built in trigger and settling time of 1.5 ms [43], the data points were collected approximately every 4.167 ms or at 240 Hz. With ~1150 samples per data run each sweep lasted ~4.8 seconds, thus avoiding contamination and ensured

that there were enough cycles of the plasma frequency to allow the plasma to settle between data points.

However, there was also a need to allow the plasma to settle after striking before sweeps were taken to allow the matching network and the bulk of the plasma to come to equilibrium. This took approximately 25 seconds and was controlled using the global lead in option of the data acquisition application.

Appendix G

Sample MathCAD Worksheet

The following section is a collaboration of work from the author of this thesis, J. Alexander and another author, B. Pathak [1].

Langmuir Probe Data Analysis

At its simplest, a Langmuir probe is simply a wire (or disk) placed in the plasma. The probe collects mostly electrons when biased positively and mostly ions when biased negatively. When the bias is negative, the electrons that are collected are the ones with sufficient energy to overcome the potential barrier of the probe. In this exercise we will analyze data from a cylindrical Langmuir probe. The random current of electrons to a surface in a plasma is

$$J_{sat} = n_e q \sqrt{kT_e / 2\pi m_e}$$

where J_{sat} is the current density, n_e is the electron density, m_e is the electron mass, and q is the elementary charge. The surface is assumed to be at the plasma potential. The electron temperature T_e will be written in electron volts below, which means that the thermal energy will be qT_e rather than kT_e. When the probe is at the plasma potential, the current collected is the **saturation current** I_{sat}:

$$I_{sat} = A_p J_{sat} = 2\pi a L J_{sat}$$

where a is the probe radius, L is the probe length and A_p is the probe area.

When the probe voltage is negative relative to the plasma potential, Vplasma, the current is estimated as:

$$I(V) = I_{sat} \exp[(V - V_{plasma})/T_e]$$

Vplasma is the potential in the space between plasma electrons and ions.

Characteristics of the probe used to acquire the data:

$D_p := 0.25 \cdot 10^{-3}$ Probe diameter in m. The wire diameter is $D_p \cdot m = 0.25\,mm$.

$L_p := 0.8 \cdot 10^{-2}$ Probe length in m. The length is approximately $L_p \cdot m = 0.8\,cm$.

$A_p := \pi \cdot D_p \cdot L_p$ Probe surface area in m^2. The area is approximately $A_p \cdot m^2 = 6.283\,mm^2$

Required Physical Constants

$q_e := 1.602 \times 10^{-19} C$ Elementary Charge (of an electron)

$m_e := 9.109 \times 10^{-31} kg$ Mass of an Electron

$eV := 1.602 \times 10^{-19} J$

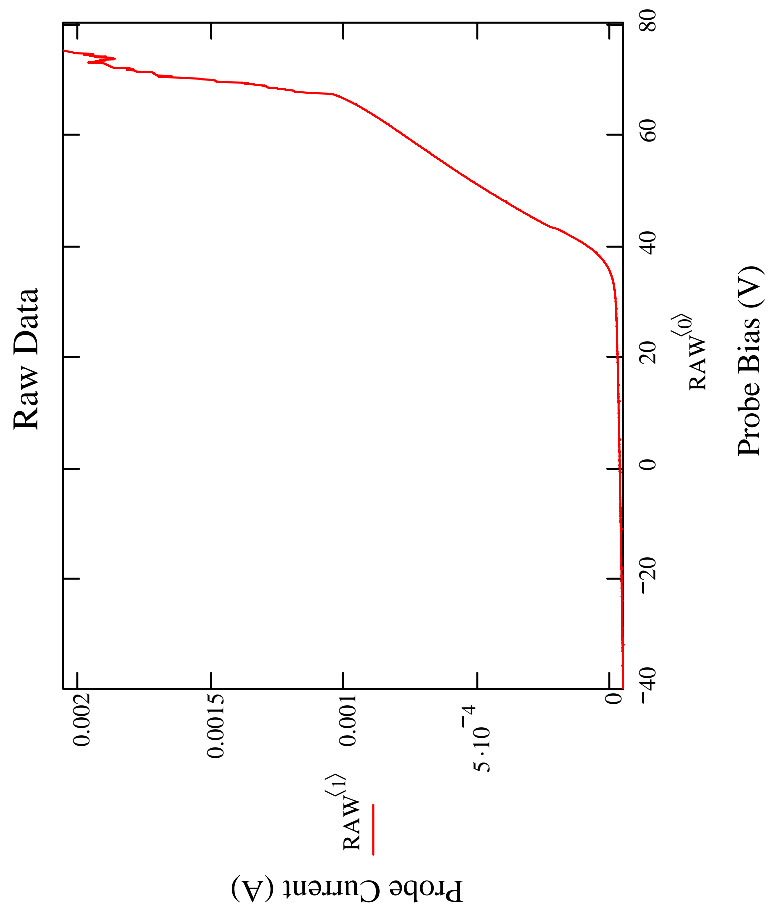
Import the sweep data from a CSV File:

$RAW :=$ Probe current in amps versus probe voltage

$rows(RAW) = 1151$ Rows in the file...

$dV := \left| RAW_{1,0} - RAW_{0,0} \right|$ $dV = 0.1$

$$RAW := \begin{cases} reverse(RAW) & \text{if } RAW_{1,0} > RAW_{2,0} \\ RAW & \text{otherwise} \end{cases}$$



Raw Data
Probe Current (A)
RAW⟨1⟩
0.002
0.0015
0.001
5·10−4
0
−40
−20
0
20
40
60
80
RAW⟨0⟩
Probe Bias (V)

Limit the sweep data to a useful region.

$VRaw_{min} := RAW_{0,0}$ $\quad$ $VRaw_{max} := RAW_{rows(RAW)-1,0}$

$VRaw_{min} = -40$ $\quad$ $VRaw_{max} = 75$

$V_{min} := -40$ $\quad$ $idx_{min} := rows(RAW) - 1 - floor\left(\frac{VRaw_{max} - V_{min}}{dV}\right)$ $\quad$ $idx_{min} = 1$

$V_{max} := 60$ $\quad$ $idx_{max} := rows(RAW) - 1 - floor\left(\frac{VRaw_{max} - V_{max}}{dV}\right)$ $\quad$ $idx_{max} = 1001$

Create an initial DATA array that has the current data, the first derivative, and the second derivative.

$DAT := submatrix(RAW, idx_{min}, idx_{max}, 0, 1)$ $\quad$ $jdx := 0 .. rows(DAT) - 1$ $\quad$ $kdx := 2, 3 .. rows(DAT) - 3$

$DAT^{\langle 1 \rangle} := 10^6 \cdot DAT^{\langle 1 \rangle}$ Convert currents to microamps $\quad$ $DatRows := rows(DAT) - 1$

Do Preliminary Localized Curve Fitting/Smoothing: prelimsmoothpts overrides prelimsmoothvolts, set it to 0 if you want to use prelimsmoothvolts. If you don't want to do a preliminary smooth, set both to 0

$prelimsmoothpts := 0$ $\quad$ $prelimsmoothvolts := 1.5$

$$span(smoothpts, smoothvolts) := \begin{cases} \frac{smoothpts}{DatRows} & \text{if } smoothpts \neq 0 \\ \frac{smoothvolts}{DatRows \cdot dV} & \text{if } smoothpts = 0 \wedge smoothvolts \neq 0 \\ 0 & \text{otherwise} \end{cases}$$

$\text{prelimspan} := \text{span}(\text{prelimsmoothpts}, \text{prelimsmoothvolts})$ $\text{prelimspan} = 0.015$

$\text{prelimpointsused} := \text{prelimspan} \cdot \text{DatRows}$ $\text{prelimpointsused} = 15$

$\text{prelimvoltsused} := \text{prelimspan} \cdot \text{DatRows} \cdot \text{dV}$ $\text{prelimvoltsused} = 1.5$

$$\text{vs} := \begin{cases} \text{loess}\left(\text{DAT}^{\langle 0 \rangle}, \text{DAT}^{\langle 1 \rangle}, \text{prelimspan}\right) & \text{if prelimspan} \neq 0 \\ 0 & \text{otherwise} \end{cases}$$

$$\text{DATtmp}_{\text{jdx}} := \begin{cases} \text{interp}\left(\text{vs}, \text{DAT}^{\langle 0 \rangle}, \text{DAT}^{\langle 1 \rangle}, \text{DAT}_{\text{jdx},0}\right) & \text{if prelimspan} \neq 0 \\ \text{DAT}_{\text{jdx},1} & \text{otherwise} \end{cases}$$

$$\text{fit}(x) := \text{interp}\left(\text{vs}, \text{DAT}^{\langle 0 \rangle}, \text{DAT}^{\langle 1 \rangle}, x\right)$$

$$\text{dfit}(x) := \frac{d}{dx}\text{fit}(x)$$

$\text{DAT}^{\langle 1 \rangle} := \text{DATtmp}$

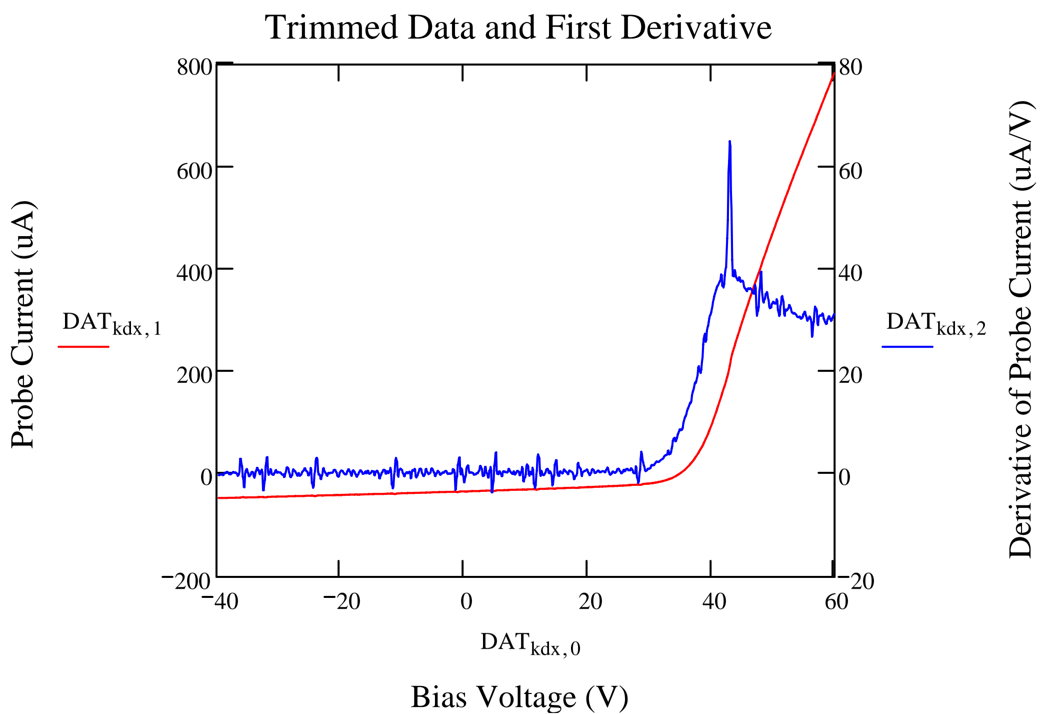
$$\text{d2fit}(x) := \frac{d^2}{dx^2}\text{fit}(x)$$

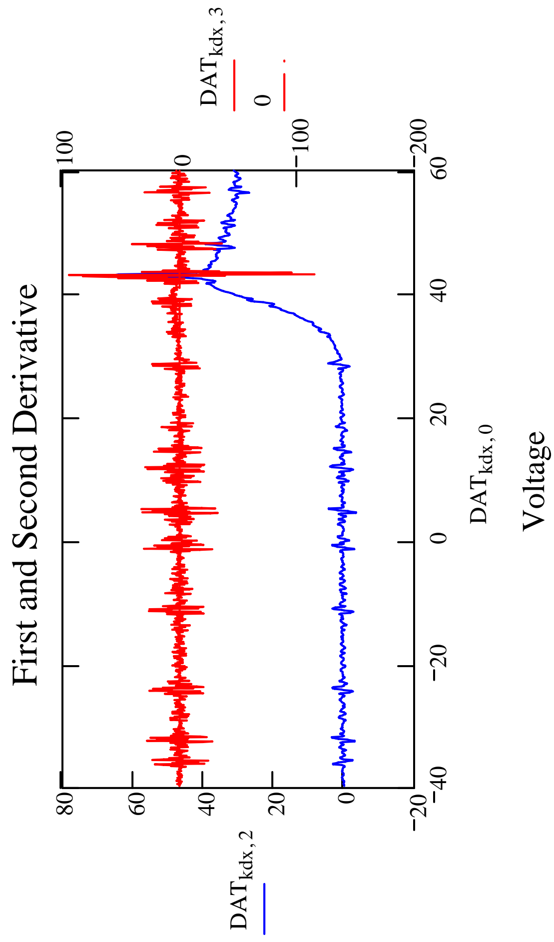
$\text{DAT}^{\langle 0 \rangle} := \text{DAT}^{\langle 0 \rangle} + 0.5 \cdot \text{dV}$ $\text{DATsec}^{\langle 1 \rangle} := \text{DAT}^{\langle 1 \rangle}$

Take the first and second derivatives of the data, plot the first derivative...

$$DAT_{kdx,2} := \mathrm{dfit}\left(DAT_{kdx,0}\right)$$

$$DAT_{kdx,3} := \mathrm{d2fit}\left(DAT_{kdx,0}\right)$$





First and Second Derivative
Voltage
$DAT_{kdx,0}$
$DAT_{kdx,2}$
$DAT_{kdx,3}$
0
80
60
40
20
0
−20
100
0
−100
−200
−40
−20
0
20
40
60

Smooth the original data, the first derivative, and the second derivative to see if they can be more usable.

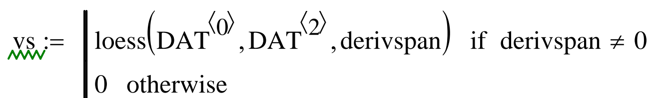
$\text{derivsmoothpts} := 0 \qquad \text{derivsmoothvolts} := 1.7$

$\text{secderivsmoothpts} := 0 \qquad \text{secderivsmoothvolts} := 1.7$

$\text{derivspan} := \text{span}(\text{derivsmoothpts}, \text{derivsmoothvolts}) \qquad \text{derivspan} = 0.017$

$\text{derivpointsused} := \text{round}(\text{derivspan} \cdot \text{DatRows}) \qquad \text{derivpointsused} = 17$

$\text{derivvoltsused} := \text{derivspan} \cdot \text{DatRows} \cdot \text{dV} \qquad \text{derivvoltsused} = 1.7$



$$\text{vs} := \begin{cases} \text{loess}\left(\text{DAT}^{\langle 0 \rangle}, \text{DAT}^{\langle 2 \rangle}, \text{derivspan}\right) & \text{if derivspan} \neq 0 \\ 0 & \text{otherwise} \end{cases}$$

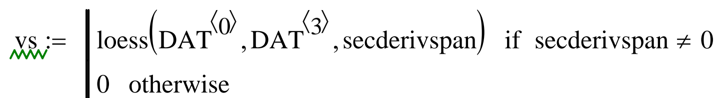
$$\text{DATtmp}_{\text{jdx}} := \begin{cases} \text{interp}\left(\text{vs}, \text{DAT}^{\langle 0 \rangle}, \text{DAT}^{\langle 2 \rangle}, \text{DAT}_{\text{jdx},0}\right) & \text{if derivspan} \neq 0 \\ \text{DAT}_{\text{jdx},2} & \text{otherwise} \end{cases}$$

$$\text{DAT}^{\langle 2 \rangle} := \text{DATtmp}$$

secderivspan := span(secderivsmoothpts, secderivsmoothvolts secderivspan = 0.017

secderivpointsused := round(secderivspan·DatRows) secderivpointsused = 17

secderivvoltsused := secderivspan·DatRows·dV secderivvoltsused = 1.7

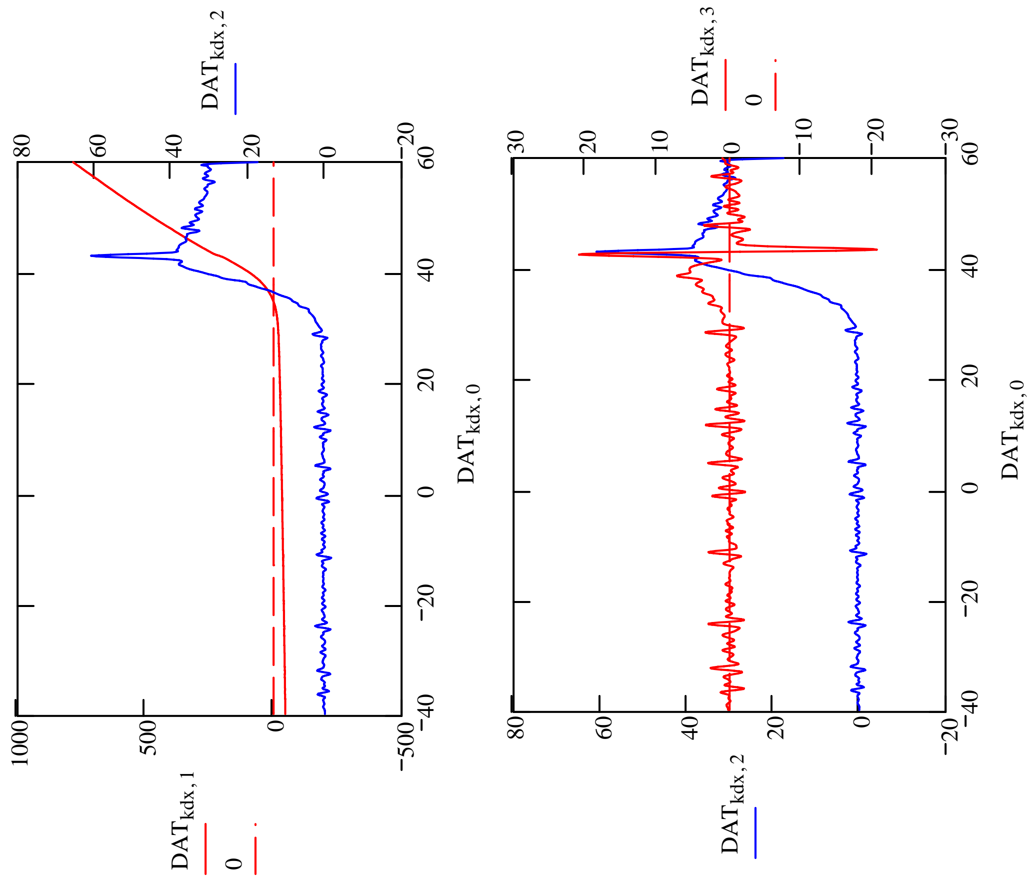


$$vs := \begin{cases} \text{loess}\left(DAT^{\langle 0\rangle}, DAT^{\langle 3\rangle}, \text{secderivspan}\right) & \text{if secderivspan} \neq 0 \\ 0 & \text{otherwise} \end{cases}$$

$$DATtmp_{jdx} := \begin{cases} \text{interp}\left(vs, DAT^{\langle 0\rangle}, DAT^{\langle 3\rangle}, DAT_{jdx,0}\right) & \text{if secderivspan} \neq 0 \\ DAT_{jdx,3} & \text{otherwise} \end{cases}$$

$$DATtmp2 := \text{ksmooth}\left(DAT^{\langle 0\rangle}, DATtmp, \frac{\text{secderivsmoothvolts}}{2}\right)$$

$$DAT^{\langle 3\rangle} := DATtmp2$$



$DAT_{kdx,1}$
0
$DAT_{kdx,2}$
$DAT_{kdx,0}$
$DAT_{kdx,3}$

Find the Floating potential and the Plasma potential based on the smoothed data.

The floating potential is the potential at which the probe current is equal to zero

$$i_{Vf} := \left| \begin{array}{l} j \leftarrow \text{DatRows} - 1 \\ \text{while } \text{DAT}_{j,1} > 0 \\ \quad j \leftarrow j - 1 \end{array} \right.$$

$i_{Vf} = 746$ Find the index of Vf

$V_F := \text{DAT}_{i_{Vf},0}$ $V_F = 34.75$ This is the floating potential

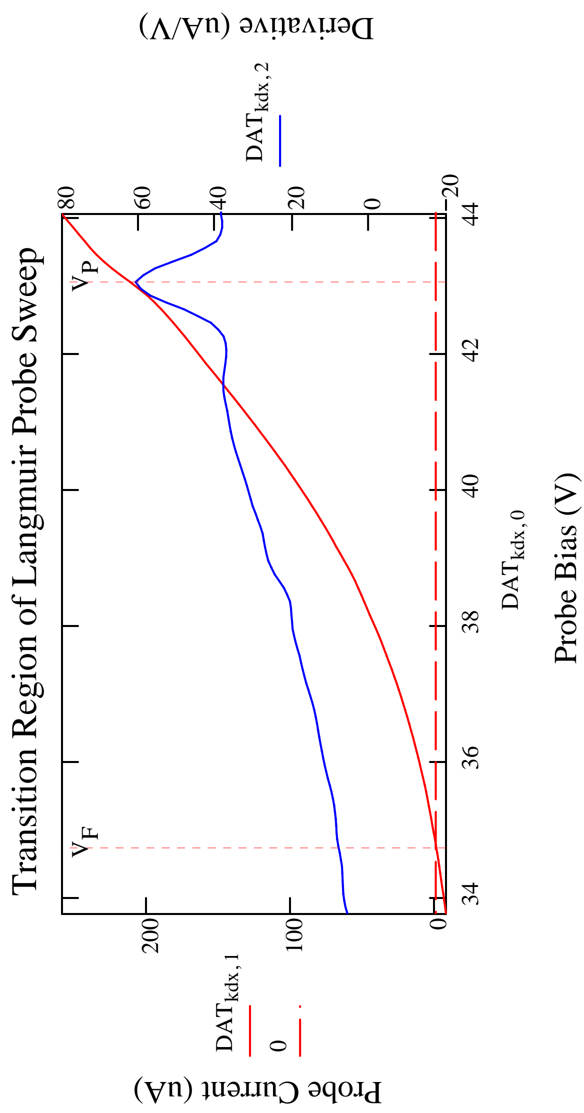
The plasma potential is at first estimation equal to the maximum of the first derivative.

$i_{Vp} := \text{match}\left(\max\left(\text{DAT}^{\langle 2\rangle}\right), \text{DAT}^{\langle 2\rangle}\right)_0$ $i_{Vp} = 829$ Find the index of Vp

$i_{Vp} := i_{Vp}$ If you don't like that Vp, pick another one...

$V_P := \text{DAT}_{i_{Vp},0}$ $V_P = 43.05$ This is the plasma potential

$\text{extension} := 10$ points to plot before and after VF and VP



Transition Region of Langmuir Probe Sweep
Probe Current (uA)
Derivative (uA/V)
Probe Bias (V)
V_F
V_P
$DAT_{kdx,0}$
$DAT_{kdx,1}$
$DAT_{kdx,2}$
0
34
36
38
40
42
44
0
100
200
-20
0
20
40
60
80

Create an EEPF and EEDF based on the second derivative and the found VP

$EERange := V_P - V_F$ How many volts the EEPF and EEDF extend out (default is to Vp-Vf)

$EERange = 8.3$ $\quad EERange := 20$ Change it here if the defaults aren't what you want

$$idx_{EEmin} := i_{Vp} - \frac{EERange}{dV}$$

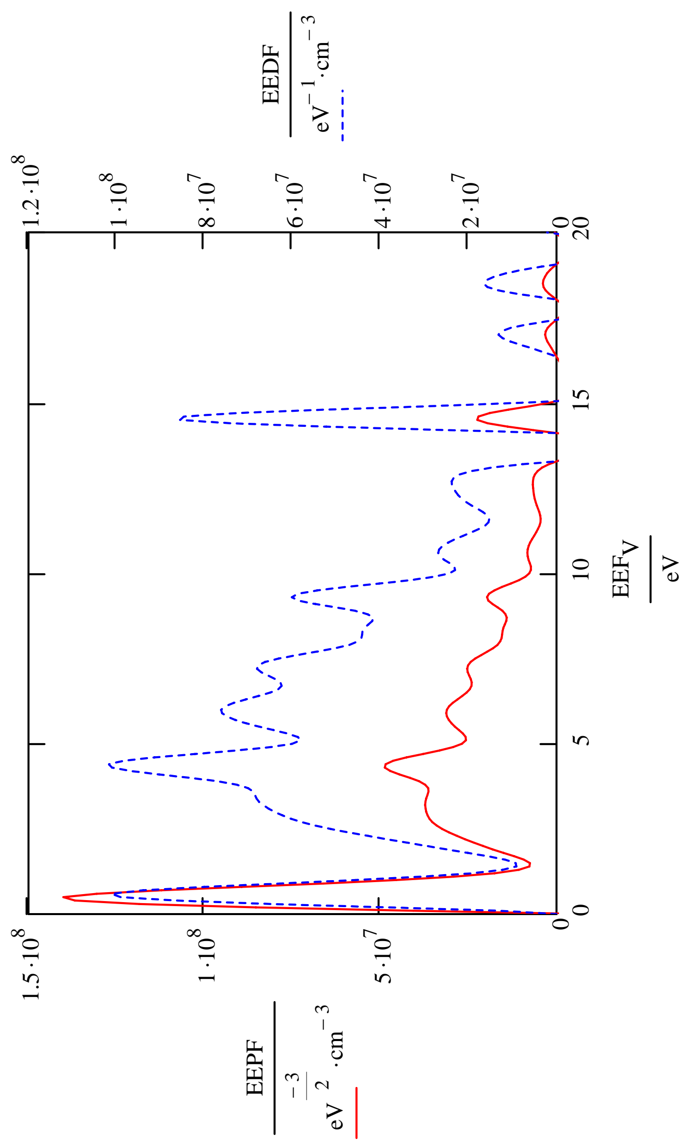
$$EEF_V := \left(-submatrix\left(DAT, idx_{EEmin}, i_{Vp}, 0, 0\right) + V_P\right) \cdot eV \qquad EEF_V := reverse\left(EEF_V\right)$$

$$EEPF := 2 \cdot \frac{\sqrt{2 \cdot m_e}}{q_e{}^3 \cdot A_p \cdot m^2} \cdot submatrix\left(DAT, idx_{EEmin}, i_{Vp}, 3, 3\right) \cdot \frac{\mu A}{V^2}$$

$EEPF := \overrightarrow{EEPF}$ $\qquad EEPF := reverse(EEPF)$ Manipulate EEPF to get it to behave...

$$EEDF := \overrightarrow{\left(EEPF \cdot \sqrt{EEF_V}\right)}$$

Note that both the EEPF and EEDF shouldn't have any negative values, so if the values are negative, we switch them to zero.


EEPF
eV^(-3/2)·cm^-3
EEDF
eV^-1·cm^-3
EEF_V
eV
1.5·10^8
1·10^8
5·10^7
0
1.2·10^8
1·10^8
8·10^7
6·10^7
4·10^7
2·10^7
0
5
10
15
20

Try and find an equivalent kTe from the EEDF

Integrate the EEDF both with and without multiplying it by the voltage...

$$qIntegral_{EEDF}(\varepsilon_{min}) := \left[\sum_{m = floor\left(\frac{\varepsilon_{min}}{dV}\right)}^{rows(EEDF)-2} \left[\frac{1}{2}\cdot\left(EEDF_m + EEDF_{m+1}\right)\left(EEF_{V_{m+1}} + -EEF_{V_m}\right)\right]\right]$$

$$qWghtedIntegral_{EEDF}(\varepsilon_{min}) := \sum_{m = floor\left(\frac{\varepsilon_{min}}{dV}\right)}^{rows(EEDF)-2} \left[\frac{1}{4}\cdot\left(EEDF_m + EEDF_{m+1}\right)\left(EEF_{V_{m+1}} + -EEF_{V_m}\right)\cdot\left(EEF_{V_{m+1}} + EEF_{V_m}\right)\right]$$

$qIntegral_{EEDF}(0) = 6.561 \times 10^{8}\,cm^{-3}$ $qWghtedIntegral_{EEDF}(0) = 3.842 \times 10^{9}\,eV\cdot cm^{-3}$

$Avg_{EE} := \dfrac{qWghtedIntegral_{EEDF}(0)}{qIntegral_{EEDF}(0)}$ $Avg_{EE} = 5.855\,eV$

$kTe_{equiv} := \dfrac{2}{3}\cdot Avg_{EE}$ $kTe_{equiv} = 3.903\,eV$

$N_e := qIntegral_{EEDF}(0)$ $N_e = 6.561 \times 10^{8}\,cm^{-3}$

Compare the EEDF to a Maxwellian and Druyvesteyn with an equal average electron energy (equivalent kTe for the Maxwellian)

$$\mathrm{dmaxwellian}_e(\varepsilon, kT_e) := \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{\varepsilon}}{\sqrt{kT_e^{\,3}}} \cdot e^{\frac{-\varepsilon}{kT_e}} \qquad 1 - \int_0^{\mathrm{EERange}} \mathrm{dmaxwellian}_e\left(\varepsilon, \frac{kTe_{equiv}}{eV}\right) d\varepsilon = 0.017$$

$$\mathrm{ddruyvesteyn}_e(\varepsilon, kT_e, \alpha) := \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{\varepsilon}}{\sqrt{kT_e^{\,3}}} \cdot \exp\left[-\left(\frac{\varepsilon}{kT_e}\right)^{\alpha}\right]$$

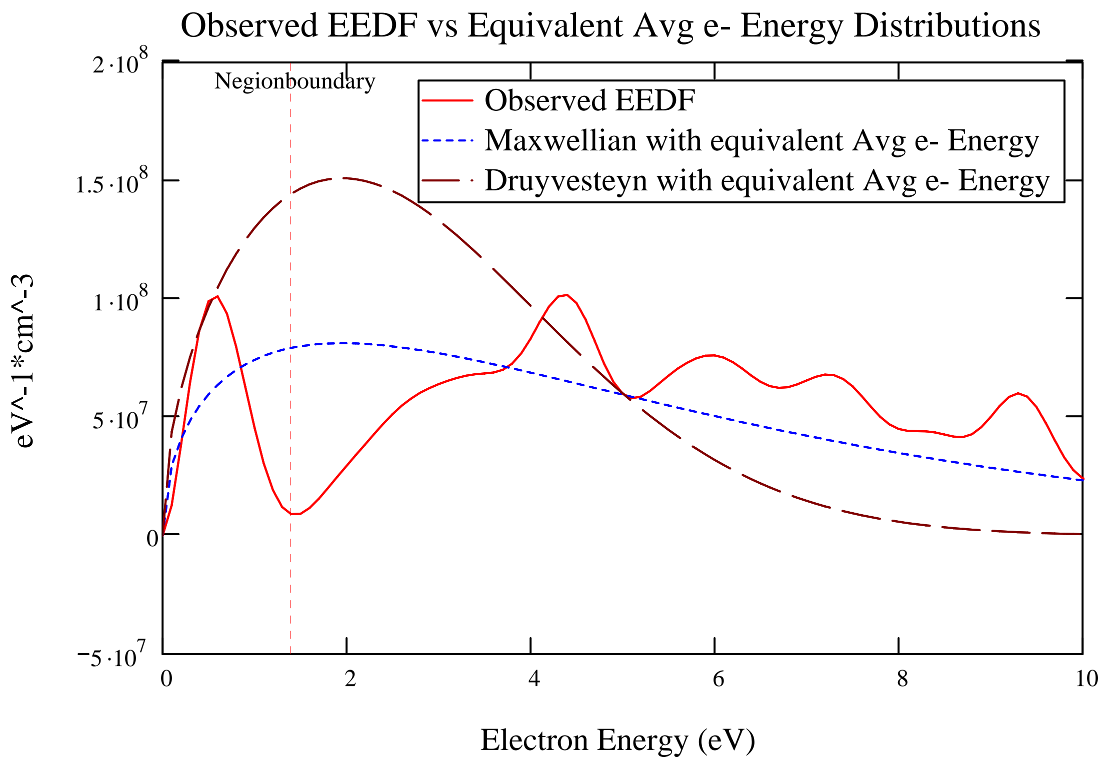
N.B. $\alpha = 2$ for a true Druyvesteyn

$$\mathrm{ndruyvesteyn}_e(\varepsilon, kT_e, \alpha) := \frac{\mathrm{ddruyvesteyn}_e(\varepsilon, kT_e, \alpha)}{\int_0^{\infty} \mathrm{ddruyvesteyn}_e(\varepsilon, kT_e, \alpha)\, d\varepsilon}$$

$$\mathrm{avgEEndruy}(kT_e, \alpha) := \int_0^{\infty} \varepsilon \cdot \mathrm{ndruyvesteyn}_e(\varepsilon, kT_e, \alpha)\, d\varepsilon \qquad \mathrm{norm}_{AvgEE}(\alpha) := \mathrm{avgEEndruy}(1, \alpha)^{-1}$$

$\alpha := 2$ $\quad$ $\alpha = 2$ for a true $\quad$ $Avg_{EE} = 5.855\ eV$ $\quad$ $E := 0, dV .. \mathrm{EERange}$

Negionboundary := 1.4



Excel Line for ease of import:

$$\mathrm{Excel} := \mathrm{augment}\left(\frac{kTe_{equiv}}{eV}, \frac{N_e}{cm^{-3}}\right)$$

Excel =

	0	1
0	3.903	$6.561\cdot10^{8}$

$$\mathrm{Excel2} := \mathrm{augment}\left(\frac{kTe_{equiv}}{eV}, \frac{N_e}{cm^{-3}}, \frac{2}{3}\,\frac{qWghtedIntegral_{EEDF}(Negionboundary)}{qIntegral_{EEDF}(Negionboundary)\cdot eV}, \frac{qIntegral_{EEDF}(Negionboundary)}{cm^{-3}}, 0, V_F, V_P, Negionboundary\right)$$

Excel2 =

	0	1	2	3	4	5	6	7
0	3.903	$6.561\cdot10^{8}$	4.346	$5.82\cdot10^{8}$	0	34.75	43.05	1.4

Error in the Distributions caused by limits

$$1 - \int_0^{EERange} dmaxwellian_e\left(\varepsilon, \frac{kTe_{equiv}}{eV}\right) d\varepsilon = 1.658\,\%$$

$$1 - \int_0^{EERange} ndruyvesteyn_e\left(\varepsilon, \frac{Avg_{EE}}{eV}, \alpha\right) d\varepsilon = 3.484 \times 10^{-4}\,\%$$

$$\frac{EEDF}{eV^{-1} \cdot cm^{-3}} =$$

	0
0	0
1	1.286·107
2	3.818·107
3	6.49·107
4	8.653·107
5	9.904·107
6	1.011·108
7	9.388·107
8	8·107
9	6.285·107
10	4.558·107
11	3.057·107
12	1.926·107
13	1.216·107
14	9.059·106
15	9.239·106

$$\frac{EEPF}{eV^{-\frac{3}{2}} \cdot cm^{-3}} =$$

	0
0	-9.754·106
1	4.068·107
2	8.536·107
3	1.185·108
4	1.368·108
5	1.401·108
6	1.306·108
7	1.122·108
8	8.944·107
9	6.625·107
10	4.558·107
11	2.914·107
12	1.758·107
13	1.067·107
14	7.656·106
15	7.543·106

$\varepsilon_{BCl2Cl} = 4.61$

$$\text{submatrix}\left(\frac{EEDF}{eV^{-1}\cdot cm^{-3}}, \text{floor}\left(\frac{\varepsilon_{BCl2Cl}}{dV}\right), 25, 0, 0\right) =$$

	0
0	$9.128\cdot10^{7}$
1	$9.831\cdot10^{7}$
2	$1.017\cdot10^{8}$
3	$1.011\cdot10^{8}$
4	$9.679\cdot10^{7}$
5	$9.029\cdot10^{7}$
6	$8.324\cdot10^{7}$
7	$7.709\cdot10^{7}$
8	$7.267\cdot10^{7}$
9	$7.01\cdot10^{7}$
10	$6.895\cdot10^{7}$
11	$6.852\cdot10^{7}$
12	$6.819\cdot10^{7}$
13	$6.761\cdot10^{7}$
14	$6.668\cdot10^{7}$
15	$6.545\cdot10^{7}$

OML THEORY

Now that we understand the electrons, Let's begin to understand the Ions. Below is a single iteration of the program at the kTe&Ne determined from the EEDF. It also uses Vp determined from the 1st derivative for iVs. As the program iterates, a few things should happen:

(1) Ne is the starting iteration of n, the pos ion density, we know that this is greater than the electron density for our chamber, hence we have to iterate on it. The iteration starting value is derived from backwards engineering of the IOML Theory.

(2) The kTe that is used in this example will change after OML iterations, this is due to the subtration of the ion current from the probe collection current. The tail of the EEDF will change. Intense EEDF calculations are used for determining kTe, we will not iterate on this value.

(3)iVs is typically lower than Vp, even though they should be equal to one another

(4) The iMass used, AN, is different for each gas species. When mixing gases, it is unknown. Therefore, we will standardize all gases to 1, and since it is a direct multiplier, we can correct it later

(4)a As a side note, setting AN to 1 actually speeds up the iterations, by lowering the "calculated density" and therefore the maximum number of iterations on density (n is iterated from Ne to 10^12, with a shortcut when the least squares sums gets worse -- 10^12 was an arbitrary value of which we shouldn't be seeing plasma densities higher than this value, even in Helium..

$$iVs := DAT_{i_{Vp},0} \qquad n := \frac{qIntegral_{EEDF}(Negionboundary)}{cm^{-3}}$$

$$kTe := \frac{2}{3}\frac{qWghtedIntegral_{EEDF}(Negionboundary)}{qIntegral_{EEDF}(Negionboundary)\cdot eV} \qquad eV_s := V_P$$

ion mass:

$$AN := 1$$

probe area in cm^2

$$A_p := A_p \cdot 10000$$

convert probe current to positive miliamps

Normalize probe potential relative to Vs, the space potential used for fitting the ion current

$$\mathrm{DATforOML}^{\langle 1\rangle} := \left(-10^{-3}\mathrm{DAT}\right)^{\langle 1\rangle} \qquad \eta := \frac{\mathrm{iVs} - \mathrm{DAT}^{\langle 0\rangle}}{\mathrm{kTe}}$$

Use some trickery to zero out all currents that are positive e.g. above floating, Vf

$$j := i_{Vf} + 1, i_{Vf} + 2 .. \mathrm{rows}\left(\mathrm{DAT}^{\langle 0\rangle}\right) - 1$$

$$\mathrm{DATforOML}_{j,1} := \begin{cases} \mathrm{DATforOML}_{j,1} & \text{if } \mathrm{DATforOML}_{j,1} > 0 \\ 0 & \end{cases}$$

Now square the "positive" miliamp ion current that doesn't deal with currents above Vf

$$\mathrm{DATsquared} := \left(\mathrm{DATforOML}^{\langle 1\rangle}\right)^2$$

Finally, Setup the OML Currents

$$\mathrm{IOML} := \frac{7.05}{10^{11}} \cdot A_p \cdot n \cdot \sqrt{\eta \cdot \frac{\mathrm{kTe}}{\mathrm{AN}}}$$

Use some trickery to zero out all currents that are above Vp

$$k := i_{Vp} + 1, i_{Vp} + 2 .. \mathrm{rows}\left(\mathrm{DAT}^{\langle 0\rangle}\right) - 1$$

$$\mathrm{IOML}_k := \begin{cases} \mathrm{IOML}_k & \text{if } \eta_{k>0} \\ 0 & \end{cases}$$

$IOMLsquared := IOML^2$

minimization

$iError := \sqrt{(DATsquared - IOMLsquared)^2}$

$h := 0, 1 .. rows\left(DAT^{\langle 0 \rangle}\right) - 1$

$\sum iError = 0.657$ $TotErr := 10^{99}$

$$n_{high} := 10^{11} \cdot \frac{DATforOML_{0,1}}{7.05 \cdot A_p \cdot \left(\frac{V_F - V_{min}}{AN}\right)^{0.5}}$$

$$n_{low} := 10^{11} \cdot \frac{DATforOML_{round\left(\frac{20}{dV}\right), 1}}{7.05 \cdot A_p \cdot \left(\frac{V_P + 7 - V_{min}}{AN}\right)^{0.5}}$$

$n := n_{low}$

$$\mathrm{OMLvalues} :=$$

$$\mathrm{TotErr} \leftarrow 10^{99}$$

$$\mathrm{iErrorLocalBest} \leftarrow 10^{99}$$

$$\mathrm{iErrorExit} \leftarrow 10^{100}$$

$$i_{Vs} \leftarrow i_{Vf}$$

$$k \leftarrow (i_{Vs}+1), (i_{Vs}+2) .. \mathrm{rows}(DAT) - 1$$

$$\text{while } n < n_{high}$$

$$\quad i_{Vs} \leftarrow i_{Vf}$$

$$\quad \text{while } i_{Vs} < i_{Vp} + \mathrm{round}\left(\frac{10}{dV}\right)$$

$$\quad\quad Vmx \leftarrow 20 \cdot \mathrm{round}\left(\frac{1}{dV}\right)$$

$$\quad\quad Vmn \leftarrow 0$$

$$\quad\quad \eta \leftarrow \frac{DAT_{i_{Vs},0} - DAT^{\langle 0 \rangle}}{kTe}$$

$$\quad\quad \eta \leftarrow \frac{DAT_{i_{Vs},0} - DAT^{\langle 0 \rangle}}{kTe}$$

$$\quad\quad IOML \leftarrow \frac{7.05}{10^{11}} \cdot A_p \cdot n \cdot \sqrt{\eta \cdot \frac{kTe}{AN}}$$

$$\quad\quad \text{for } k \in (i_{Vs}+1), (i_{Vs}+2) .. \mathrm{rows}\left(DAT^{\langle 0 \rangle}\right) - 1$$

$$\quad\quad\quad IOML_k \leftarrow \begin{cases} IOML_k & \text{if } \eta_{k>0} \\ 0 & \end{cases}$$

```
IOMLsquared ← IOML^2
iterError ← sqrt((DATsquared − IOMLsquared)^2)
while  Vmx < i_Vf − round(20/dV)
    iError ← Σ_{i = Vmn}^{Vmx} iterError_i
    if  iError < TotErr
        OMLvalues_0 ← kTe
        OMLvalues_1 ← n
        OMLvalues_2 ← i_Vs
        OMLvalues_3 ← Vmn
        OMLvalues_4 ← Vmx
        TotErr ← iError
        OMLvalues_5 ← TotErr
    iErrorLocalBest ← iError   if  iError < iErrorLocalBest
    Vmn ← Vmn + 20
    Vmx ← Vmx + 20
i_Vs ← i_Vs + 1
n ← 10^99   if  iErrorLocalBest > iErrorExit
iErrorExit ← iErrorLocalBest
```

$$\left| \begin{array}{l} \left| \begin{array}{l} iErrorLocalBest \leftarrow 10^{77} \\ n \leftarrow n + 5\cdot 10^{6} \end{array} \right. \\ OMLvalues \end{array} \right.$$

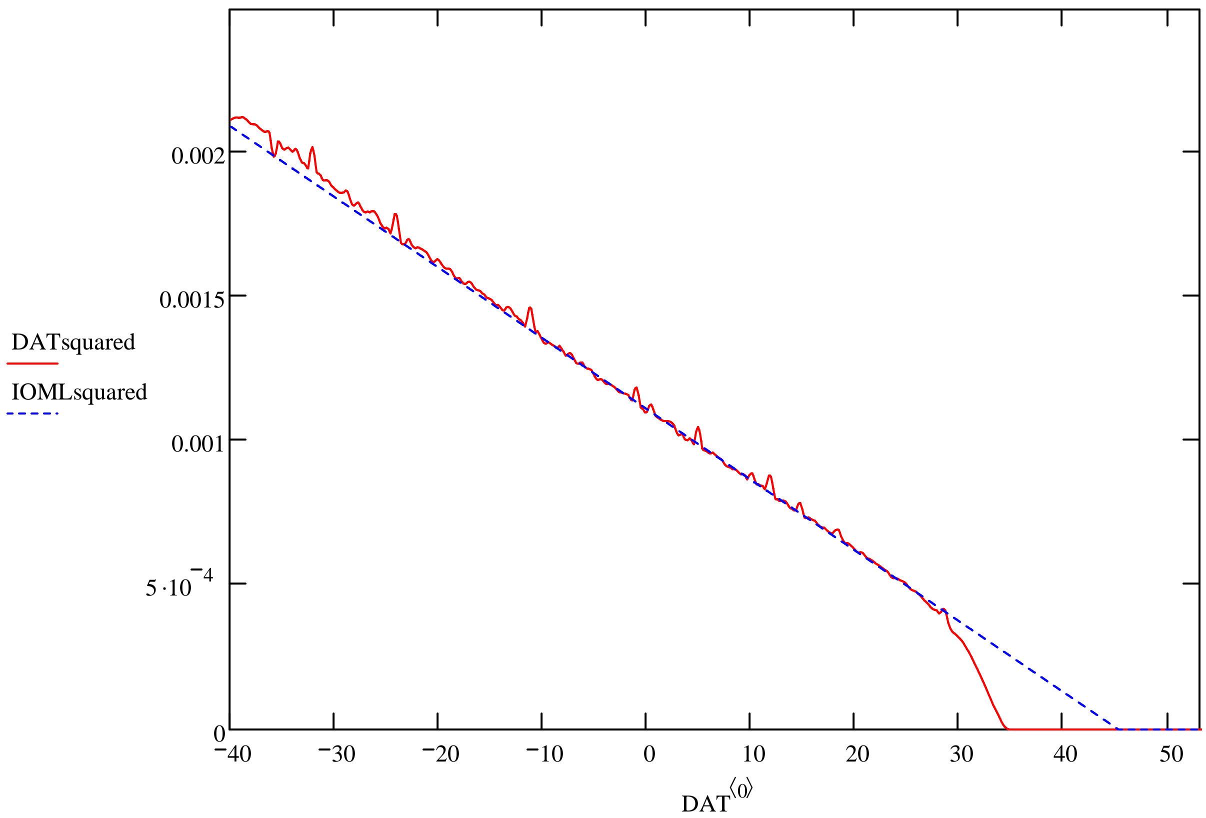
$kTe := OMLvalues_0$ $\quad n := OMLvalues_1$ $\quad i_{Vs} := OMLvalues_2$

$Vmn := OMLvalues_3$ $\quad Vmx := OMLvalues_4$ $\quad TotErr := OMLvalues_5$

$$\eta := \frac{DAT_{i_{Vs},0} - DAT^{\langle 0 \rangle}}{kTe} \qquad IOML := \frac{7.05}{10^{11}}\cdot A_p \cdot n \cdot \sqrt{\eta \cdot \frac{kTe}{AN}}$$

$k := i_{Vs} + 1, i_{Vs} + 2 .. rows\left(DAT^{\langle 0 \rangle}\right) - 1$

$$IOML_k := \left| \begin{array}{l} IOML_k \ \text{ if } \ \eta_{k>0} \\ 0 \end{array} \right. \qquad IOMLsquared := IOML^2$$


DATsquared
IOMLsquared
0.002
0.0015
0.001
5·10^−4
0
−40
−30
−20
−10
0
10
20
30
40
50
DAT⟨0⟩

$$DAT_elecurr^{\langle 0 \rangle} := DAT^{\langle 0 \rangle}$$

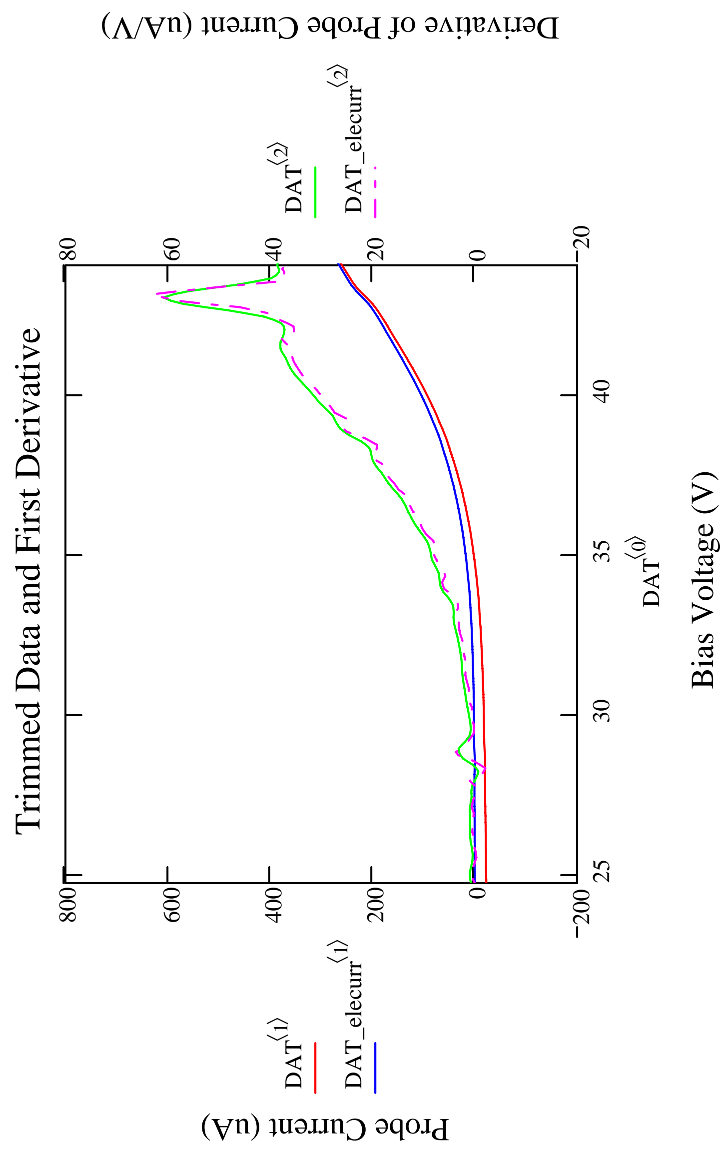
$$DAT_elecurr^{\langle 1 \rangle} := DAT^{\langle 1 \rangle} + IOML \cdot 10^{3}$$

$$iondx := 2, 3 .. rows(DAT) - 3$$

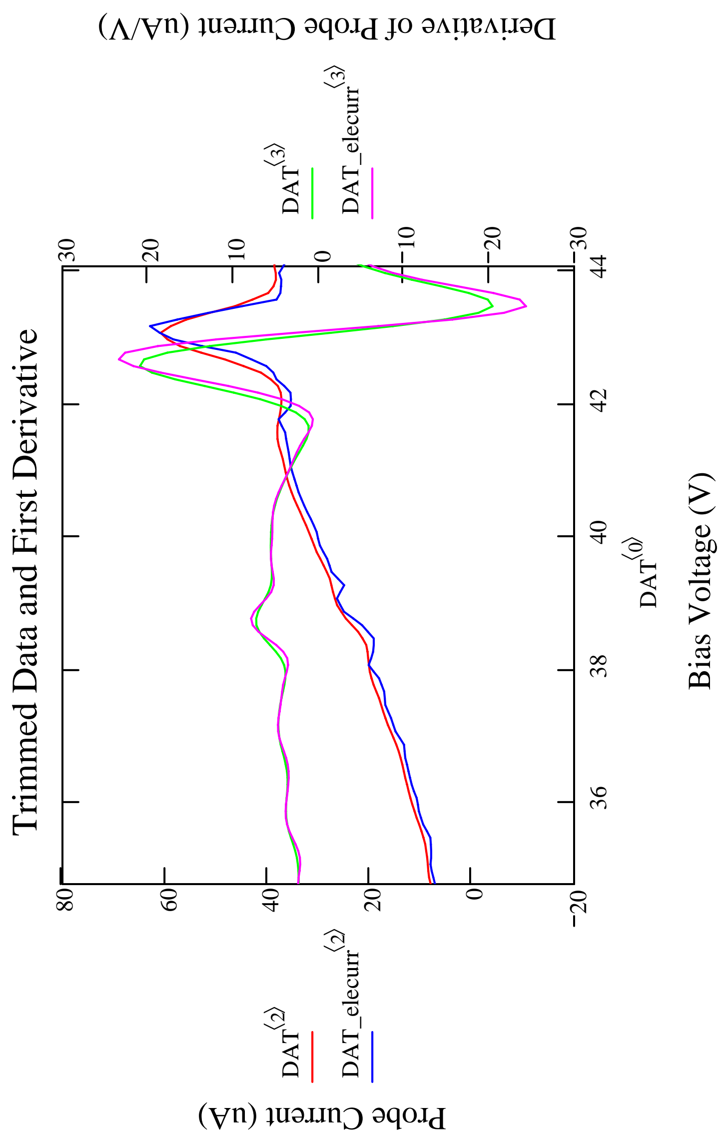
$$DAT_elecurr_{iondx, 2} := \frac{1}{12 \cdot dV} \cdot \left(-DAT_elecurr_{iondx+2, 1} + 8\, DAT_elecurr_{iondx+1, 1} - 8 \cdot DAT_elecurr_{iondx-1, 1} + DAT_elecurr_{iondx-2, 1} \right)$$

$$DAT_elecurr_{iondx, 3} := \frac{1}{12 \cdot dV^{2}} \cdot \left(\begin{array}{l} -DAT_elecurr_{iondx+2, 1} + 16\, DAT_elecurr_{iondx+1, 1} - 30 \cdot DAT_elecurr_{iondx, 1} \cdots \\ + 16 \cdot DAT_elecurr_{iondx-1, 1} - DAT_elecurr_{iondx-2, 1} \end{array} \right)$$

$$DAT_elecurr^{\langle 3 \rangle} := ksmooth\left(DAT^{\langle 0 \rangle}, DAT_elecurr^{\langle 3 \rangle}, \frac{secderivsmoothvolts}{2} \right)$$



Trimmed Data and First Derivative
Probe Current (uA)
Derivative of Probe Current (uA/V)
Bias Voltage (V)
DAT⟨0⟩
DAT⟨1⟩
DAT_elecurr⟨1⟩
DAT⟨2⟩
DAT_elecurr⟨2⟩


Trimmed Data and First Derivative
Probe Current (uA)
Derivative of Probe Current (uA/V)
Bias Voltage (V)
$DAT^{\langle 0 \rangle}$
$DAT^{\langle 2 \rangle}$
$DAT_elecurr^{\langle 2 \rangle}$
$DAT^{\langle 3 \rangle}$
$DAT_elecurr^{\langle 3 \rangle}$
80
60
40
20
0
−20
30
20
10
0
−10
−20
−30
36
38
40
42
44

recorrect Ap

$$A_p := \frac{A_p}{10000}$$

Find the index of Vp

If you don't like that Vp, pick another one...

This is the plasma potential

Create an EEPF and EEDF of the ELECTRON current based on the second derivative and the found VP

$EERange := V_P - V_F$ How many volts the EEPF and EEDF extend out (default is to Vp-Vf)

$EERange = 8.3$ $\quad EERange := 20$ Change it here if the defaults aren't what you want

$$idx_{EEmin} := i_{Vp} - \frac{EERange}{dV}$$

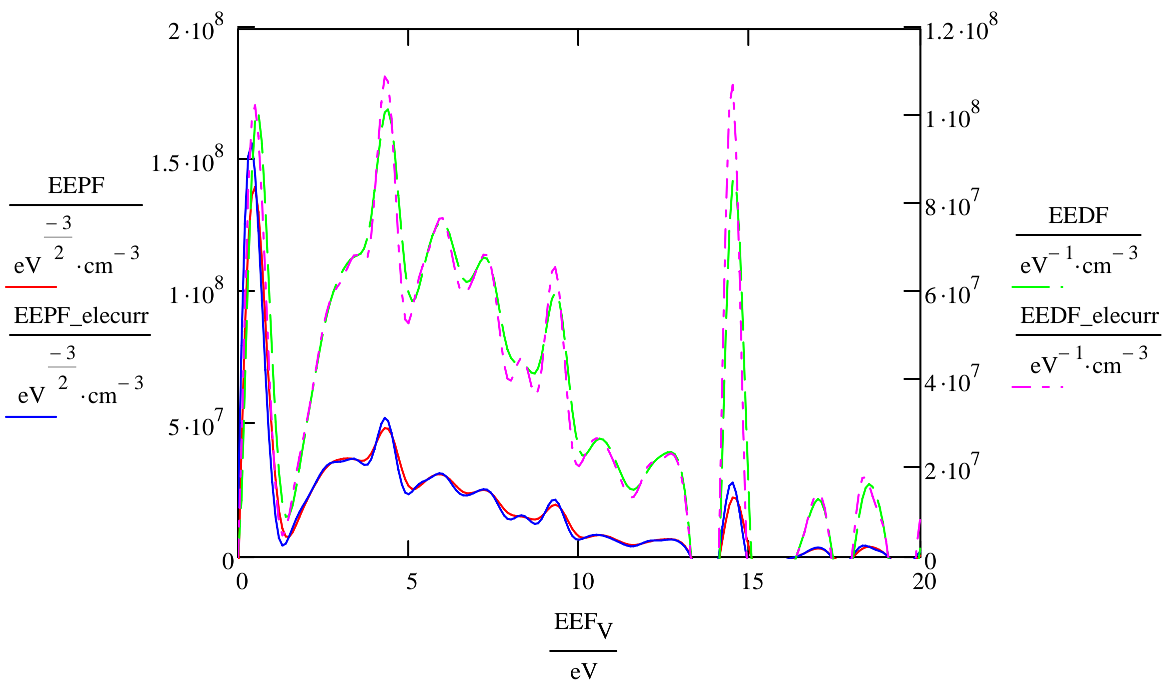
$$EEF_elecurr_V := \left(-\text{submatrix}\left(DAT_elecurr, idx_{EEmin}, i_{Vp}, 0, 0\right) + V_P\right)\cdot eV \qquad EEF_elecurr_V := \text{reverse}\left(EEF_elecurr_V\right)$$

$$EEPF_elecurr := 2\cdot\frac{\sqrt{2\cdot m_e}}{q_e^{\,3}\cdot A_p\cdot m^2}\cdot\text{submatrix}\left(DAT_elecurr, idx_{EEmin}, i_{Vp}, 3, 3\right)\cdot\frac{\mu A}{V^2}$$

$EEPF_elecurr := \overrightarrow{EEPF_elecurr}$ $\quad EEPF_elecurr := \text{reverse}(EEPF_elecurr)$ Manipulate EEPF to get it to behave...

$$EEDF_elecurr := \overrightarrow{\left(EEPF_elecurr\cdot\sqrt{EEF_elecurr_V}\right)}$$

Note that both the EEPF and EEDF shouldn't have any negative values, so if the values are negative, we switch them to zero.



Try and find an equivalent kTe from the EEDF

Integrate the EEDF both with and without multiplying it by the voltage...

$$\text{qIntegral_elecurr}_{\text{EEDF}}(\varepsilon_{\text{min}}) := \left[\sum_{m=\text{floor}\left(\frac{\varepsilon_{\text{min}}}{dV}\right)}^{\text{rows(EEDF_elecurr)}-2}\left[\frac{1}{2}\cdot\left(\text{EEDF_elecurr}_m + \text{EEDF_elecurr}_{m+1}\right)\left(\text{EEF_elecurr}_{V_{m+1}} + -\text{EEF_elecurr}_{V_m}\right)\right]\right]$$

$$\text{qWghtedIntegral_elecurr}_{\text{EEDF}}(\varepsilon_{\text{min}}) := \sum_{m=\text{floor}\left(\frac{\varepsilon_{\text{min}}}{dV}\right)}^{\text{rows(EEDF_elecurr)}-2}\left[\frac{1}{4}\cdot\left(\text{EEDF_elecurr}_m + \text{EEDF_elecurr}_{m+1}\right)\left(\text{EEF_elecurr}_{V_{m+1}} + -\text{EEF_elecurr}_{V_m}\right)\cdot\left(\text{EEF_elecurr}_{V_{m+1}} + \text{EEF_elecurr}_{V_m}\right)\right]$$

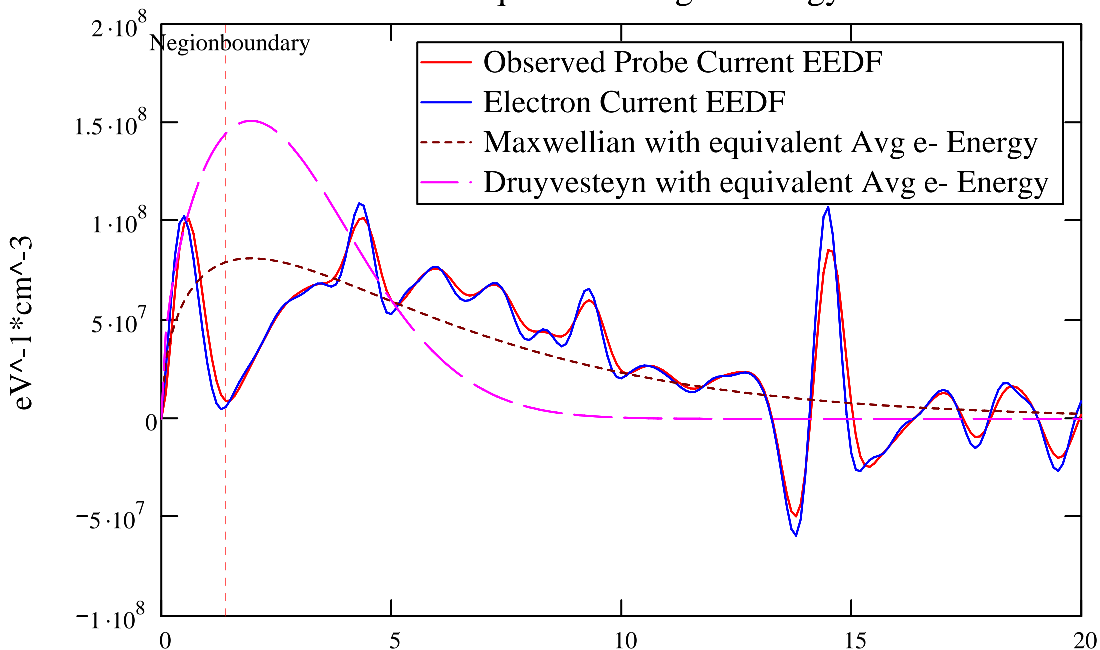
$\text{qIntegral_elecurr}_{\text{EEDF}}(0) = 6.36 \times 10^{8}\,\text{cm}^{-3}$ $\text{qWghtedIntegral_elecurr}_{\text{EEDF}}(0) = 3.67 \times 10^{9}\,\text{eV}\cdot\text{cm}^{-3}$

$\text{Avg_elecurr}_{\text{EE}} := \frac{\text{qWghtedIntegral_elecurr}_{\text{EEDF}}(0)}{\text{qIntegral_elecurr}_{\text{EEDF}}(0)}$ $\text{Avg_elecurr}_{\text{EE}} = 5.77\,\text{eV}$

$\text{kTe_elecurr}_{\text{equiv}} := \frac{2}{3}\cdot\text{Avg_elecurr}_{\text{EE}}$ $\text{kTe_elecurr}_{\text{equiv}} = 3.846\,\text{eV}$

$\text{N_elecurr}_e := \text{qIntegral_elecurr}_{\text{EEDF}}(0)$ $\text{N_elecurr}_e = 6.36 \times 10^{8}\,\text{cm}^{-3}$

$\text{Negionboundary} = 1.4$



$$Excel3 := augment\left(\frac{kTe_{equiv}}{eV}, \frac{N_e}{cm^{-3}}, \frac{2}{3}\frac{qWghtedIntegral_{EEDF}(Negionboundary)}{qIntegral_{EEDF}(Negionboundary)\cdot eV}, \frac{qIntegral_{EEDF}(Negionboundary)}{cm^{-3}}, \frac{N_e}{cm^{-3}} - \frac{qIntegral_{EEDF}(Negic}{cm^{-3}}\right.$$

Excel3 =

	0	1	2	3	4	5	6	7	8	9	10
0	3.903	6.561·108	4.346	5.82·108	7.408·107	34.75	43.05	1.4	3.846	6.36·108	4.28

$n_{low} = 9.594 \times 10^8$ $n_{high} = 1.201 \times 10^9$