

# **Diagnostic Studies of Silicon and Silicon Dioxide Etching in Fluorine and Chlorine-Containing Inductively Coupled Plasmas**

by

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## Abstract

Plasma etching processes are widely used to produce patterns in the fabrication of microelectronic devices. The recent development of micro-/nano- technologies for micro-electro-mechanical systems, as well as the reduction of critical dimensions in transistors towards 7 nm and below, has brought out the need to control plasma etching processes. The very severe requirements in terms of etch rate, selectivity, profile control and surface damage caused by ion bombardment have been at the origin of the development of mechanistic studies by means of plasma diagnostics and surface analysis.

In the present study, chemical reaction probabilities, defined as the number of silicon atoms removed per incident fluorine atom, have been investigated in mixtures of  $\text{NF}_3$  and  $\text{SF}_6$  plasmas in an inductively-coupled plasma reactor. Fluorine atom densities were measured by optical emission actinometry, and isotropic etching rates were measured by the degree of undercutting of  $\text{SiO}_2$ -masked silicon, using cross-sectional scanning electron microscopy (SEM). The F atom reaction probabilities derived from isotropic etching rates indicate a  $\sim 30$ -fold higher reaction probability in  $\text{SF}_6$  plasmas compared with values in  $\text{NF}_3$  plasmas. This surprising enhancement of reaction probabilities for F with Si in  $\text{SF}_6$  plasmas is further investigated based on the mechanism of adsorbed sulfur acting as a catalyst to greatly enhance the etching rate of Si.

Further, we discussed the use of glow discharge optical emission spectroscopy (GD-OES) for in-situ, real-time characterization of surfaces exposed to plasmas. A small coupon piece was mounted on an rf-biased electrode and inserted into an opening in the reactor wall. Silicon or  $\text{SiO}_2$  substrates on a separately rf-biased electrode were etched in

an inductively-coupled plasma (ICP) of  $\text{Cl}_2/\text{Ar}/\text{O}_2$  or  $\text{C}_4\text{F}_8/\text{O}_2$ , respectively. Pulsed bias was applied to sputter the surface of the coupon piece. Optical emission from the region above the coupon surface was collected and spectrally resolved. The difference in intensity between the coupon bias on and off condition was used to determine what species were present on the surface. A quantification method for converting emission intensities into atomic composition depth profiles is presented.

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## **Chapter 1 – Introduction**

### **1.1 Plasma etching in semiconductor industry**

In 1965, Gordon E. Moore - co-founder of Intel (NASDAQ: INTC) postulated that the number of transistors that can be packed into an integrated circuit will double about every two years. Driven by Moore's law, the feature size of the semiconductor devices has shrunk by nearly two orders of magnitude, from 1  $\mu\text{m}$  in the 1980s to 10 nm in 2017<sup>6</sup>. With the help of innovative design in structures such as fin field effect transistors (FinFETs)<sup>7</sup>, 3D NAND (short for NOT AND in Boolean logic) flash memory<sup>8</sup>, through-silicon vias (TSV)<sup>9</sup> and new processing techniques, like high dielectric constant (so-called high k) metal gate, multi patterning, atomic layer etching (ALE)<sup>10-14</sup>, Moore's law has governed the semiconductor industry from 1965 to today, shown in Fig. 1.1.



diffraction limit, plasma processes have been called upon to trim photoresist line widths<sup>16</sup> and allow doubling and tripling of pattern densities<sup>17</sup>. Even with extreme ultra-violet lithography (EUV) at 13.5 nm beginning to be used for state-of-the-art device manufacturing<sup>18</sup>, plasma etching continues to provide the equally critical pattern transfer steps.

Plasma etching occurs as a sequence of three surface reactions, namely, adsorption, reaction, and desorption<sup>19</sup>. This atomic scale cycle occurs sequentially in plasma etching. Isotropic or chemical etching (Fig. 1.2a) is carried out by chemically reactive neutral species, such as radicals. Neutral species do not have any directionality, so they can etch equally in all directions undercutting the mask (e.g., etching of Si by F atoms). The sputtering process (Fig. 1.2b) represents the ejection of surface atoms induced by positive ion bombardment (e.g.,  $\text{Ar}^+$ )<sup>2</sup>. This is a physical rather than a chemical mechanism, and has very low selectivity. For ion energies of interest, the etch rate due to sputtering is given by

$$ER_s = Y_s \frac{J_+}{\rho_s}, \quad (1.2)$$

where  $Y_s$  is the sputtering yield (atoms of substrate removed per incident ion),  $J_+$  is the ion flux, and  $\rho_s$  is the density of the substrate material. Reactive ion etching (RIE) is performed by radicals and directional energetic ion bombardment (Fig. 1.2c). The total etch rate is equal to the sum of the three mechanisms. These processes are depicted in Fig. 1.2.

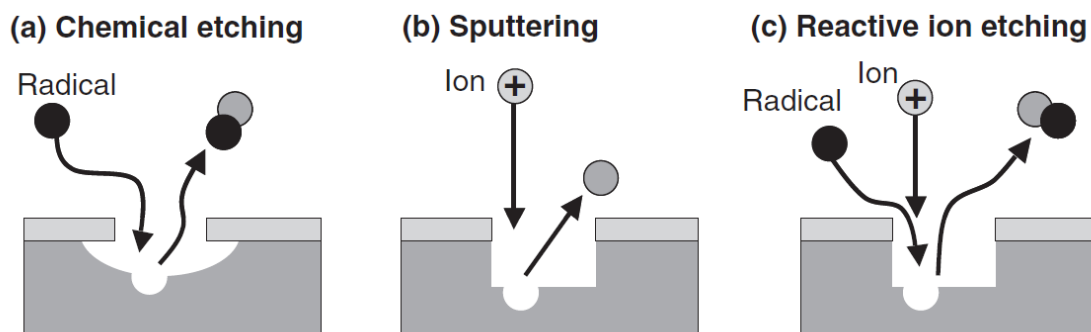


FIG. 1.2. Basic etching mechanisms : (a) chemical etching<sup>1</sup>, (b) sputtering<sup>2</sup>, and (c) reactive ion etching (RIE)<sup>1,3</sup>.

The mechanism of ion-enhanced etching of silicon was first elucidated in the well-known experiment by Coburn and Winters<sup>20</sup>, shown in Fig. 1.3. The etching rate of poly-Si was monitored as first (0–200 s) a flux of the very reactive gas  $\text{XeF}_2$  was directed onto the Si. Then at 200 s, a 450 eV  $\text{Ar}^+$  beam was turned, while leaving the  $\text{XeF}_2$  on. Finally at 660 s the  $\text{XeF}_2$  gas is turned off leaving just the  $\text{Ar}^+$  beam on. The fact that the etch rate with both beams incident on the Si surface is much greater than the sum of the etch rates observed with the two beams separately, clearly demonstrates the synergism between the ion beam and the reactive neutral species. Subsequently, numerous studies have focused on the synergistic effect of ions and radicals<sup>21–26</sup> to simulate the ion enhanced surface reactions.

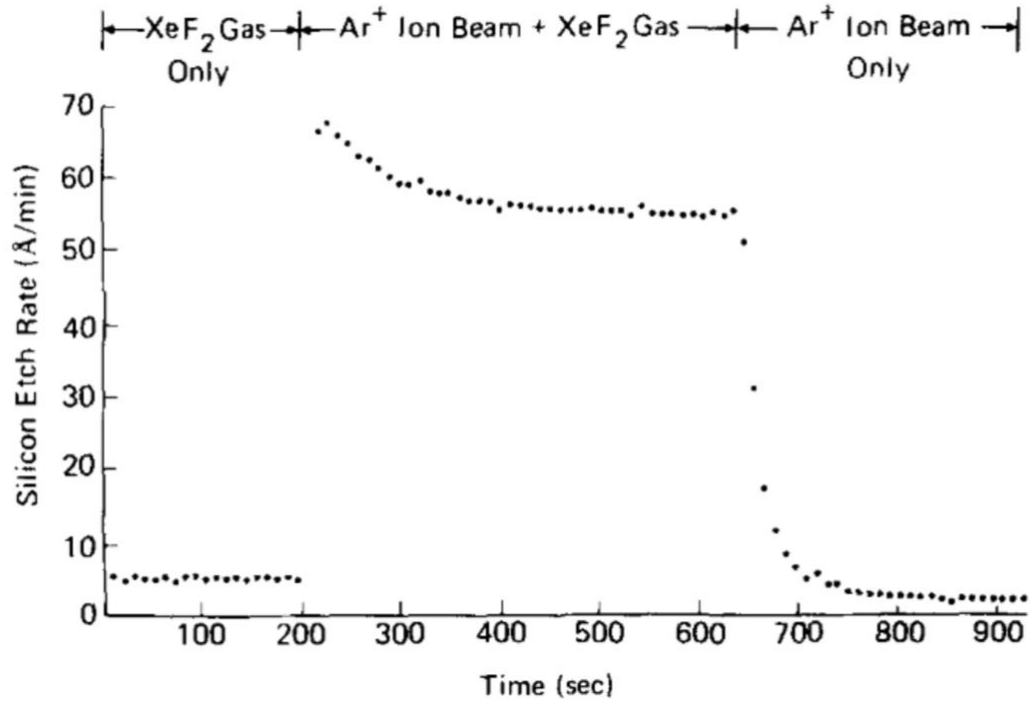


FIG. 1.3. Ion-assisted gas-surface chemistry using Ar<sup>+</sup> and XeF<sub>2</sub> on silicon.

## 1.2 Inductively and capacitively coupled plasma

Early on, etching was primarily done using capacitively-coupled plasma (CCP) reactors<sup>27-29</sup>. Power at radio frequency (rf), often at 13.56 MHz, was applied to one of two parallel electrodes, while the other electrode (often the chamber walls) was grounded. In the most common reactor configuration, the substrate electrode had a smaller area compared to the grounded electrode. A negative dc self-bias voltage was developed on the substrate electrode, causing energetic positive ion bombardment of the substrate, promoting anisotropic etching<sup>2,6,7</sup>. More recently, dual frequency CCP reactors were developed, with high frequency power (typically 10 to 100 MHz) applied to the upper electrode to control the plasma density, and low frequency power (typically less than 10

MHz applied to the lower substrate electrode to control the ion energy by generating high-voltage sheaths on the lower electrode that holds the wafer.<sup>28</sup> These are considered moderate-density discharges. High-density discharges are produced by inductively coupled plasmas (ICP)<sup>28</sup>. ICP reactors deliver rf power to the plasma through a dielectric barriers such as a flat window<sup>28</sup>. These systems exhibit low-voltage sheaths adjacent to bounding surfaces, including the wafer<sup>28</sup>. This allows for better ion energy control by providing separate rf power to the substrate electrode<sup>28</sup>. Higher etching rates and better selectivity can be achieved with ICPs<sup>28</sup> compared to CCP reactors.

### **1.3 Plasma-surface interactions**

Plasma-surface interactions are an important yet poorly understood and controlled aspect of plasma science and technology. In plasma etching, materials exposed to the plasma are often inadequate in that they erode too fast, resulting in an uncontrolled drift in chamber surface chemistry<sup>30, 31</sup>. Even with an inert chamber wall surface, the surface chemistry can still change over time by deposition of etching byproducts. For example, the silicon oxy-chloride layers that deposit on chamber walls during Si etching not only changes the heterogeneous reaction rate over time, but also can flake off and contaminate the wafer. These effects usually require a chamber-cleaning plasma step before each etching process. Plasmas containing NF<sub>3</sub>, SF<sub>6</sub> and CF<sub>4</sub>/O<sub>2</sub> are commonly used. By performing brief plasma cleans in the absence of the wafer (typically a few minutes or less), the chamber walls are restored to the same state before each wafer is etched, improving wafer-to-wafer reproducibility. However, this clean process is always

conducted in corrosive gases-based plasmas, which will also modify the reactor surface. Therefore, drift of plasma processing between cleaning and etching still exists. Changes of chamber wall conditions can occur over short (seconds) to long (days) time scales in high-throughput industrial etching reactors.

Plasma surface interactions can be investigated by both *in situ* and *ex situ* methods. For *in situ* methods, surface reaction information can be gathered from either surface measurement (*directly*) or bulk plasma (*indirectly*). On one hand, surface layers on reactor walls have been detected *directly* by multiple total internal reflection Fourier transform infrared (MTIR-FTIR)<sup>31-34</sup>, spectroscopic ellipsometry (SE), and laser-induced thermal desorption (LD-LIF/LD-PIE)<sup>35-38</sup>. On the other hand, surface information can also be acquired *indirectly* by analyzing bulk plasma composition, like optical emission spectroscopy (OES) and broadband absorption spectroscopy<sup>39-43</sup>. For *ex situ* methods, typical surface analysis can be carried out by X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES).

## 1.4 Power modulated plasma

Power-modulated plasmas are increasingly being used in etching and deposition processes for manufacturing of semiconductor devices<sup>28, 44</sup>. They will likely continue to emerged as increasingly important methods to address the formidable challenges of fabricating future generations of micro-devices. Square wave modulation, shown in Fig. 1.4, is most frequently used. The duration of the power ON fraction of the cycle (active glow) is  $\tau_{ON}$ , while that of the power OFF fraction of the cycle (afterglow) is  $\tau_{OFF}$ . The

pulse period is  $\tau_P = \tau_{ON} + \tau_{OFF}$ . Usually 100% power modulation depth is applied, the power in the afterglow is zero. Partial power modulation has also been used, for the purpose of measuring the kinetics of plasma-chemical or surface reactions<sup>45, 46</sup>.

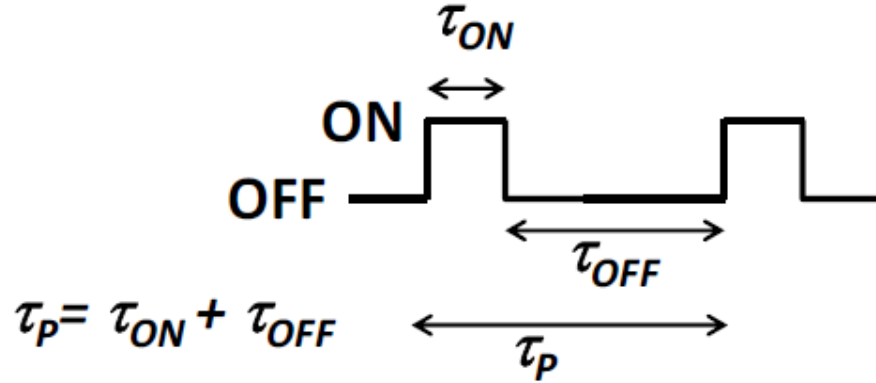


FIG. 1.4. In pulsed plasmas, power is square-wave modulated. Within each pulse, the power is ON for time  $\tau_{ON}$  and OFF for time  $\tau_{OFF}$ . The pulse period is  $\tau_P = \tau_{ON} + \tau_{OFF}$  and the duty ratio is  $\tau_{ON} / \tau_P$ .

There are four common configurations of pulsed plasmas being employed for plasma etching, as shown in Fig. 1.5: (a) modulation of the power that sustains the plasma (source pulsing) with no power on the substrate electrode, (b) modulation of the power that sustains the plasma (source pulsing) with continuous wave (cw) power on the substrate electrode, (c) cw power that sustains the plasma with modulation power on the substrate electrode (bias pulsing), (d) modulation of both the source and bias powers with or without a phase shift between the two (synchronous pulsing).

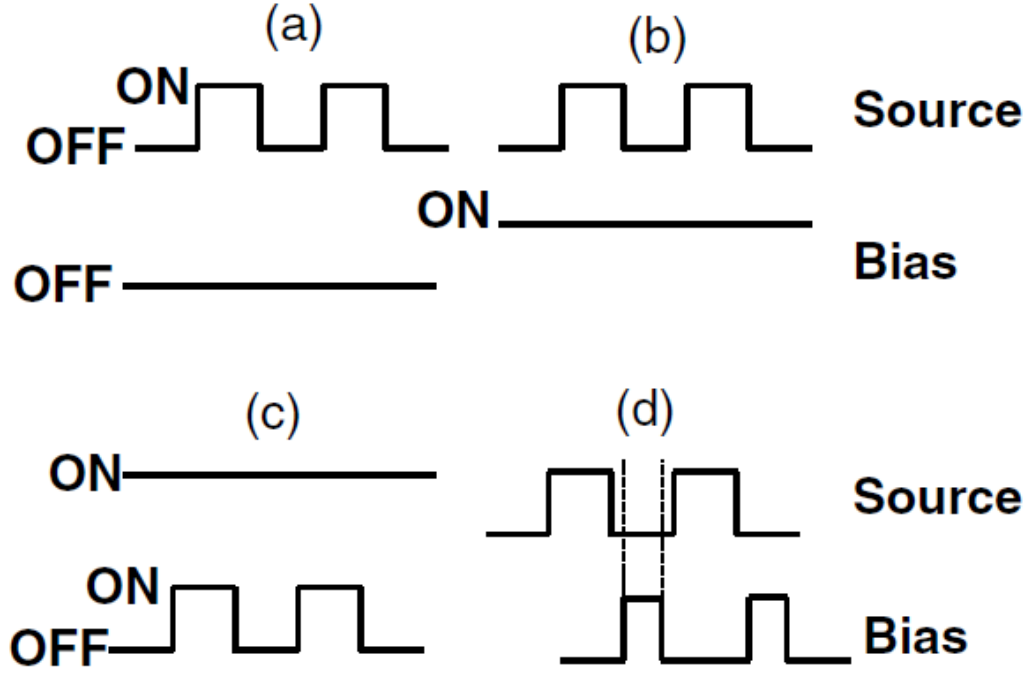


FIG. 1.5. Common pulsed plasma schemes. a) Source pulsing with no substrate bias. b) Source pulsing with cw substrate bias. c) Bias pulsing with cw source power. d) Synchronous source and bias pulsing, where bias power may be phase shifted with respect to source power.

By tuning the operating parameters such as pulse frequency, duty cycle and modulation depth, plasma properties such as electron temperature ( $T_e$ ), electron density ( $n_e$ ), ion energy distribution (IED) and electron energy distribution function (EEDF) can be manipulated, which give more flexibility in etching and deposition processes<sup>4, 47-49</sup>. Pulsed plasmas have been shown to offer some advantages over continuous wave (CW) plasmas in terms of etching rate uniformity and selectivity, as well as less electrical, structural or radiation damage<sup>29, 50</sup>. For example, Samukawa<sup>51</sup> has demonstrated that by pulsing the power to a  $\text{CHF}_3$  electron cyclotron resonance plasma, selectivity of  $\text{SiO}_2$  etching over Si is enhanced. The selectivity increase was because of the relative increase of  $\text{CF}_2$ . Shin *et al.*,<sup>52</sup> have employed pulsed plasmas to obtain nearly monoenergetic ion energy distributions (IEDs) for improved control of ion-bombardment-stimulated

processes, especially near the energy threshold. Samukawa has also shown that pulsed chlorine containing plasmas have better selectivity and anisotropy with less damage in Si etching<sup>53</sup>. Ahn *et al.*, suggested that pulsed electronegative plasmas can suppress undesirable etching anomalies (such as notching or bowing), attributed to injection of negative ions into the bottom of the features to neutralize accumulated positive charge<sup>54</sup>.

Pulsed plasma with partial depth modulation (i.e., rapid switching from high to low power) can have advantages over more commonly studied fully modulated pulsed plasmas<sup>55</sup>. The principle is that negative ions can escape during the afterglow of fully modulated plasmas but remain confined by the sheath of a weak afterglow plasma during partial-depth power modulation. For example, Courteille and co-workers<sup>55</sup> have shown that the sheath does not collapse and anions cannot escape unless the modulation depth of the rf voltage exceeds  $\sim 85\%$ . Power modulation can affect not only the relative concentration of radicals, but also the spatial distribution of these radicals in the plasma reactor. For example, as the gas flows through the plasma, the gas is depleted by electron-impact dissociation. As a result, the etch or deposition rate can vary greatly along the flow path of the gas<sup>56</sup>. Power modulation can be used to alleviate these rate variations and therefore improve uniformity.

## 1.5 Plasma diagnostic technique - OES actinometry

OES is the dominant optical diagnostic tool for plasma applications. The equation that governs optical emission is,

$$I_{X,i,j,k} = 4a(\lambda_{X,j,k})n_XQ_{X,k}b_{X,j,k}\int_0^\infty \sigma_{X,i,k}(v)v^3f_e(v)dv, \quad (1.3)$$

where the emission intensity of a given species ( $I_{X,i,j,k}$ ) depends on the number density of the ground state of the species  $n_x$ , but also other terms such as the quantum yield ( $Q_{x,k}$ ), the branching ratio ( $b_{x,j,k}$ ) and an integral over the electron energy distribution function (EEDF). Many of the parameters within equation (1.3) are not well known, therefore number density cannot be extracted from simple optical emission measurements. The most common way to address this problem and derive relative and even absolute number densities of species from optical emission is through actinometry<sup>57, 58</sup>. The technique of actinometry involves the injection of a small amount of inert gas into the reactor, typically a noble gas such as Xe, Ar, or Kr. The amount of gas added should be small enough such that the plasma is only minimally perturbed. If one chooses an inert gas that has a similar electron energy dependence of the relative excitation cross section, then the integral over the EEDF in equation (1.3) can be cancelled out, and a much simpler expression for number density can be obtained,

$$n_X = a_{X,A} n_A \left( \frac{I_{X,i,j,k}}{I_{A,i,j,k}} \right), \quad (1.4)$$

where  $n_A$  is the number density of the inert gas, which is known and not changing with time, and  $a_{X,A}$  is a calibration factor that encompasses all the parameters in Eq. (1.3) for both the species of interest and the rare gas. Another assumption in Eq. (1.4) is that the emission of the species is due to electron impact excitation and no other process.

Although OES actinometry is a very powerful and minimally invasive plasma diagnostic, it has some disadvantages that make its application for quantitative determination of relative and absolute number densities possible for only a small number of species. The first assumption that is difficult to meet for most species is that the

excitation energy dependencies of the actinometer gas and the species are similar. For example, the actinometer gas for measuring Cl number density is Xe because the excitation energy threshold of Cl is 10.50 eV and that of Xe is 9.94 eV<sup>58</sup>. If one were to try and measure SiCl, SiCl<sub>2</sub>, or SiCl<sub>3</sub> number density using the actinometer gas of Xe, the energy mismatch between these species would likely cause a large error in the measured number density, if the electron energy distribution is changing under varying plasma conditions (e.g., changes in pressure).

## 1.6 Dissertation outline

In this dissertation, five independent studies on fluorine and chlorine containing gas chemistries are presented. First, the series of experiments shown in chapter 2 investigate etching SiO<sub>2</sub>-masked silicon in mixed NF<sub>3</sub>/SF<sub>6</sub> plasmas. Optical emission actinometry is applied to monitor F emissions, while Si etching rates are determined from the extent of mask undercutting. In particular, the chapter addresses reaction mechanisms for higher etching rates of silicon with smooth surface morphology in the presence of SF<sub>6</sub> plasmas<sup>5</sup>.

In chapter 3, Glow Discharge-Optical Emission Spectroscopy is developed for *in-situ* characterization of chamber wall surfaces exposed to the plasma. A small coupon piece of aluminum covered with yttria, a common chamber wall coating in reactors used in plasma etching, is mounted on an rf-biased electrode and inserted into an opening in the reactor wall. Silicon or SiO<sub>2</sub> substrates on a separately rf-biased electrode are etched in an inductively-coupled plasma (ICP) of Cl<sub>2</sub>/Ar or C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>, respectively. Pulsed bias was applied to sputter the surface of the coupon piece in the wall at the edge of the ICP, either

during etching in a halogen ( $\text{Cl}_2$ )-containing plasma, or after etching in an Ar ICP. The difference in optical emission intensity between the coupon bias on and off condition is used to determine what species were present on the surface.

Chapter 4 presents the power modulation method to measure recombination coefficients ( $\gamma_{\text{Cl}}$ ) in  $\text{Cl}_2$  and  $\text{Cl}_2/\text{O}_2$  ICPs. Reaction probabilities for Cl to form mainly  $\text{Cl}_2$  are determined by fitting global model predictions to time-dependent Cl number densities measured by actinometry at the beginning and end of the powered portion of the modulation period.

Chapter 5 demonstrates diagnostics of power modulated chlorine plasmas. Time resolved OES, broadband emission detected with a photomultiplier tube (PMT), Langmuir probe (LP) measurements, and power delivery measurements are presented. Two different transients are obtained, one in which no delay occurs and one with a substantial pre-ignition period in the transition from high power to low power, or less commonly from low to high power. This latter mode can have many forms with complex dynamics that can even have periods corresponding to two modulation periods.

The experiments presented in chapter 6 investigate fluorocarbons plasmas and reveal concentrations of different fluorocarbon species using UV absorption spectroscopy. Each of these five projects are detailed with background literature, experimental procedure, and relevant results in separate chapters. The dissertation ends with a brief section summarizing the findings in this dissertation and providing an overview of future directions.

## Chapter 2 – Etching Silicon in Mixtures of NF<sub>3</sub>/SF<sub>6</sub> Plasma

### 2.1 Motivation

Fluorine-containing plasmas generated from gases such as NF<sub>3</sub>, SF<sub>6</sub>, and CF<sub>4</sub>/O<sub>2</sub> are commonly used to etch silicon in applications requiring high etching rates<sup>59-61</sup>. Rapid isotropic chemical etching by F atoms produces mask undercutting<sup>59,60,62</sup>, however, requiring sidewall-passivating gas additives<sup>61,63,64</sup> and/or cryogenic substrate temperatures<sup>65, 66</sup> to suppress this effect. SF<sub>6</sub> plasmas have been found to produce higher etching rates, while tending to leave smoother etched Si surfaces<sup>67-70</sup>. These are essential requirements for most applications, including etching of high aspect ratio features for microelectromechanical system (MEMS) devices through the Bosch process<sup>71</sup>.

Many studies of reaction mechanisms and primary etching products in fluorine containing plasmas have been reported<sup>60, 72-76</sup>. Chemical reaction probabilities ( $\epsilon_F(Si)$ ) of F atoms have been measured by several groups as shown in Fig. 2.1<sup>60, 70, 75-82</sup>. All sources of F except SF<sub>6</sub> fall on a “universal curve” and reflect a large (~30-fold) decrease in the reaction probability with increasing F flux, from 0.03 at a F flux  $10^{12}\text{cm}^{-2}\text{s}^{-1}$  to 0.001 at a flux of  $10^{20}\text{cm}^{-2}\text{s}^{-1}$ <sup>83</sup>. On the other hand, F atoms generated in SF<sub>6</sub> plasmas don’t follow the same trend; they are ~20 to 100-times higher at comparable F fluxes of  $10^{18}$ - $10^{19}\text{cm}^{-2}\text{s}^{-1}$ <sup>83</sup>.

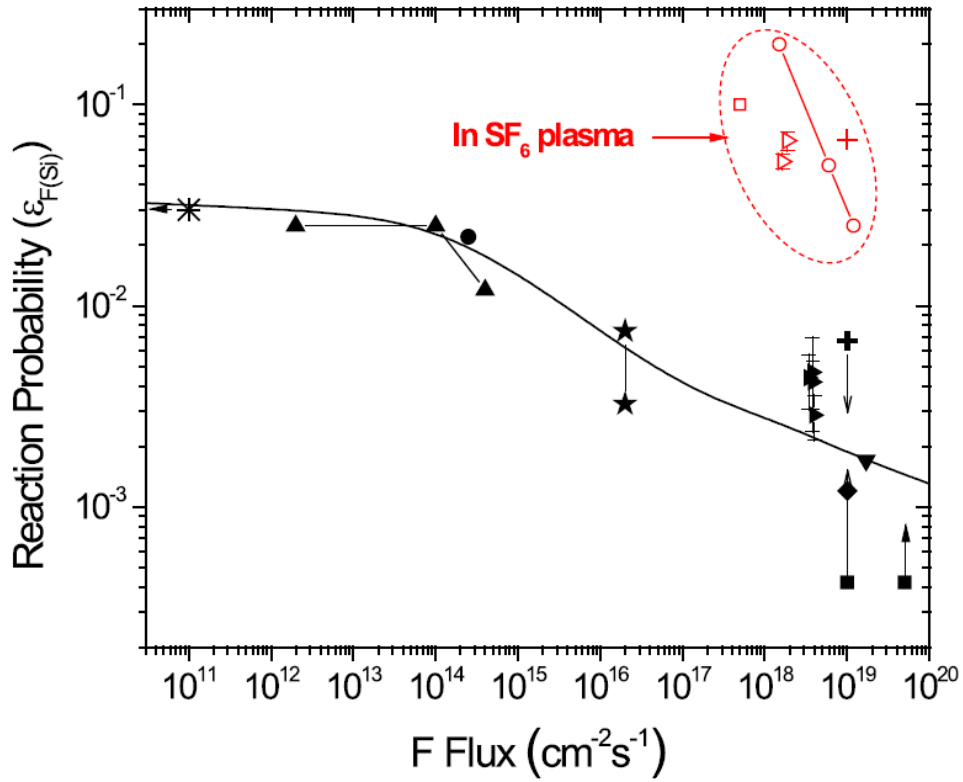


FIG. 2.1. Reaction probabilities, reported by different research groups, plotted as a function of measured or estimated F atom flux. Values measured with  $\text{CF}_4$ ,  $\text{F}_2$ , and  $\text{NF}_3$  sources of beams or plasmas are in solid black. The black line is an “eyeball” fit to all these data. Points labeled ( $\blacktriangleright$ ) and ( $\Delta$ ) are from our lab, using  $\text{NF}_3$  and  $\text{SF}_6$  plasmas, respectively<sup>5</sup>.

In the present study, reaction probabilities of F atoms with Si in the absence of ion bombardment were measured in  $\text{NF}_3/\text{SF}_6/\text{Ar}$  plasmas as a function of  $\text{NF}_3/\text{SF}_6$  ratio<sup>5</sup>. Optical emission actinometry was applied to monitor F emissions along with Si etching rates from mask undercutting. The role of adsorbed sulfur acting as a catalyst was demonstrated as the explanation for the high chemical reaction probabilities. The etched Si surface morphology was examined by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). A mechanism for the enhancement in etching rate and smoothening of the surface by adsorbed sulfur is proposed.

## 2.2 Experimental

A schematic of the experimental reactor, shown in Figure 2.2, has been described in a previous publications from our lab<sup>84, 85</sup>. The inductively coupled plasma (ICP) is generated using a 13.56 MHz radio frequency (RF) source that delivers power through an impedance-matching network to a planar spiral coil above an alumina window. A removable,  $\text{Y}_2\text{O}_3$ -coated Al liner confines the plasma. Openings in the liner allows for optical emission spectroscopy (OES) to be performed, as shown in Fig. 2.2. Radial gas flow is delivered near the top, just below the alumina window. Optical emission spectra were recorded with a spectrometer (Ocean Optics HR4000 with 0.17 nm resolution) that covered the 570–790 nm region. The sample stage was not powered and was grounded in all experiments, thus only low energy ions bombarded the sample.

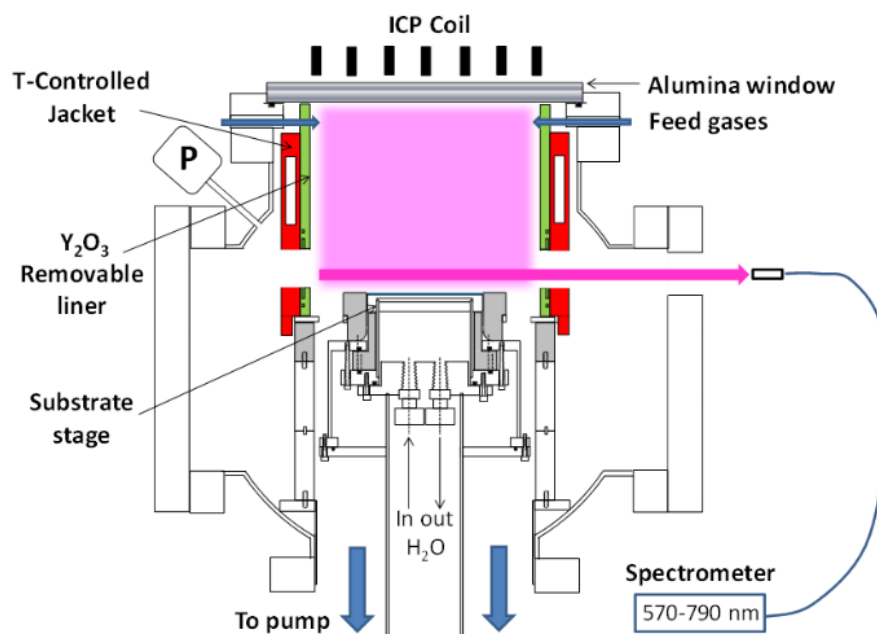


FIG. 2.2. Schematic of the inductively coupled plasma main chamber. The water-cooled, bias able substrate stage was grounded in the present study. Radial pumping is mainly through the open portions of the support structure, not shown in this view. P = capacitance manometer pressure gauge.

8" diam. p-type Si wafers patterned with 1  $\mu\text{m}$  thick  $\text{SiO}_2$  stripes, with 1  $\mu\text{m}$  to 500  $\mu\text{m}$  wide open trenches (NOVATI Technologies INC.) were used to measure etching rates. The pattern consisted of repeated dies (20 mm x 20 mm) of same-size trenches spaced 1  $\mu\text{m}$  to 500  $\mu\text{m}$  from each other. These dies were cleaved from the wafer and pasted onto a 3" diam. Si wafer for each experiment. Samples were etched for typically 5 mins. in a 400 W plasma at 50 mTorr pressure and a total gas flow rate of 50 sccm. Mixtures of  $\text{SF}_6$  and  $\text{NF}_3$  were used in varying ratios. Ar (25 sccm) was added for carrying out actinometry measurements of F-atom number densities.

After etching, samples were cleaved and cross-sections were examined, using scanning electron microscopy (SEM). The isotropic etching rate was calculated by dividing the mask undercut by etching time. Vertical etching rates were also measured, using etched depths at the center of the trench. The isotropic etching rate was used to calculate chemical reaction probabilities,  $\varepsilon_{F(\text{Si})}$ , that can be defined as the number of Si atoms removed per incident F atom in the absence of ion bombardment.  $\varepsilon_{F(\text{Si})}$  is given by<sup>83</sup>

$$\varepsilon_{F(\text{Si})} = \frac{1.667 \times 10^{-10} N_A \rho_{\text{Si}} R_{\text{Si}}}{M_{\text{Si}} [n_F v_F/4]}, \quad (2.1)$$

where,  $N_A$  is Avogadro's number,  $\rho_{\text{Si}}$  and  $M_{\text{Si}}$  are the density and atomic weight of Si, and  $v_F$  is the mean thermal velocity of F. The etching rate ( $R_{\text{Si}}$ ) is in  $\text{\AA}/\text{min}$ . (It is converted into cm/s by multiplying by  $1.667 \times 10^{-10}$ ). F atom number density ( $n_F$ ) was obtained using optical emission actinometry and the expression

$$n_F = a_{F,\text{Ar}} n_{\text{Ar}} \frac{I_F}{I_{\text{Ar}}}, \quad (2.2)$$

where  $I_F$  and  $I_{Ar}$  are the emission intensities, of respectively, the 703.7 nm F line and 750.4 nm Ar line,  $n_{Ar}$  is the number density of Ar added to the feed gas, and  $a_F = 4.1$  is a calibration factor, obtained previously<sup>86</sup>.

In addition to SEMs, atomic force microscopy (AFM) was used to examine Si surface morphology after etching in  $NF_3/SF_6$  plasmas. All AFM measurements were performed on an Asylum Research Cypher ES instrument (Santa Barbara, CA), using a gold coated silicon nitride cantilever. AFM images were collected in tapping mode to minimize tip–substrate contact. Root mean square (RMS) roughness of etched Si surfaces was obtained by measurements of multiple  $1\ \mu m^2$  scanned areas.

## 2.3 Results and Discussion

### 2.3.1 – Si etching rate and F flux in mixed $NF_3/SF_6$ plasmas

Fig. 2.3 shows cross section SEM images of masked features etched for 5 min. in  $NF_3/Ar$  (Fig. 2.3a, 10  $\mu m$  features) or  $SF_6/Ar$  (Fig. 2.3b, 50  $\mu m$  features) plasmas. The mask was found to be undercut by 500 nm for  $NF_3/Ar$ , and 6000 nm for  $SF_6/Ar$  plasmas, corresponding to etching rates of 1000 and 12000  $\text{\AA}/\text{min}$ , respectively. Similar large vertical etching rates were found for  $SF_6/Ar$  vs.  $NF_3/Ar$  plasmas (15650 vs. 2000  $\text{\AA}/\text{min}$ , respectively).

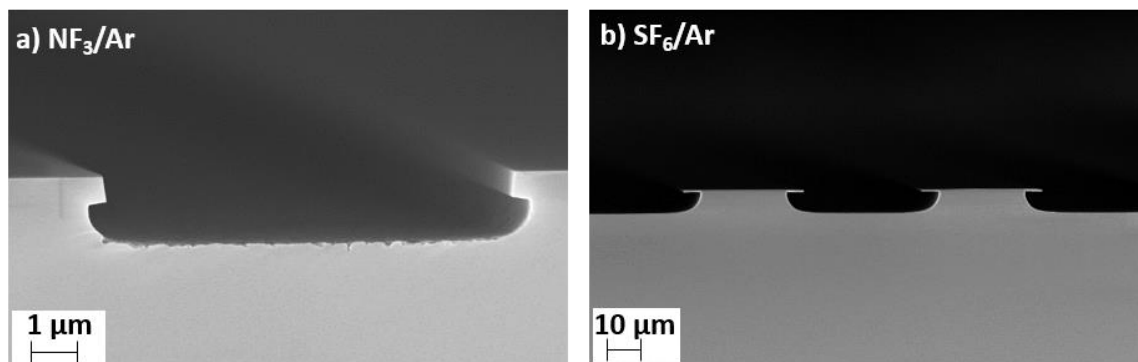


FIG. 2.3. SEM micrographs of SiO<sub>2</sub>-mask Si patterned samples after etching in a) NF<sub>3</sub>/Ar and b) SF<sub>6</sub>/Ar plasmas. Flow rates: NF<sub>3</sub>:Ar = 25:25 sccm, SF<sub>6</sub>:Ar = 25:25 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min.

Fig. 2.4(a) presents both isotropic and vertical etching rates as a function of NF<sub>3</sub>:SF<sub>6</sub> ratio. The Ar flow was kept constant at 25 sccm. As the percentage of SF<sub>6</sub> increased from 0 to 30%, the isotropic etching rate increased ~12-fold, with further additions of SF<sub>6</sub> having little effect. A similar effect was found for the vertical etching rate, though the difference was less severe. As shown in Fig. 2.4(b), fluorine number density *decreased* with increasing addition of SF<sub>6</sub>, counter to the etching rates trends. Subtracting the horizontal rate from the vertical rate yields the small ion-assisted etching component for the low-energy ion bombardment condition with no stage bias. Within the scatter of the measurements, there was no apparent dependence of the ion-assisted etching rates on the NF<sub>3</sub>:SF<sub>6</sub> ratio.

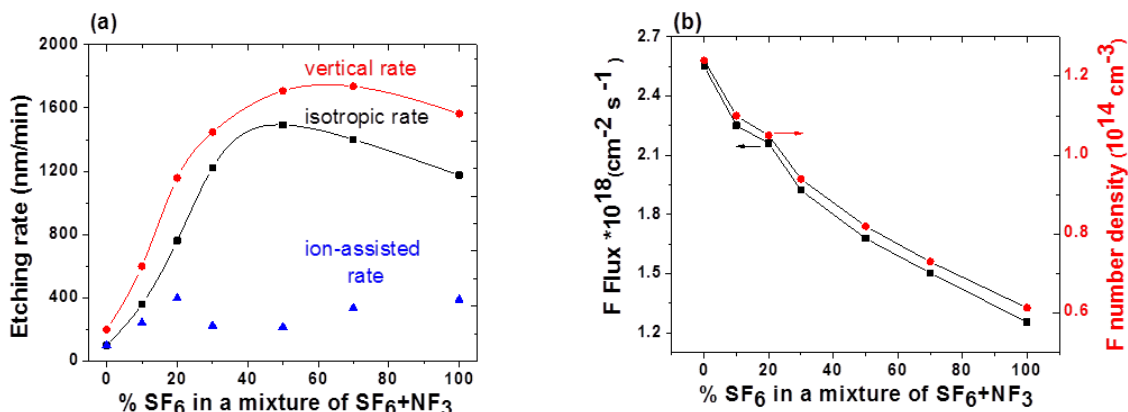


FIG. 2.4. Etching results in the absence of stage bias. Total flow = 50 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min. (a) isotropic and vertical etch rates vs % of SF<sub>6</sub> gas in a mixture of NF<sub>3</sub>/SF<sub>6</sub> plasma, (b) F number density and flux (at an assumed constant gas temperature of 600 K) vs % of SF<sub>6</sub> gas in a mixture of NF<sub>3</sub>/SF<sub>6</sub>.

### 2.3.2 – Reaction probabilities for F atoms with Si in NF<sub>3</sub>/SF<sub>6</sub>/Ar plasmas

Isotropic reaction probabilities defined by eqn. (2.1), derived from the data in Fig. 2.4, are presented in Fig. 2.5. Values range from ~0.003 in a NF<sub>3</sub>/Ar plasma to ~0.08 in a SF<sub>6</sub>/Ar plasma. Addition of only 10% SF<sub>6</sub> to an NF<sub>3</sub> plasma produced a ~5-fold increase in reaction probability. Beyond ~50% SF<sub>6</sub> addition, a constant  $\varepsilon_{F(Si)}$  was observed.

As addressed recently, the wide range in reported values for  $\varepsilon_{F(Si)}$  (0.00042 to 0.2) has been ascribed to two effects<sup>83</sup>. First, when CF<sub>4</sub>, F<sub>2</sub> or NF<sub>3</sub> plasmas are the source of F-atoms,  $\varepsilon_{F(Si)}$  follows a universal trend of decreasing with F flux. Second, the very high values for  $\varepsilon_{F(Si)}$  are all for cases where the source of F-atoms was a SF<sub>6</sub> plasma. The mechanism proposed for this surprising enhancement of reaction probabilities for F with Si in SF<sub>6</sub> plasmas is the role of adsorbed sulfur, acting as a catalyst to greatly enhance the F etching reaction with Si<sup>83</sup>.

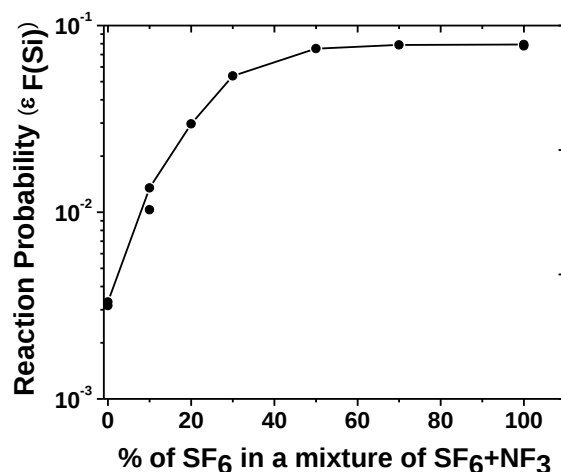


FIG. 2.5. Isotropic reaction probabilities of F atom with Si, vs % of SF<sub>6</sub> gas in a mixture of NF<sub>3</sub>/SF<sub>6</sub>. Total flow = 50 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min.

This latter mechanism is further investigated in the present study. Dilute solutions of sulfur in isopropyl alcohol were allowed to evaporate on the masked Si samples. Surface tension caused the solution to evaporate last at the line edges. The final stage of solvent evaporation resulted in  $\sim 2\ \mu\text{m}$  diameter periodic “strings of beads” forming along the mask edge, depositing the highest concentrations of sulfur in these regions. When this sample was placed side by side with one not exposed to sulfur, and then etched in a NF<sub>3</sub>/Ar plasma, hemispherical volumes of Si were etched away in the regions of highest sulfur coverage, one of which is labelled as point **A** in the SEM images in Fig. 2.6. Using edge-on SEMs (not shown), reaction probabilities for the sulfur-dosed sample were estimated in several ways. First, the maximum range in the degree of undercutting of the mask was measured, yielding  $\varepsilon_{F(Si)} = 0.0052\text{--}0.0087$ . (The sulfur-free surface exhibited the expected slower isotropic rate, with  $\varepsilon_{F(Si)} = 0.0018$ .) Second, the vertical etched depth indicated by point **A** in Fig. 2.6 was determined from a number of edge-on cleaved samples. From this depth was subtracted the ion-assisted etching component (from Fig. 2.4a for pure NF<sub>3</sub> plasmas).

The remaining chemical etching component was used to obtain  $\epsilon_{F(Si)} = 0.0053\text{-}0.0087$ . Using the latter procedure, the flat region far from the mask edge (point **B** in Fig. 2.6), where much less sulfur was left by the IPA solution, as surface tension caused it to be drawn to the line edges, was used to obtain  $\epsilon_{F(Si)} = 0.0029$ .

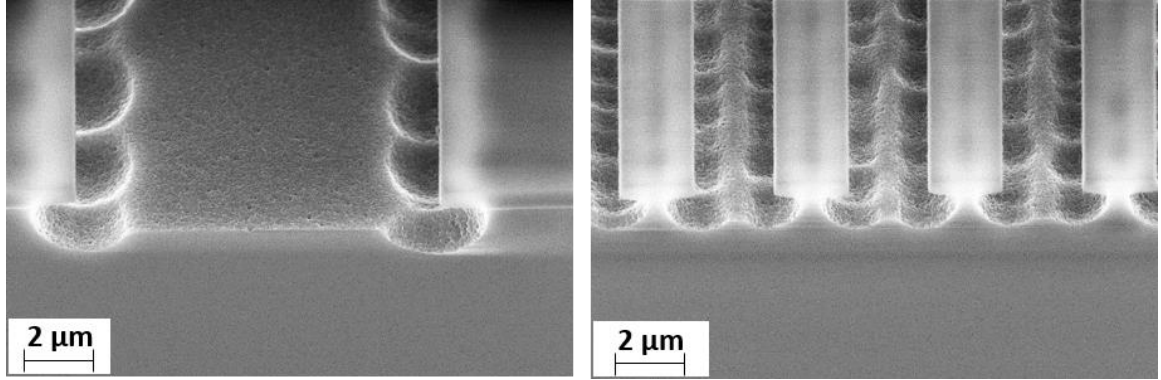


FIG. 2.6. Scanning electron micrographs of S dosed Si pattern samples with SiO<sub>2</sub> mask after etching in a NF<sub>3</sub>/Ar plasma. NF<sub>3</sub>:Ar = 25:25 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min.

### 2.3.3 – Measurements of Si roughness after etching in NF<sub>3</sub>/SF<sub>6</sub> plasmas

Etched Si surface morphology was examined qualitatively by SEM as shown in Fig. 2.7. NF<sub>3</sub> plasma-etched Si surfaces (Fig. 2.7(a)) appeared cloudy to the eyes and revealed a rough, pitted surface, compared to SF<sub>6</sub> plasma-etched Si surfaces (Fig. 2.7(d)), which were quite smooth and relatively free of etch pits, despite the much larger etched depth. As the % SF<sub>6</sub> in NF<sub>3</sub>/SF<sub>6</sub> plasmas was increased, the surface morphology transitioned from rough-to-smooth in much the same manner as the etching probability of Si by F increased (Fig. 2.6). Also, sulfur-exposed Si surfaces after etching in the NF<sub>3</sub> plasmas were significantly smoother (Fig. 2.7) relative to non-exposed sulfur on Si after etching in NF<sub>3</sub> plasma (Fig. 2.8(a)).

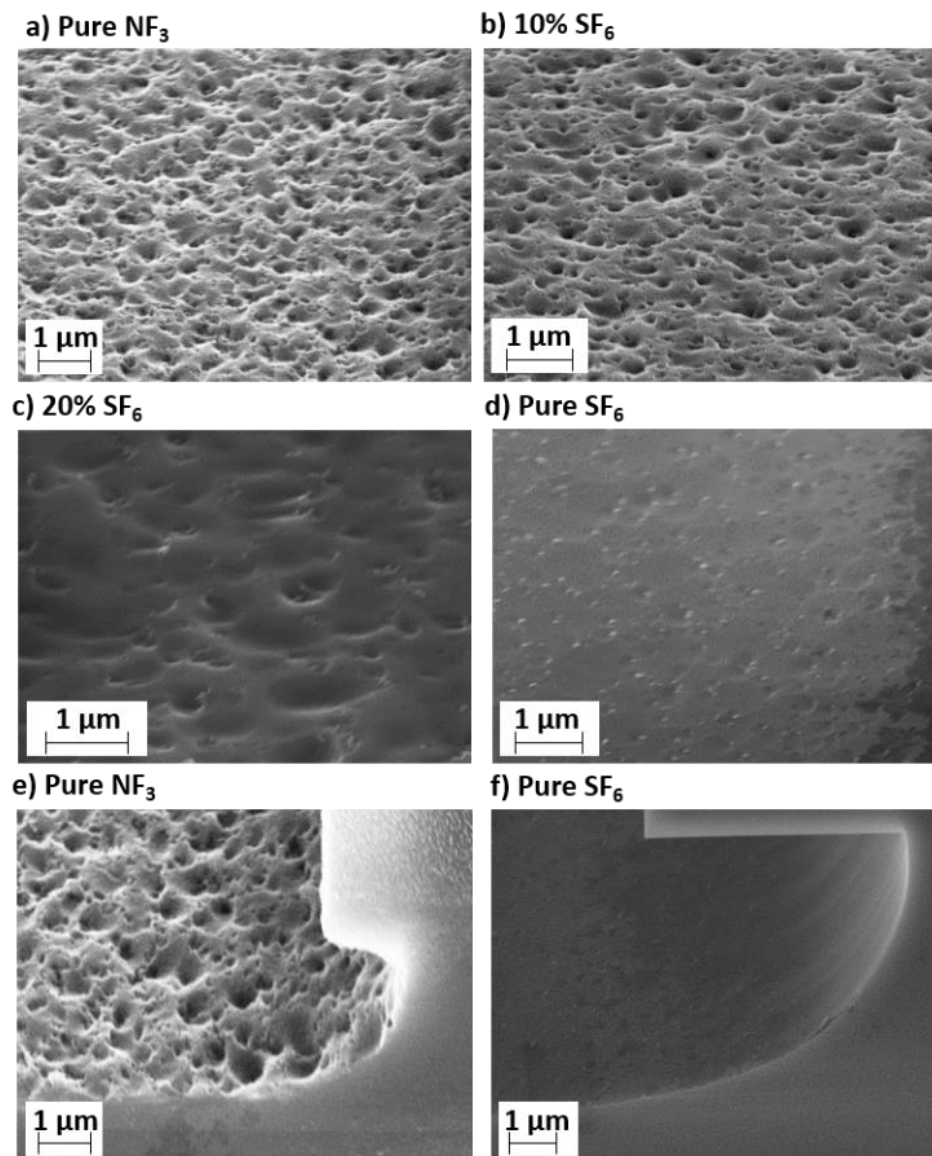


FIG. 2.7. Scanning electron micrographs of Si after etching in a various composition of  $\text{NF}_3/\text{SF}_6$  plasmas. Total flow = 50 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min.

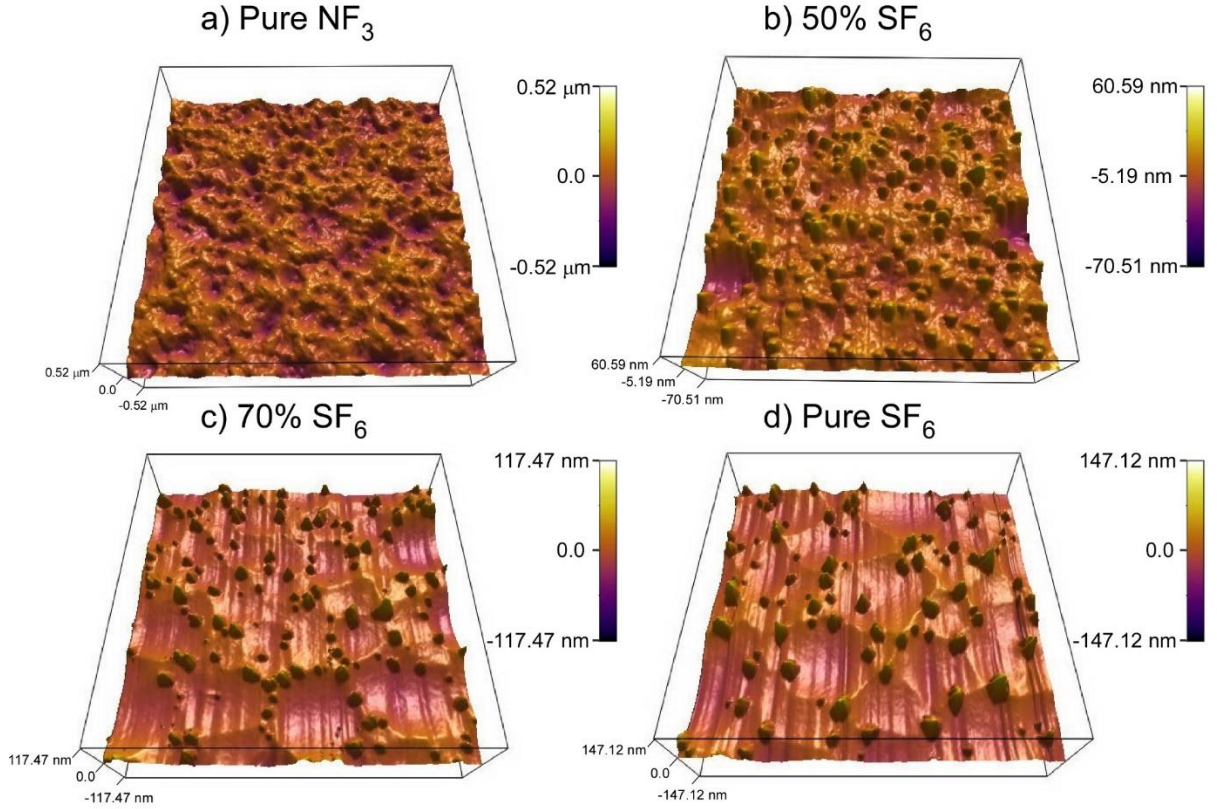


FIG. 2.8. (a-d) AFM scans of Si surfaces after plasma etching in different percentages of  $\text{SF}_6$  in 25 sccm of  $\text{NF}_3 + \text{SF}_6$ . Ar flow rate = 25 sccm, total flow rate = 50 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min. The scanned areas displayed are  $5 \times 5 \mu\text{m}$ .

A more quantitative measure of surface morphology was obtained from AFM measurements, shown in Fig. 2.9. For  $\text{NF}_3$  plasmas (Fig. 2.8(a)), the surface topography spans several hundred nanometers, whereas for the  $\text{SF}_6$  plasma (Fig. 2.8(d)) the surface is smoother with a sparser occurrence of relatively smaller hillocks that are of the order of 20 nm in height. The root mean square (RMS) roughness for the etched surfaces is reported in Fig. 2.9 as a function of % of  $\text{SF}_6$  addition to mixtures of  $\text{NF}_3/\text{SF}_6$  plasmas. For  $\text{NF}_3$  plasmas, RMS roughness lies in the range of 34 nm to 42 nm; for  $\geq 50\%$   $\text{SF}_6$  feed gas mixtures, RMS roughness ranges from 4 nm to 12 nm. The samples shown in Figs. 2.8 and 2.9 were etched for the same 5 min. Since the vertical etching rate for  $>50\%$   $\text{SF}_6$  are about 9 times higher than in  $\text{NF}_3$  plasmas (Fig. 2.3a), the etched depths were about 8500 nm for

the >50% SF<sub>6</sub>-containing plasma-etched samples and 1000 nm for the NF<sub>3</sub> plasma-etched sample. Thus the **relative** decrease in roughness for >50% SF<sub>6</sub> is even more dramatic than indicated by the data in Figs 2.7 and 2.8. The origin of the small (~20 nm high, or 0.2% of the etched depth) hillocks, surrounded by a very smooth surfaces etched in >50% SF<sub>6</sub> plasmas, is unclear. The hillock bases seem to be mostly oriented along a particular direction (not apparent in Fig. 2.8, but in other images shown in Fig. 2.10), suggesting some crystallographic-dependent etching, perhaps initiated by brief masking caused by contaminants that come from the chamber walls during etching. More definitive, four-sided hillocks with {110} facets, and bases oriented along <100> directions, have been observed in 50% Cl<sub>2</sub>/Ar plasmas, under conditions where trace contaminants were observed and ion bombardment energies were <10 eV, below the threshold for ion-assisted etching<sup>87</sup>.

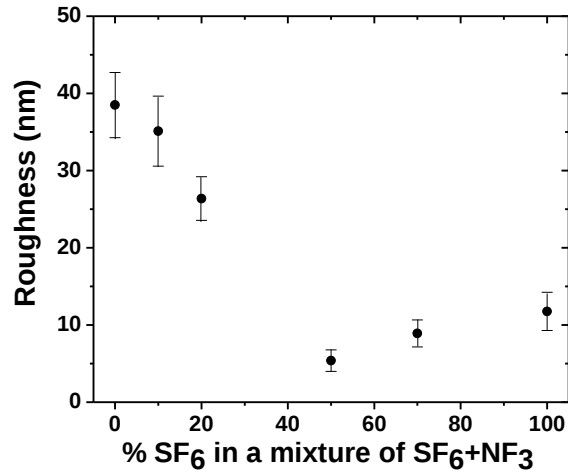


FIG. 2.9. RMS roughness determined from AFM scans in Fig 2.8, and others for the conditions given in Fig. 2.8.

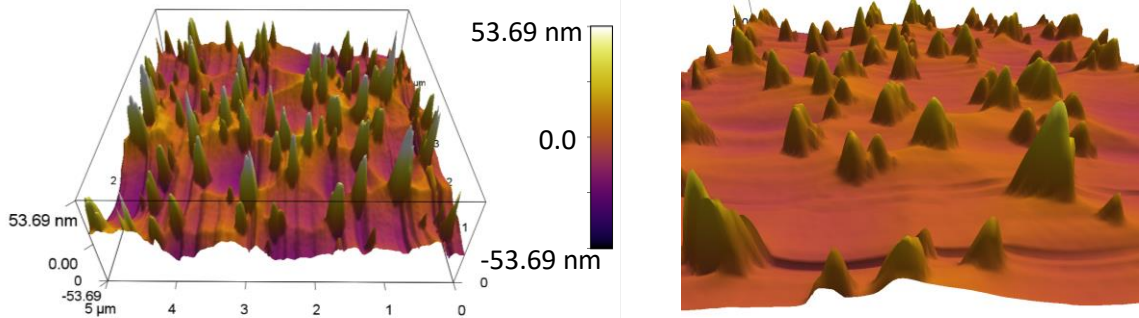


FIG. 2.10. AFM scans of Si surfaces after etching in  $\text{SF}_6$  /Ar plasma.  $\text{SF}_6$ :Ar = 25:25 sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min.

After etching, unmasked Si sample surfaces were analyzed by X-ray photoelectron spectroscopy (XPS), with intermediate air exposure. Spectra shown in Fig. 2.11 reveal that the near-surface region of Si etched in the  $\text{NF}_3$  plasma contained much more F than did Si etched in the  $\text{SF}_6$  plasma. Both samples oxidized to a similar extent and picked up similar levels of carbon, due to air exposure. The rise in the background on the high binding energy side of the F(1s) peak for the  $\text{NF}_3$  plasma-etched sample indicates that much of the fluorine is sub-surface. Most of this fluorine is not bound to Si, since the Si(2p) region reveals nearly equal intensities of features corresponding to elemental Si near 99 eV and  $\text{SiO}_x\text{F}_y$  at  $\sim 103$  eV, similar to observations for the  $\text{SF}_6$  plasma-etched sample. Winters, et al. found similarly large amounts of excess fluorine after etching Si with F atoms and attributed it to  $\text{F}^-$  that had penetrated deeply (at least 25 nm) into Si<sup>88</sup>. It has also been shown definitively that F rapidly penetrates through a 10 nm thick Si film, when exposed to even a low flux of F in a molecular beam<sup>89</sup>. This deep penetration of fluorine into Si was not captured in

the molecular dynamics simulations of Humbird and Graves<sup>76, 90</sup>, due to limitations of the method to shorter spatial and temporal domains.

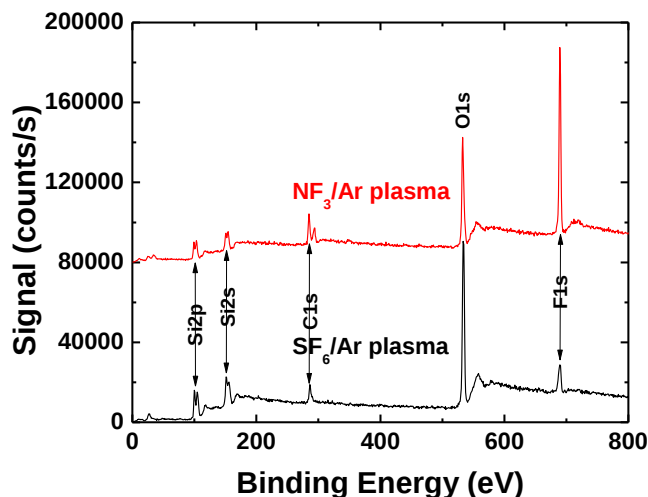


FIG. 2.11. XPS spectra of Si surfaces after etching in  $\text{NF}_3/\text{Ar}$  and  $\text{SF}_6/\text{Ar}$  plasmas. Flow rates:  $\text{NF}_3:\text{Ar} = 25:25$  sccm,  $\text{SF}_6:\text{Ar} = 25:25$  sccm, pressure = 50 mTorr, ICP power = 400 W, etching time = 5 min.

### 2.3.4 – Proposed reaction mechanism for surface roughness

It is often reported that roughening of Si surfaces is related to the presence of species that redeposit or remain as residuals on the wafer, leading to micro-masking<sup>91, 92</sup>. Martin and Cunge have attributed roughness in ion-assisted etching of Si in  $\text{SF}_6$  and  $\text{CF}_4$  plasmas to micro-masking by  $\text{AlF}_x$  sputtered from the chamber walls.<sup>92</sup> After 10 min of etching in a  $\text{SF}_6$  plasma, they observed  $3 \times 10^{14} \text{ Al/cm}^2$  on the surface, i.e., about 1 monolayer. In the present study, no metals such as Y or Al from erosion of the Yttria liner or alumina ICP window are detected by XPS (i.e., <1% of a monolayer). Furthermore, the roughness persists up the sidewall right up to the overhanging  $\text{SiO}_2$  mask, as shown in Fig. 6(e). Metal contaminants would not deposit up the sidewalls to the same extent as in open

areas. Also the sidewalls receive very little ion bombardment, a necessary part of the micro-masking mechanism for roughness, and yet are equally rough. Indeed, micro-masking is not a plausible explanation for conditions where isotropic, chemical etching dominates. Therefore, it is unlikely that the surface roughness is due to micro-masking in this case of isotropic etching by F, in the absence of sulfur and significant ion-enhancement.

Several other mechanisms have been proposed for surface roughening during Si etching in fluorine and chlorine-containing plasmas. Rough surfaces produced in  $\text{CF}_4/\text{O}_2$  plasmas that generate large amounts of F atoms, similar to the  $\text{NF}_3$  plasma case in the present study, have been ascribed to a F that impinges on the side of a surface feature and then desorbs and is re-absorbed deeper into the feature, where it causes etching.<sup>93</sup> Although this would lead to a faster etching rate at the bottoms of features, increasing roughness, as pointed out by Martin and Cunge, it is not reasonable that F would have a low reactive sticking coefficient on the upper region of a feature and a high reactive sticking coefficient on the surface below<sup>92</sup>.

Kokkoris, et al.,<sup>94</sup> also attribute surface roughness for Si etched in a  $\text{SF}_6$  plasma to a F re-emission mechanism similar to that offered by Zhao, et al.,<sup>93</sup> with the further inclusion of ion-initiated micro-masking by “hard inhibitor” deposits, and a “soft inhibitor” that could be  $\text{SF}_x$  species that have a higher sticking coefficient than F. This proposed soft inhibitor mechanism cannot explain the enhanced roughness in  $\text{NF}_3$  vs.  $\text{SF}_6$  plasmas found in the present study and elsewhere<sup>70</sup>, since surfaces are *smoother* in  $\text{SF}_6$  plasmas, where  $\text{SF}_x$  and  $\text{S}_x$  species that could possibly act as such soft inhibitors are prevalent, than in  $\text{NF}_3$  plasmas, where no nitrogen is detected by XPS on  $\text{NF}_3$  plasma-etched Si, ruling out possible  $\text{NF}_x$  inhibitors that are rapidly converted in the plasma to  $\text{N}_2$  (negligible sticking

coefficient on fluorinated Si) and F atoms, by fast electron attachment of  $\text{NF}_3$ , and secondary bi-molecular reactions of  $\text{NF}_x$  species<sup>95-97</sup>. Silicon etched downstream of pure  $\text{F}_2$  plasmas also exhibits a rough surface<sup>2</sup>. Furthermore, depositing sulfur on Si before etching in  $\text{NF}_3$  plasmas also leads to a *smoother* surface.

It is noteworthy that no sulfur was detected by XPS on the Si surface after etching. It has been reported that Si surfaces etched in  $\text{SF}_6$  plasmas and then transferred under vacuum to a surface analysis chamber do contain substantial sulfur<sup>98, 99</sup>. On the other hand, Si samples that were exposed to air between being etched in an  $\text{SF}_6$  plasma and analyzed by XPS, as was the case in the present study, contain little if any sulfur<sup>100, 101</sup>. Gaseous  $\text{SO}$ ,  $\text{SO}_2$  and  $\text{H}_2\text{S}$  formed in reactions with  $\text{H}_2\text{O}$  are likely, leading to loss of S from the surface. Thus, it is likely in the work presented here that S was on the Si surface during and immediately after etching.

In the present study, there is a strong correlation between surface roughness and sub-surface penetration by F, as demonstrated by the XPS measurements. It is likely that the roughness is the cause of enhanced F uptake and vice versa. When F (or  $\text{F}^-$ ) penetrates below the surface, it will insert into Si-Si bonds. This then leaves a dangling bond that will be rapidly fluorinated as fluorine builds up in the layer. The fluorination of lattice bonds enhances the diffusion rate of F into Si, leading to further breaking of lattice bonds.

Fluorine is not expected to bridge bond Si atoms, due to the strong Si-F bond. Sulfur, on the other hand can bridge bond between two Si atoms. (This process is similar to that in the vulcanization of rubber, where small sulfur chains crosslink adjacent C atoms.) More highly fluorinated  $\text{SF}_x$  species are unlikely to be present at high number densities, given the high degree of dissociation of  $\text{SF}_6$  in the plasma. Sulfur is likely to

impinge on the surface in the form of S, S<sub>2</sub>, SF or SF<sub>2</sub>. These species likely have high sticking coefficients on Si. Therefore,  $\equiv\text{Si-SF}_{x=0-2}\text{-Si}\equiv$  and similar moieties are expected to form. This bridge bonding will suppress the diffusion of F into Si, leading to a smoother surface morphology during etching. Since the etching rate is limited by reactions at the surface or the first couple of monolayers below the surface, the rate should not be affected by the slower rate of diffusion of F deep into Si. This is also indicated by the fact that the products of Si etching are widely reported to be SiF<sub>4</sub>, a small amount of Si<sub>2</sub>F<sub>6</sub>, as well as SiF<sub>2</sub><sup>83, 88</sup>. If deep penetration of F were important in causing etching, then larger Si<sub>x</sub>F<sub>y</sub> molecules and clusters would be expected to form.

### 2.3.5 – Proposed reaction mechanism for higher $\epsilon_{F(Si)}$ in SF<sub>6</sub> plasma

The large enhancement in the F atom probability for Si etching in SF<sub>6</sub> plasmas is now addressed. F is expected to have a large sticking coefficient on a Si dangling bond site, forming a strong covalent bond. At steady-state, this leads to the several monolayers thick surface layer composed mainly of SiF<sub>x</sub>, with little free F or F<sup>-</sup>, similar to the simulations of Humbird and Graves<sup>76, 90</sup>. It is on this fluorinated surface that F will relatively weakly adsorb (i.e., physisorb), after which it can diffuse, desorb (first order rate constant  $k_d$ ) combine with another F to form F<sub>2</sub>, or go on further to react and form a volatile etching product. Assuming an oversimplified mechanism in which a sparse coverage of physisorbed F, [F<sub>phys</sub>], reacts with SiF<sub>3</sub> in this layer (second order rate constant,  $k_r$ ) to form SiF<sub>4</sub>, which immediately desorbs, and further assuming that the sum of etching and

desorption is fast compared to  $F_2$  formation, steady state expressions for the etching rate (ER) and physisorbed F coverage  $[F_{(phys)}]$  are,

$$ER = k_r [F_{phys}] [SiF_3] \quad (2.3)$$

$$\text{and } [F_{phys}] = \frac{\Gamma_F s}{k_d + k_r [SiF_3]}, \quad (2.4)$$

where  $\Gamma_F$  is the F flux to the surface, and  $s$  is the sticking coefficient on the fluorinated surface. Combining (3) and (4),

$$ER = \frac{\Gamma_F s k_r [SiF_3]}{k_d + k_r [SiF_3]}. \quad (2.5)$$

Since  $\varepsilon_{F(Si)} < 0.1$  (see Fig. 2.4), most F atoms leave the surface as F and not incorporated into  $SiF_4$ , therefore

$$ER \approx \frac{\Gamma_F s k_r [SiF_3]}{k_d}. \quad (2.6)$$

Assuming similar coverages of  $SiF_3$  in  $NF_3$  and  $SF_6$  plasmas, as is suggested by the XPS spectra in the Si(2p) region, the ratio of the Si etching reaction probability for F in  $SF_6$  plasmas ( $\varepsilon_{F(Si),S}$ ), to  $\varepsilon_{F(Si)}$  in  $NF_3$  plasmas is then

$$\frac{\varepsilon_{F(Si),S}}{\varepsilon_{F(Si)}} \approx \frac{s_S k_{r,S} k_d}{s k_r k_{d,S}}, \quad (2.7)$$

where the subscript S indicates the coefficient for the process in the presence of sulfur. Hence some combination of enhanced F sticking coefficient and/or decreased desorption rate on a surface covered with sulfur would lead to the observed enhancement of etching in  $SF_6$  plasmas. If F that reacts with  $SiF_3$  is not bound to S, then  $k_{r,S}$  is equivalent to  $k_r$ . If

not, then it is likely that  $k_{r,S} < k_r$ , and the ratio  $\frac{s_S k_d}{s k_{d,S}}$  would need to be larger to explain the large enhancement in SF<sub>6</sub> plasmas.

This mechanism for enhancement of the F reaction probability for Si surfaces with adsorbed S is similar to the large increase in etching rate for Si in XeF<sub>2</sub> gas (i.e no plasma).<sup>102</sup> In this case, dissociative chemisorption of XeF<sub>2</sub> leads to etching of Si by adsorbed F atoms, equivalent to isotropic etching by F atom-generating plasmas. With XeF<sub>2</sub>, it was found that the etching rate increased strongly with decreasing temperature. This was attributed to the longer residence time for XeF<sub>2</sub> on the surface, increasing the possibility for dissociation, physisorbed F formation and Si etching. In the present case, SF<sub>x</sub> plays a similar role, increasing the coverage and residence time for F on the surface until the etching reaction can occur.

There have been other reports of surface catalytic enhancement of Si etching in the gas phase. Coburn found that the F atom etching of Si was enhanced by a relatively small amount (nearly 2-fold) by the simultaneous impingement by Cl<sub>2</sub>.<sup>103</sup> Formation of inter-halogen compounds (ClF or ClF<sub>3</sub>) that are known to etch Si was ruled out. Instead, the increase in etching rate was ascribed to an enhancement in the F atom reaction probability, though the underlying cause was not elaborated on. Trace amounts of adsorbed Cu have been reported to catalyze etching of Si by F<sub>2</sub>, increasing etching rates ~100-fold<sup>104,105</sup>. The proposed mechanism was an enhancement in the dissociative chemisorption of F<sub>2</sub> at 2 adjacent Cu sites, leading to the formation of CuF that then undergoes a F exchange reaction with Si and SiF<sub>x</sub>, leading eventually to formation of volatile SiF<sub>4</sub> and/or SiF<sub>2</sub> and regeneration of active Cu sites, completing the catalytic cycle.

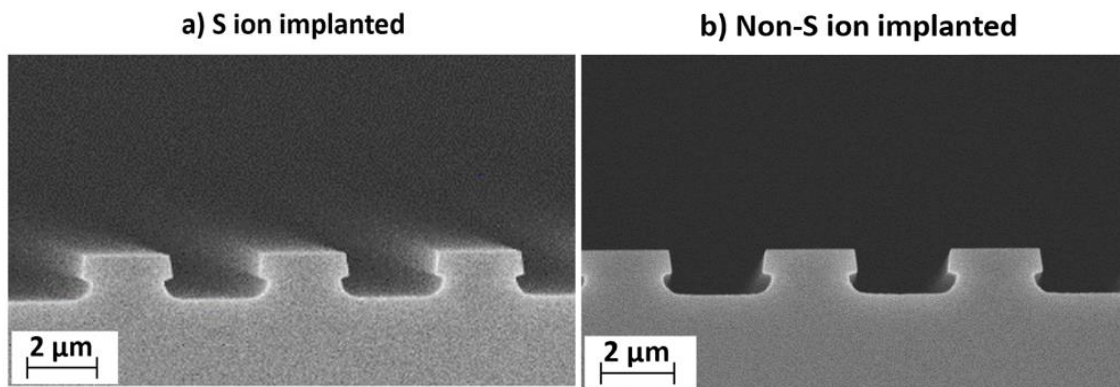


FIG. 2.12. Scanning electron micrographs of a) S ion implanted Si pattern sample b) Non-sulfur ion implanted Si with SiO<sub>2</sub> mask after etching in NF<sub>3</sub>/Ar plasma, Etching Conditions : NF<sub>3</sub>/Ar : 25:25 sccm , 50 mTorr pressure, 400 W ICP, 5 min etching time.

Another possible mechanism for the large enhancement in reaction probabilities of F with Si in SF<sub>6</sub> plasmas could be an electronic effect involving S states within the Si bandgap and modified band bending at the surface<sup>83</sup>. To confirm or rule out electronic effects, further experiments were performed, using sulfur ion implantation into masked sample at 30-60 KeV ion energies with a dose of 10<sup>15</sup> ions/cm<sup>2</sup>, followed by post-annealing at 500 °C for 30 min. This will produce a layer 100 nm deep with a sulfur concentration of 10<sup>20</sup> cm<sup>-3</sup>. When this sample was placed side by side with one not exposed to ion implantation, and then etched in NF<sub>3</sub>/Ar plasma for a time (300 s) required to etch the ion-implanted layer, the etching profiles looked similar for both the samples, as seen in the SEM images in Fig. 2.12. The S-implanted sample isotropically etched with a reaction probability of 0.0023 at a F flux of  $\sim 2.0 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ , which is equivalent to the one with the non-sulfur implanted sample at the same flux. Hence, this rules out electronic effects and confirms the surface reaction mechanism.

The  $\epsilon_{F(Si)}$  values derived from mask undercutting and from the depth of the hemispherical regions are equal (0.0052-0.0087). This seems to indicate that not only does

sulfur “ride” on the Si surface as it is isotropically etched by F atoms (similar to what was observed for Cu-catalyzed etching of Si by  $F_2^{104, 105}$ , but it also diffuses along the surface and up the sidewall to catalyze etching right up to the interface of Si with the undersurface of the mask. Presumably the decrease in  $\epsilon_{F(Si)}$  over the first  $\sim 1\text{-}2\ \mu\text{m}$  from the mask (see Fig. 2.6) is due to a decreasing amount of deposited S. What is surprising is the abrupt transition at distances  $> \sim 2\ \mu\text{m}$  from the mask edge to a very constant  $\epsilon_{F(Si)} = 0.0029$  (i.e., flat surface in Fig. 2.6) that still exceeds that for S-free surfaces ( $\epsilon_{F(Si)} = 0.0018$ ). The surface also remains quite smooth in this flat region, relative to surfaces etched in  $NF_3$  plasmas with no adsorbed S. Without a controlled dosing of S it is not possible to determine the dependence of the catalytic enhancement on the S surface coverage.

## 2.4 Conclusions

Reaction probabilities of F atom with Si in the absence of ion bombardment were measured for various gas ratios of  $NF_3$  and  $SF_6$  plasmas in an inductively-coupled plasma reactor. Optical emission actinometry was applied to measure F number densities and cross-sectional SEM was used to measure the degree of undercutting of  $SiO_2$ -masked Si.  $NF_3/Ar$  and  $SF_6/Ar$  plasmas produced isotropic etching rates of 1000 and 12000 Å/min, respectively. Corresponding reaction probabilities were measured with values ranged from  $\epsilon_{F(Si)} \sim 0.003$  in  $NF_3/Ar$  plasma to  $\sim 0.08$  ( $\sim 30$ -fold larger) in a  $SF_6/Ar$  plasma. Addition of only 10%  $SF_6$  to an  $NF_3$  plasma produced a  $\sim 5$  fold increase in  $\epsilon_{F(Si)}$ .

The large enhancement of reaction probabilities for F with Si in  $SF_6$  plasma was shown to be caused by adsorbed sulfur acting as a catalyst to enhance etching by F. This mechanism was confirmed by allowing dilute solutions of sulfur in isopropyl alcohol to

evaporate on the masked Si samples.  $\text{NF}_3/\text{Ar}$  plasma etching of these sulfur-dosed samples produced a reaction probability of  $\sim 0.0076$ , while the sulfur-free surface had a lower  $\epsilon_{R(\text{Si})} = 0.0018$ . An increase in the F sticking coefficient and/or decrease in F desorption rate on a surface covered with sulfur leads to increased F coverage on the surface, less F diffusion into the subsurface region, and hence an enhancement of the F reaction probability leading to Si etching.

The second question addressed here is the rough vs. smooth surface morphology in  $\text{NF}_3$  vs.  $\text{SF}_6$  mixtures. AFM measurements indicated an RMS roughness of 34 nm to 42 nm for Si etched in  $\text{NF}_3$  plasmas, and 4 nm to 12 nm in  $\text{NF}_3/\text{SF}_6$  plasmas for  $>50\%$   $\text{SF}_6$ . Several mechanisms of micro-masking were ruled out as the cause of the surface roughness in  $\text{NF}_3$  plasmas. A strong correlation was found between surface roughness and sub-surface penetration by F in  $\text{NF}_3$  plasmas. In  $\text{SF}_6$  plasmas it was proposed that S bridge bonded adjacent Si atoms suppresses diffusion of F into Si, leading to the smooth surface morphology.

## **Chapter 3 – Glow Discharge-Optical Emission Spectroscopy for In-Situ Analysis of Surfaces in Plasmas**

### **3.1 Motivation**

In-situ, real-time characterization of surfaces exposed to plasmas is of great interest. Chemical analysis methods are limited, however. The two most common chemical analysis methods, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)<sup>106</sup>, cannot be used because they require energy-resolved detection of electrons, as well as high-vacuum conditions. Consequently, samples must be moved from the plasma chamber to an analysis chamber for XPS or AES. Sample transfer under vacuum eliminates reactions of adsorbed layers with air (especially with H<sub>2</sub>O), but does not prevent weakly adsorbed species from leaving the surface in the time it typically takes to terminate plasma exposure, pump the reactor to a reasonably low pressure, transfer the sample, and begin analysis (typically several minutes for conventional sample transfer). This time can be shortened to <1 ms by the spinning wall method<sup>107-110</sup>, which is best suited for cylindrical samples. Fourier transform infrared absorption can probe the surface of prisms by the total-internal-reflection method<sup>112,113</sup>. The technique is limited to a few substrates that are transparent over broad regions of the infrared, is difficult to quantify, cannot detect many species of interest, and is not very sensitive, thus requiring long accumulation times.

A technique that could analyze surfaces without moving or rotating the sample out of the plasma reactor would be very useful. This measurement should be made immediately after plasma exposure, or especially during plasma processing. The ability to determine the chemical compositions and thicknesses of reaction layers and deposited films would

provide insights into etching and deposition mechanisms, as well as changing heterogeneous chemistry on reactor walls.

One technique that has not been applied to surface analysis in plasma processes is secondary ion mass spectroscopy (SIMS). SIMS has much greater sensitivity than XPS or AES. It also provides depth profiles by sputtering the sample surface. While the plasma precludes introduction of a focused ion beam to carry out conventional SIMS analysis, by applying a large negative bias to a sample, ions in the plasma can serve as the source of sputtering. The sputtered products are expected to be mostly neutrals, and detection of neutrals or secondary ions by mass spectrometry is problematic, especially if sputtered products are not volatile, since they would deposit on the chamber walls before reaching the mass spectrometer. Consequently, another method for detection of sputtered species is needed.

Optical emission spectroscopy is ideally suited for this purpose. In fact, the materials characterization technique known as glow discharge-optical emission spectroscopy (GD-OES) is based on the sputtering of samples in a plasma with detection by optical emission excited by collisions of sputtered species with high-energy electrons<sup>114-117</sup>. In this case, the sample to be analyzed is placed to a small chamber and either negative direct current (DC) or radio-frequency (rf) voltage is applied to the sample (the latter for insulators) to produce a plasma, usually in argon, and induce energetic ion bombardment of the sample. Optical emission intensities of selected species are monitored as a function of time as the sample is sputtered, providing relative or absolute (with calibration standards) atomic concentrations as a function of depth<sup>111</sup>. The plasma is therefore an analysis tool, and is not involved in formation of the material to be analyzed.

## 3.2 Experimental

A schematic of the GD-OES is shown in Fig. 3.1. Plasmas with positive ion densities of about  $3 \times 10^{11} \text{cm}^{-3}$  were generated near the center of the reactor 2 cm above a substrate. The substrate (here a bare Si wafer or  $\text{SiO}_2$ ) was mounted on a 3" diam. electrode that was powered with a second CW RF (18 MHz) supply. This produced a negative DC self-bias voltage on the wafer to promote ion-assisted etching. A removable 6" i.d.  $\text{Y}_2\text{O}_3$ -coated cylindrical Al liner confined the plasma. A grounded thermocouple and grounded feed gas connections were electrically connected to bare Al in the liner. The insulating  $\text{Y}_2\text{O}_3$  coating on the liner would be expected to be at the plasma floating potential.

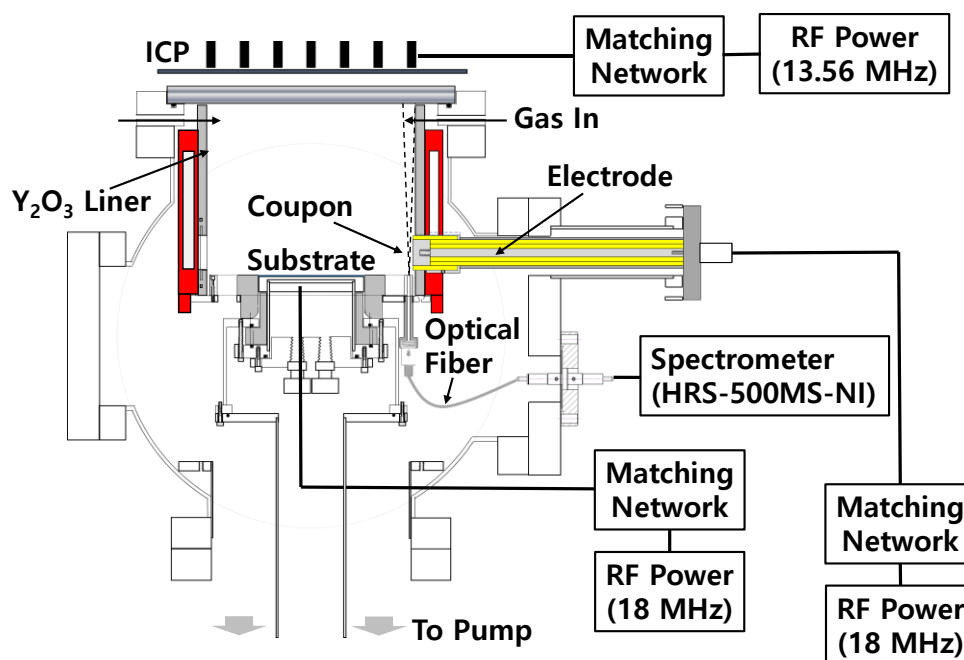


FIG. 3.1. Schematic of the inductively coupled plasma main chamber, and electrode holding the coupon piece. The dashed lines represent the approximate cone of acceptance of the optical fiber probe assembly.

Thin coupon pieces of 0.75" diam. were bonded to the surface of a 0.75" diam. aluminum electrode. The electrode and coupon piece were inserted through a hole in the liner. The surface of the coupon was flush with the walls of the liner. The electrode was intermittently powered with 18 MHz rf voltage through an impedance-matching network. With 35 W forward and 5 W reflected power, the measured direct current (DC) self-bias voltage produced on the electrode was -320 V. All experiments were performed with a 1 mm thick  $\text{Y}_2\text{O}_3$  disc coupon.

Optical emission near the surface was recorded, using an optical fiber cable with a collimating lens, and high aspect ratio tube (2.0 mm i.d., 38 mm long), mounted inside the plasma chamber along the liner wall, as shown in Fig. 3.1. The tube minimizes deposition of species on the surface of the lens. It also provides a collection angle of only  $1.5^\circ$  and therefore a spatial isolation of the signals of species sputtered from the coupon surface, and then excited by electron-impact excitation within a few mm of the surface. The dashed lines in Fig. 3.1 represent the approximate acceptance cone of the optical detection system. Emission is line-integrated over the region above the substrate, but also extends to the top of the reactor. Therefore, background emission from the plasma for Cl and O, and to a lesser extent, etching products, is much more intense than the products sputtered from the coupon.

An optical fiber vacuum feedthrough and fiber cable directed optical emission to a spectrometer (Princeton Instruments HRS-500 MS-NI), equipped with a CCD camera (Princeton Instruments model PIXIS<sup>TM</sup> 2KBUV). The input slit width was 60  $\mu\text{m}$ , resulting in a resolution of 0.2 nm full width at half maximum.

Emission spectra were recorded every 0.5 s and stored continuously. Spectra recorded with just the ICP on (sometimes with substrate bias power) provided the background of emission arising from electron impact of species in the plasma. Periodically, the coupon bias was turned on for 0.5 s and spectra were recorded. Subtracting the background signal just after from the coupon-bias-on spectra provided an instantaneous signal of species sputtered from the coupon. A labview program was used to control the pulsing sequences and data collection. Results are presented for etching of Si in  $\text{Cl}_2/\text{O}_2/\text{Ar}$  plasmas, and  $\text{SiO}_2$  etching in a  $\text{C}_4\text{F}_8$  plasma.

### **3.3 Results and Discussion**

#### **3.3.1 – Sputter-depth profiling in an Ar plasma after Si etching in $\text{Cl}_2/\text{Ar}/\text{O}_2$ plasmas**

A silicon substrate on a separately rf-biased 3” diameter electrode was etched in a  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma for 15 min. After etching, pulsed bias was applied to sputter the surface of the  $\text{Y}_2\text{O}_3$  coupon piece in an Ar ICP. Spectra were then recorded with and without coupon bias, as described above. Typical spectra are given below for conditions just after Si etching in a  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma (Figs. 3.2(a) and 3.2(b)) and after 6 min of sputtering of the coupon (Figs. 3.2(c) and 3.2(d)) in Ar plasmas only. Subtracting the bias-off from the bias-on intensity provides a “difference spectrum” of the optical emission of the sputtered material. Such a difference spectrum is shown in Fig. 3.3 for the region dominated by Si and SiCl emission.

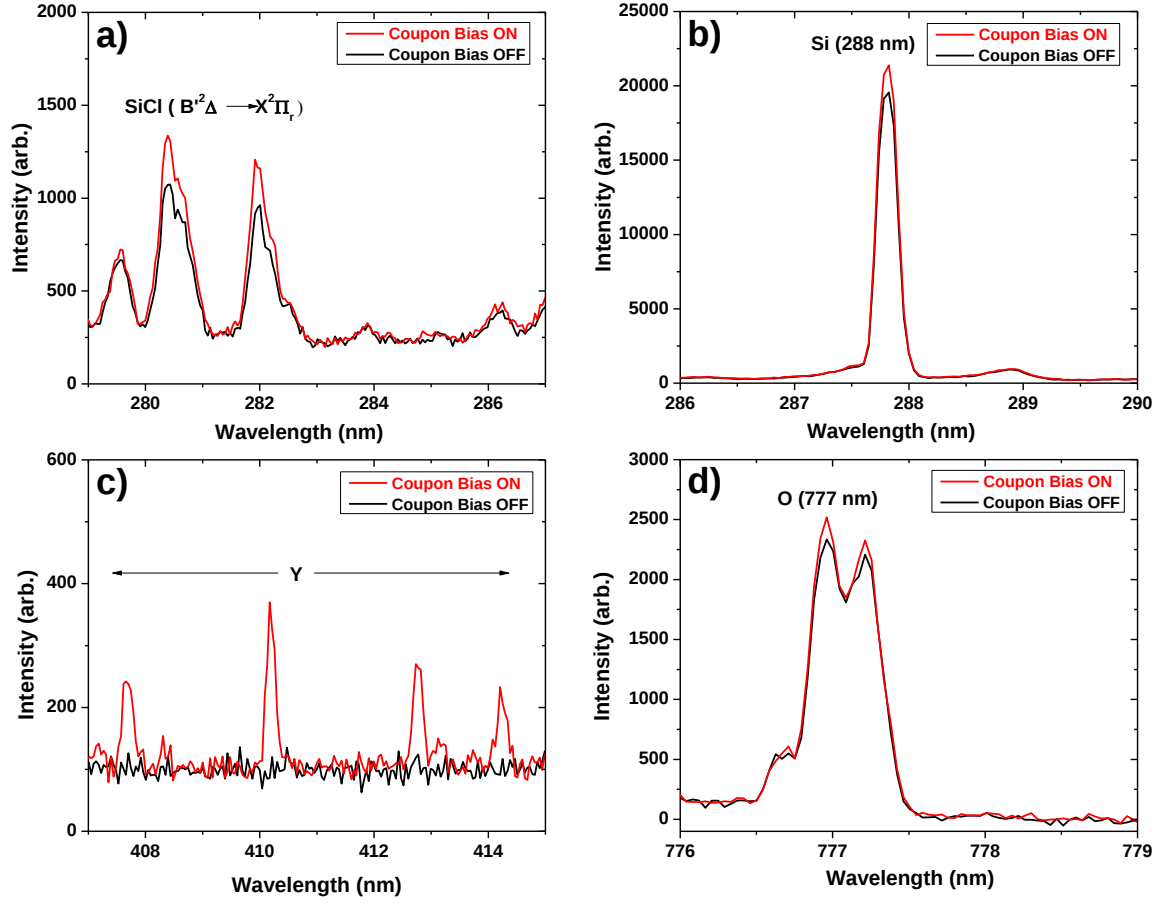


FIG. 3.2. Optical emission spectra with coupon bias on (red) and off (black) in an Ar plasma with 20 sccm Ar, 9 mTorr, 160 W ICP, -320 (ON) or 0 (OFF) V<sub>DC</sub> coupon self-bias. a) SiCl and b) Si just after Si etching in a Cl<sub>2</sub>/Ar/O<sub>2</sub> plasma. c) Y and d) O 6 min. after etching.

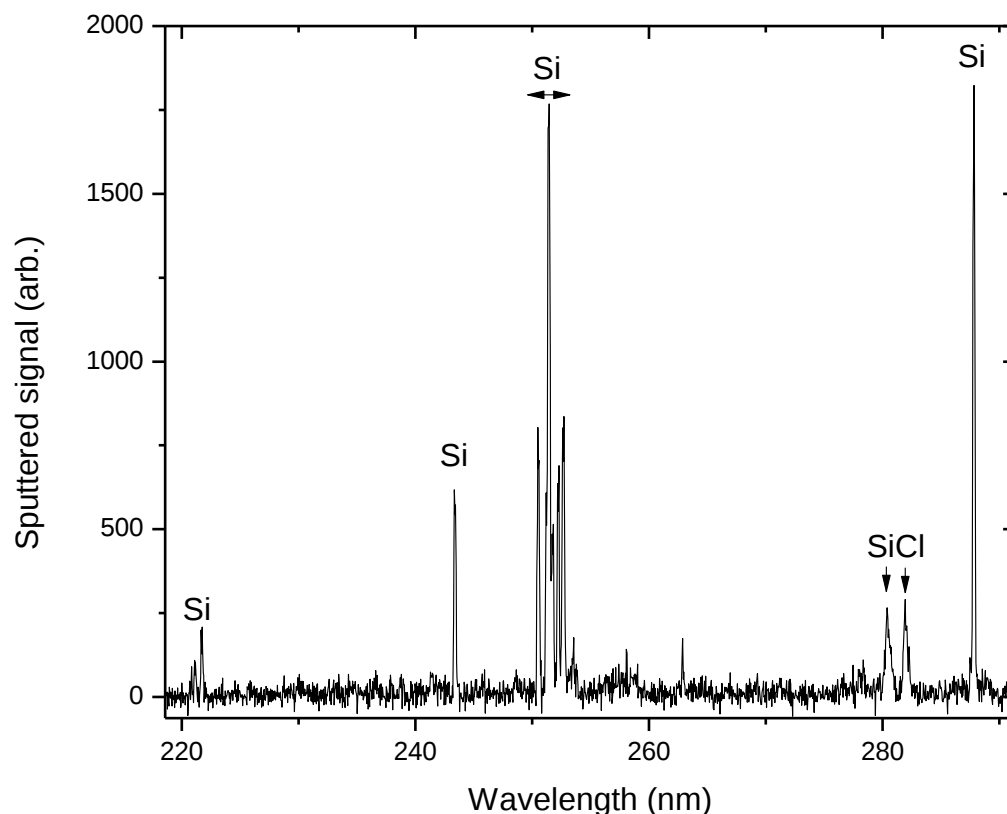


FIG. 3.3. Difference spectrum (coupon bias-on minus coupon bias-off) of optical emission of the sputtered products in an Ar plasma just after Si etching in  $\text{Cl}_2/\text{Ar}/5\%\text{O}_2$  plasma for the conditions in Fig. 3.2.

It is possible that the plasma properties could be altered slightly by the application of coupon bias, causing the electron impact excitation rate leading to emission to change slightly, perhaps mimicking the desired signal from the coupon. Emission from Ar at 750.4 nm was also monitored with bias on and off. No difference in Ar emission intensity was found, hence the small difference signals such as those in Fig. 3.3 are due to the species sputtered from the coupon. (It should be pointed out that emission from  $\text{Ar}^+$  increases by a very small, but statistically significant amount. Production of this emission requires either higher energy electrons than those responsible for the emissions of interest here, or is a

result of e-impact on  $\text{Ar}^+$ . Either mechanism is unrepresentative of that for excitation of emission from Si, SiCl and other sputtered products.) Also, the complimentary drop in sputtered species and rise in coupon species (i.e., Y and O) are a strong indication that the difference signals are not artifacts.

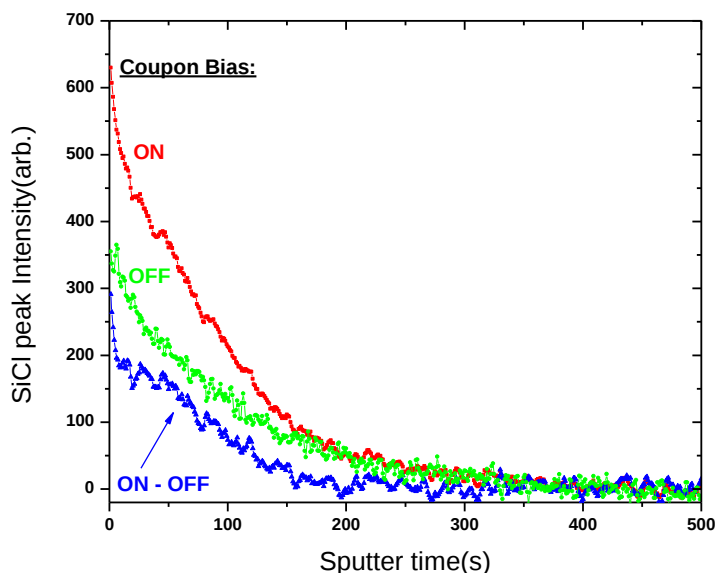


FIG. 3.4. Time resolved SiCl (280 nm) emission intensity in an Ar plasma after etching in  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma for 15 min. Etching conditions: Flow rates of  $\text{Cl}_2:\text{Ar}:\text{O}_2 = 20:2:1$  sccm, pressure = 20 mtorr, ICP power = 400 W, Si substrate  $V_{\text{DC}} = -80\text{V}$ . Ar plasma conditions for coupon sputtering: 20 sccm, pressure = 9 mTorr, ICP power = 160 W, coupon bias =  $-320 V_{\text{DC}}$ .

Intensities of emissions from sputtered species were recorded as a function of time in the Ar plasma. An example of such measurements is given in Fig. 3.4 for SiCl emission intensity at 280 nm ( $\text{B}'^2\Delta \rightarrow \text{X}^2\Pi_r$ ) with the coupon bias on and off. The difference in these signals is also plotted.

The SiCl emission is produced by electron impact on SiCl, and possibly by electron impact dissociation of  $\text{SiCl}_2$ ,  $\text{SiCl}_3$  and/or  $\text{SiCl}_4$  and with simultaneous excitation of the  $\text{B}'^2\Delta$  state of SiCl. Due to the added energy required to break one, two or three Si-Cl bonds

(Cl<sub>2</sub> formation is unlikely), direct excitation of ground state SiCl to the B'<sup>2</sup>Δ state by electron impact is most likely the predominant process. Si chlorine products desorbing from the chamber walls and diffusing to the observation region are assumed to dominate the emissions detected when the coupon bias is off, due to the very large area ratio (150:1) of all surfaces, relative to the coupon surface. When the coupon bias was turned on, SiCl emission intensity increased, due to the enhanced sputtering of the SiO<sub>x</sub>Cl<sub>y</sub> film that deposited on the surface of the coupon during etching. The difference in these two signals provides a measure of the net signal coming from just the coupon. In this example, the Si-containing film was removed from the coupon in ~150 s.

In another example, presented in Fig. 3.5, net intensities of Si, SiCl, Y and O emission were recorded as a function of coupon sputtering time. Without O<sub>2</sub> in the feed gas, Si and SiCl decayed to baseline in ~100 s. Y and O signals were not detected initially (first ~50 s) and then rose to a nearly constant level by ~130 s, indicating complete removal of the SiCl<sub>y</sub> film. With 5% O<sub>2</sub> in the feed gas, SiCl signal decayed to undetectable levels in ~170 s. Si emission followed a similar but slower decay, and reached baseline near 300 s. O emission decayed from its maximum initial level to a steady, non-zero intensity in the same ~170 s required for SiCl to decay to baseline. No Y signal was detected initially, but as the SiO<sub>x</sub>Cl<sub>y</sub> film was sputtered away, Y emissions from sputtering the underlying substrate increase to a steady-state level. O emission also decays to a steady-state level, after which the Y<sub>2</sub>O<sub>3</sub> substrate is sputtered at a constant rate. The times for Si and SiCl signals to decay to baselines and Y and O signals to reach steady-state correspond to the time for removal of the surface layer that was deposited during etching.

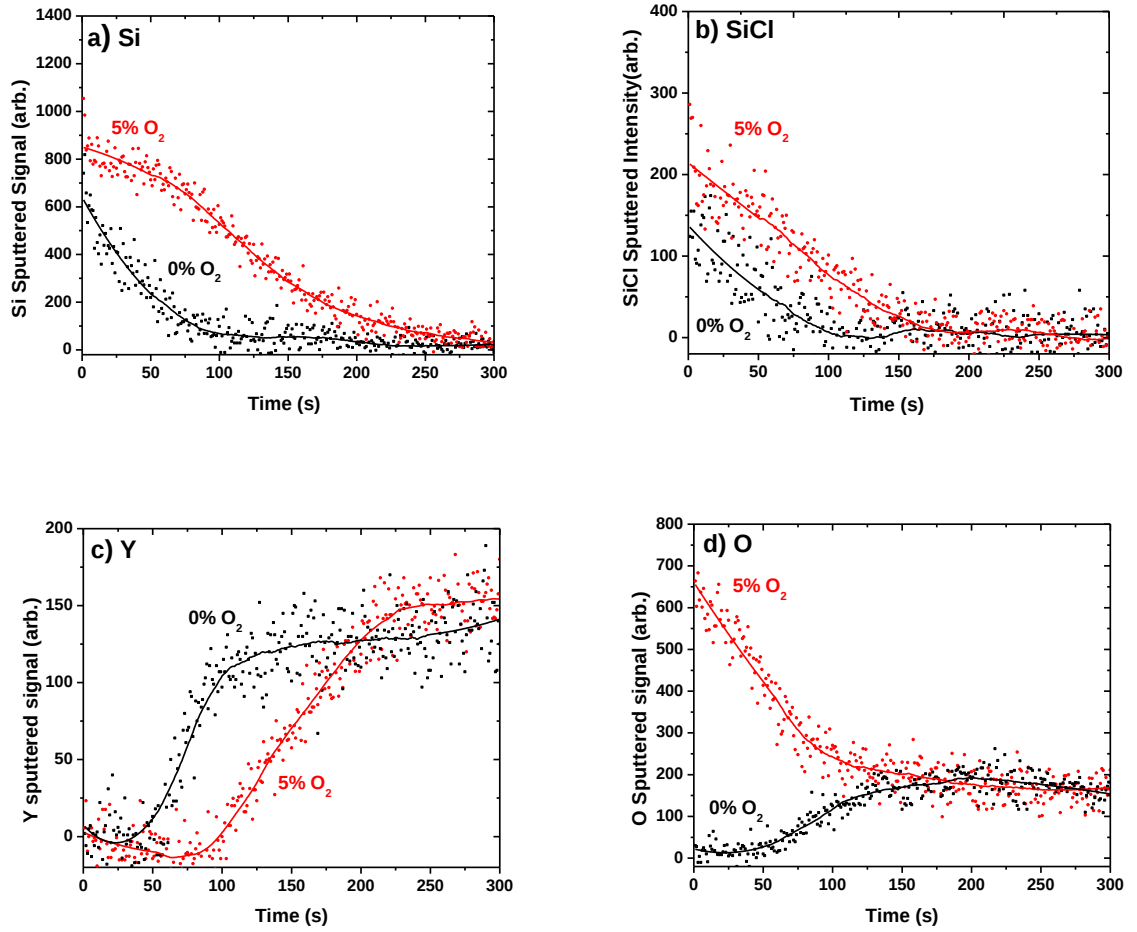


FIG. 3.5. Time-resolved optical emission intensities (coupon bias ON minus coupon bias OFF) of a) Si, b) SiCl, c) Y and d) O in an Ar plasma just after etching Si in  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma. Points: raw measurements, lines: 100 point Savitzky-Golay smooth.

It should be noted that although the  $\text{SiO}_x\text{Cl}_y$  film contains substantial Cl, the large background emission from Cl in the Ar plasma makes it very difficult to detect a difference in Cl emission with and without substrate bias. No other emissions were identified in the difference spectra, including  $\text{SiCl}_2$ ,  $\text{SiCl}_3$ ,  $\text{YCl}$  and  $\text{YO}$ , indicating that these species are not sputtered from the surface.

### 3.3.2 – Sputter-depth profiling in Ar plasma after SiO<sub>2</sub> etching in C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasmas

Films deposited on the Y<sub>2</sub>O<sub>3</sub> coupon after etching SiO<sub>2</sub> in C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub> plasmas were also investigated. Spectra were recorded with and without coupon bias, as above. Emission from CF<sub>2</sub> and O were detected in the initial difference spectra, indicating sputtering of a CO<sub>x</sub>F<sub>y</sub> film. A sputter depth profile plot is shown in Fig. 3.6 for a C<sub>4</sub>F<sub>8</sub>/10%O<sub>2</sub> plasma. It took ~4 min to remove the fluorocarbon film that deposited on the walls. Pure C<sub>4</sub>F<sub>8</sub> plasmas deposited a somewhat thicker film that requires about 5 min to remove (not shown), while the film deposited in a C<sub>4</sub>F<sub>8</sub>/40%O<sub>2</sub> plasma was sputtered away in ~2 min (also not shown). This is to be expected as a result of the consumption of CF<sub>x</sub> film precursors in the plasma by reactions with O<sup>118, 119</sup>.

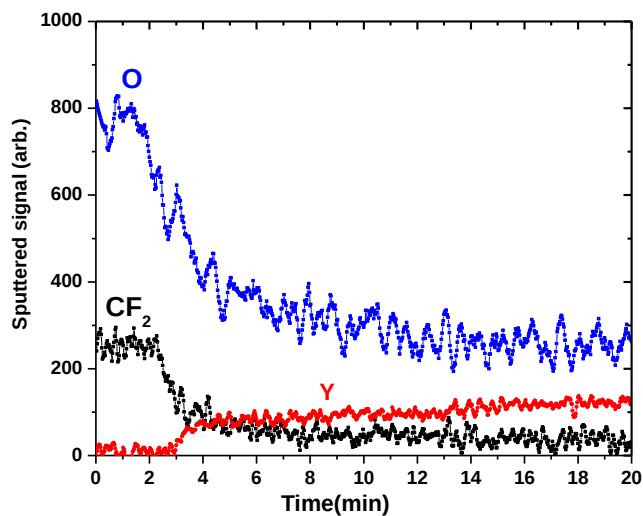


FIG. 3.6. Time-resolved optical emission intensities of CF<sub>2</sub>, O and Y in an Ar plasma just after etching SiO<sub>2</sub> in a C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub> plasma. Etching conditions: C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar flow rates: 10:1:2 sccm, pressure = 20 mtorr, ICP power = 400 W, V<sub>DC</sub> = -140V, etching time = 9 min. Sputtering conditions: 20 sccm Ar, pressure = 80 mtorr, ICP power = 160 W, V<sub>DC</sub> = -400 V.

### 3.3.3 – Sputter-depth profiling in $\text{Cl}_2/\text{Ar}/\text{O}_2$ plasma after Si etching in $\text{Cl}_2/\text{Ar}/\text{O}_2$ plasmas

A goal of this study is to demonstrate the use of glow discharge optical emission spectroscopy for real time analysis of surfaces in plasmas during etching processes. This can be carried out by simply turning off the Si substrate bias, while continuing to record emission spectra as a function of time. An example of such an experiment is shown in Fig. 3.7. Differences in emission intensities of Si, SiCl, YCl ( $B^1\Pi \rightarrow X^1\Sigma$ ) and O with and without coupon bias were recorded as a function of sputtering time, including the 10 s period before turning off substrate bias.

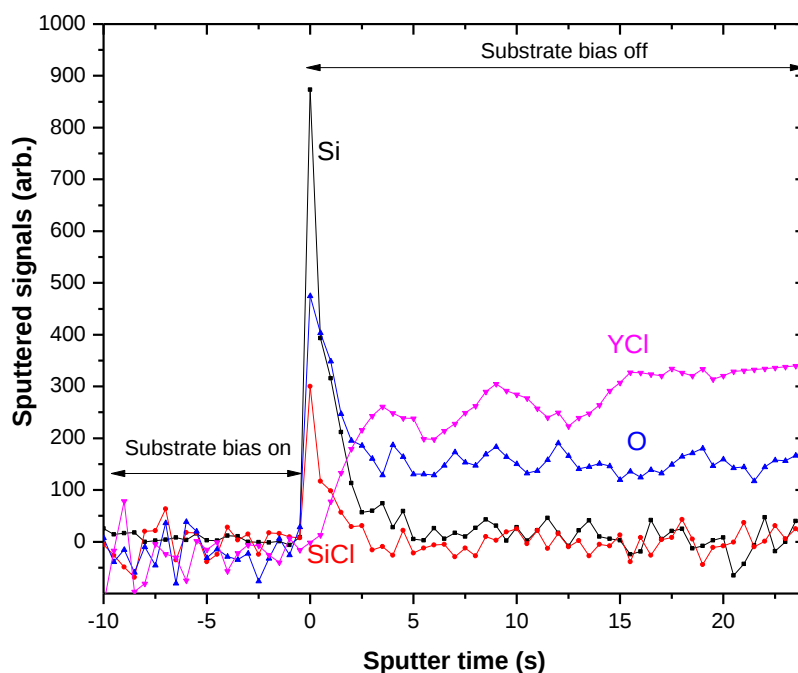


FIG. 3.7. Time-resolved optical emission intensity of Si, SiCl, YCl and O in a  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma during ( $t < 0$ ) and just after ( $t > 0$ ) etching Si in the same plasma. Etching conditions :  $\text{Cl}_2/\text{Ar}/\text{O}_2$ : 20:2:1 sccm; 40 mtorr, 200 W ICP CW,  $V_{\text{DC}}=-150\text{V}$ ; 15 min etching. Sputtering conditions: no substrate bias power, coupon power = 25 W, coupon  $V_{\text{DC}} = -250\text{V}$

Unfortunately, during Si substrate bias, the very intense emission from Si and SiCl in the plasma masks any small difference between the coupon bias on and off emission intensities, and the net signals are indistinguishable from zero. As the substrate bias was turned off, however, emissions from Si, SiCl and O sputtered off the coupon are immediately detected rising out of a decaying background. Within 5 s, Si and SiCl signals decayed to baseline and YCl and O signals reach a near-steady-state level. No Y signal was detected after sputtering away the  $\text{SiO}_x\text{Cl}_y$  film in the  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma. Instead, YCl is detected after the deposited film is removed. Apparently, Cl bonds to Y, making it easier to sputter  $\text{Y}_2\text{O}_3$  coupon, but with the product being  $\text{YCl}_x$ , with very little sputtered Y. This may also explain why the Si and SiCl signals in the chlorine plasma are much weaker than when an Ar plasma is used to sputter the coupon; adsorbed Cl bonds to Si and shifts the sputtered products to mostly  $\text{SiCl}_y$  ( $y > 1$ ) species.

The 5s required to sputter the  $\text{SiO}_x\text{Cl}_y$  film from the surface of the  $\text{Y}_2\text{O}_3$  coupon is much shorter than the  $\sim 150$  s needed to remove the film in the Ar plasma. The  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma would be expected to sputter the  $\text{SiO}_x\text{Cl}_y$  film much faster than does an Ar plasma, at least for small  $\text{O}_2$  additions. Thus, not only would the film be removed faster once the Si substrate bias is extinguished and film deposition stops, but the periodic sputtering of the film during deposition would lead to a thinner film being deposited, both of which could lead to the observed short time to sputter away the film for the conditions in Fig. 3.7

Many other experiments would be needed to sort out these effects. In addition, much can be done to reduce the contributions from emission in the plasma, especially from Si, SiCl, Cl and O, making it much easier to extract these emissions resulting from

sputtering of the film deposited on the coupon. Ongoing efforts are focused on blocking the light coming from the plasma, especially near the ICP coil, by installing a black anodized aluminum sheet just above the electrode and optical fiber.

### 3.3.4 – Quantification of sputter depth profiles

An analytical method similar to sputter depth profiling with AES, XPS or SIMS can be applied to extract atomic concentrations from GD-OES sputter depth profiles<sup>120-123</sup>. The emission intensity,  $I_X$  for an atom X in the film is proportional to its number density in the gas above the sample that is probed by the optical emission spectrometer. This is in turn proportional to the product of its number density in the film,  $N_X$ , and the sputtering rate for the sample,  $S_d$ , which may depend on the film composition and hence sputter depth,  $d$ . The proportionality constant is a sensitivity factor,  $F_X$ , that we assume has no composition dependence.  $F_X$  contains the dependences on the electron impact cross section of the emitter, the electron energy distribution in the probed region rear the sample, and the wavelength-dependent relative detection efficiency of the spectrometer. The absolute spectrometer sensitivity, electron number density, and ion flux and energy can be lumped into one proportionality constant,  $a$ , that is the same for all species. It will cancel out in the final analysis. The number density,  $N_X$  of X is then,

$$N_X = \frac{I_X}{aS_dF_X} . \quad (3.1)$$

Total atomic concentration present in the film is the summation of concentrations of individual species present on the sputtering surface. In the example of Ar plasma sputtering after Si etching in  $\text{Cl}_2/\text{O}_2$  plasmas that leads to deposition of a  $\text{SiO}_x\text{Cl}_y$  film on

a  $\text{Y}_2\text{O}_3$  coupon piece, the total atomic concentration ( $N_T$  in atoms/cm<sup>3</sup>) is the sum of the atomic concentrations (also in atoms/cm<sup>3</sup>) of yttrium ( $N_Y$ ), oxygen ( $N_O$ ), silicon ( $N_{Si}$ ) and chlorine ( $N_{Cl}$ ),

$$N_T = N_Y + N_O + N_{Si} + N_{Cl} , \quad (3.2)$$

The total number density is therefore,

$$N_T = \frac{1}{aS_d} \left( \frac{I_Y}{F_Y} + \frac{I_O}{F_O} + \frac{I_{Si}}{F_{Si}} + \frac{I_{Cl}}{F_{Cl}} \right) . \quad (3.3)$$

For each species, the composition expressed in atomic percent,  $C_X$ , is given by

$$C_X = 100 \frac{N_X}{N_T} = 100 \frac{I_X}{F_X} / \left( \frac{I_Y}{F_Y} + \frac{I_O}{F_O} + \frac{I_{Si}}{F_{Si}} + \frac{I_{Cl}}{F_{Cl}} \right) . \quad (3.4)$$

Note that the determination of concentrations expressed in atomic % does not require a knowledge of the sputtering rate. (Actually, the method used here to determine  $F_{Cl}$  and  $F_{Si}$  does require a determination of relative sputtering rates, as detailed below.) Of course, converting sputtering time into depth requires a determination of the absolute sputtering rate,  $S_d$ , as it does with any sputter depth profile analysis method.

Here the atomic emission lines at 410 nm and 777 nm were used to obtain the intensities of Y and O. For Cl, we use the SiCl emission, since Cl emission was unreliable due to the large background signal. For Si, either the same SiCl emission or Si emission could be chosen, or even an average of the two. Since the Si emission persisted after the SiCl emission was no longer observed in the difference spectrum, we chose the 288 nm line of Si.

The most difficult task in obtaining quantitative depth profiles is the determination of the sensitivity factors.  $F_Y$  was determined from the emission during sputtering of the  $Y_2O_3$  coupon, after the  $SiO_xCl_y$  film was removed,

$$F_Y = \frac{3}{2} \frac{I_Y}{I_O} F_O. \quad (3.5)$$

One factor can be set to unity; here we choose  $F_O = 1$ . Using the measurements in Fig. 3.5 at longer times ( $t = \sim 600$  s, not shown in the figure),  $I_Y/I_O = 185/156$  and  $F_Y = 1.78$ .

For Si and Cl sensitivity factors, we first obtain  $F_{Cl}$  relative to  $F_{Si}$ ,

$$F_{Cl} = \frac{1}{y} \frac{I_{Cl}}{I_{Si}} F_{Si} = r F_{Si}, \quad (3.6)$$

from the SiCl and Si emission intensity measurements in Fig. 3.5 (b) and Fig. 3.5 (a), in the early stage of sputtering, when no O is present, and the  $Y_2O_3$  substrate is still covered with the  $SiCl_y$  film. For the period when the signal is relatively constant (12-14 s),  $\frac{I_{Cl}}{I_{Si}} = 0.29$ . For  $y$ , we assume that the Cl content in this  $SiCl_y$  layer is equal to that found when Si(100) is exposed to a  $Cl_2$  ICP at the very low ion energy ( $\sim 5$  eV) in the present study at the unbiased coupon. The Cl surface coverage on Si(100) under these conditions is  $1.5 \times 10^{15} \text{ cm}^{-2}$ <sup>35</sup>, hence given a Si density of  $6.8 \times 10^{14} \text{ cm}^{-2}$  on the (100) surface,  $y \approx 2$ , and  $r = 0.15$ .

To then obtain  $F_{Cl}$  and  $F_{Si}$ , relative to  $F_O$ , we assume that the  $SiO_xCl_y$  film has the same atom number density as  $SiO_2$ ,  $N_{SiO_2}$ , hence

$$N_{SiO_2} = \frac{3 \rho_{SiO_2} N_A}{M_{SiO_2}} = \frac{1}{aS_d} \left( \frac{I_O}{F_O} + \frac{I_{Si}}{F_{Si}} + \frac{I_{Cl}}{F_{Cl}} \right), \quad (3.7)$$

where  $\rho_{SiO_2}$  and  $M_{SiO_2}$  are the density and atomic weight of  $SiO_2$ , and  $N_A$  is Avogadro's number. To eliminate  $a$ , we write a similar expression for  $Y_2O_3$  at a depth sufficiently large ( $d \rightarrow \infty$ ) that the film deposited on the coupon has been completely sputtered away

$$N_{Y_2O_3} = \frac{5 \rho_{Y_2O_3} N_A}{M_{Y_2O_3}} = \frac{1}{aS_\infty} \left( \frac{I_{Y,\infty}}{F_Y} + \frac{I_{O,\infty}}{F_O} \right), \quad (3.8)$$

where  $\rho_{Y_2O_3}$  and  $M_{Y_2O_3}$  are the density and atomic weight of  $Y_2O_3$ , and  $S_\infty$  is the  $Y_2O_3$  sputtering rate. Combining (3.6), (3.7) and (3.8), approximating  $N_{SiO_2}/N_{Y_2O_3}$  as unity, and solving for  $F_{Si}$ ,

$$F_{Si} = \frac{I_{Si} + \frac{I_{Cl}}{r}}{\frac{S_d}{S_\infty} \left( \frac{I_{Y,\infty}}{F_Y} + \frac{I_{O,\infty}}{F_O} \right) - \frac{I_O}{F_O}}. \quad (3.9)$$

For  $I_{Si}$ ,  $I_{Cl}$ , and  $I_O$ , we use the measurements in Fig. 3.5 (a, b and d) for 5% $O_2/Cl_2$  plasmas near 25 s (780, 170 and 550, respectively), when the signals are nearly constant and none of the O signal is originating from the substrate, based on the absence of Y emission in Fig. 3.5(c). We did not measure the sputtering rates of the film and  $Y_2O_3$  in this study. Such a determination is necessary to complete the extraction of the sensitivity factors for Si and Cl.

If we assume that the O emission is proportional to relative sputtering rate, then

$$\frac{S_d}{S_\infty} = \left( \frac{I_O}{I_{O,\infty}} \right) \left( \frac{3}{x} \right), \quad (3.10)$$

where  $x$  is  $\sim 1.5$  for  $SiO_xCl_y$ , hence  $\frac{S_d}{S_\infty} = \left( \frac{550}{160} \right) \left( \frac{3}{1.5} \right) = 6.9$ . Using this and the other required values in (3.9), we obtain the sensitivity factor for Si,  $F_{Si} = 1.21$ .  $F_{Cl} = 0.18$  is then obtained from eqn (3.6).

Atomic concentrations,  $C_X$ , from eqn. (3.4) for  $X = \text{Si, Cl, O, and Y}$ , determined from the Savitzky-Golay 100 points filtered data followed by 40 point FFT smoothing in Fig. 3.5, are plotted in Fig. 3.8. Si atomic concentration rose to 40% within 100 s followed by a slower decay, and reached baseline near 500 s. Chlorine started with the highest atomic concentration of 47% and decayed faster to 10% within 200 s. No Y atomic concentration was present initially, but as the  $\text{SiO}_x\text{Cl}_y$  film was sputtered away, Y concentration from sputtering the underlying substrate increased to 40%. Also, O atomic concentration rose to a steady-state concentration of ~55%, when  $\text{Y}_2\text{O}_3$  substrate is sputtered at a constant rate.

We have therefore demonstrated a method for obtaining quantitative depth profiles of atomic species number densities in adsorbed films deposited on chamber walls during plasma processing. Improvements in background emission suppression, and calibration standards should make it possible to simplify the analysis and enhance its accuracy and information content.

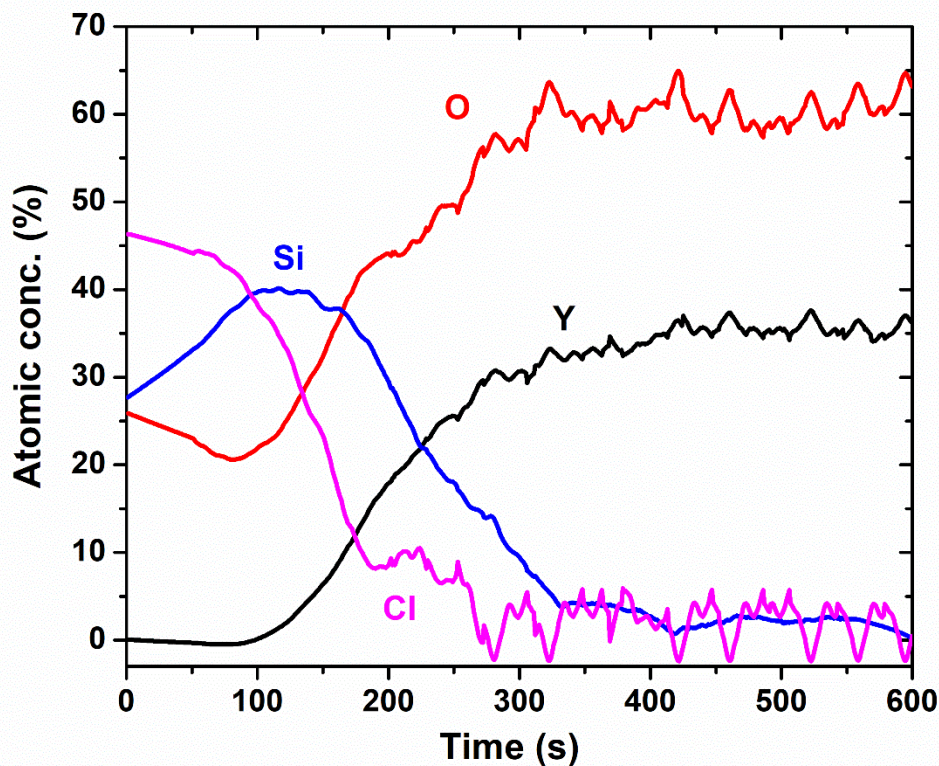


FIG. 3.8. Time-resolved relative atomic concentrations of Si, Cl, O and Y in an Ar plasma just after etching Si in a  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma. Etching Conditions :  $\text{Cl}_2/\text{Ar}/\text{O}_2$  : 20:2:1 sccm ; 20 mtorr, 400 W ICP CW,  $V_{\text{DC}}=-80\text{V}$ ; 15 mins etching. Sputtering Conditions: 20 sccm Ar, 9 mtorr, 160 W ICP,  $-320\text{ V}_{\text{DC}}$ .

### 3.4 Conclusions

Glow discharge optical emission spectrometry was developed and demonstrated for *in-situ* measurement of the chemical composition of surfaces exposed to plasmas. Pulsed bias was applied to sputter the surface of a yttria-covered aluminum coupon piece, in the wall at the edge of an inductively-coupled plasma. Optical emission was collected from the region of the plasma above the surface of the coupon. The difference in intensity between the coupon bias on and off condition was used to determine what species were present on the surface. Si or  $\text{SiO}_2$  substrates on a separately rf-biased electrode were etched in  $\text{Cl}_2/\text{Ar}$

or  $\text{C}_4\text{F}_8/\text{O}_2$  ICPs, respectively. Measurements were made after etching in an Ar ICP, as well as during etching.

After Si etching in a  $\text{Cl}_2/\text{O}_2/\text{Ar}$  plasma, sputtering in an Ar ICP produced optical emission from Si, SiCl, Y and O. As the  $\text{SiO}_x\text{Cl}_y$  film that deposited on yttria during Si etching was sputtered away, SiCl emissions decayed to baseline somewhat faster than Si emissions. Y emissions began to be observed as the SiCl and Si emission decayed, indicating sputtering of the underlying substrate. Y emissions increased to a steady-state level after complete removal of the  $\text{SiO}_x\text{Cl}_y$  film. O emissions that initially arose from the film, also reached to a steady-state level resulting from yttria sputtering. Similar analysis was done by depositing films on the  $\text{Y}_2\text{O}_3$  coupon after etching  $\text{SiO}_2$  in  $\text{C}_4\text{F}_8/\text{O}_2$  plasmas. Emissions from  $\text{CF}_2$  and O were detected in the initial difference spectra, indicating sputtering of a  $\text{CO}_x\text{F}_y$  film.

An analytical method similar to sputter depth profiling in XPS, AES or SIMS was developed to extract atomic concentration vs. depth profiles from GD-OES sputtering in Ar plasmas after etching in  $\text{Cl}_2/\text{O}_2/\text{Ar}$  plasmas. Sensitivity factors were obtained for sputtered species Si, Cl, O and Y. A sample depth profile was obtained for the film deposited on Yttria during Si etching.

Additionally, GD-OES was demonstrated for real time analysis of surfaces in plasmas during etching processes. Optical emission intensities of Si, SiCl, YCl and O with and without coupon bias were recorded as a function of sputtering time in  $\text{Cl}_2/\text{O}_2/\text{Ar}$  plasma. The  $\text{SiO}_x\text{Cl}_y$  film was sputtered much faster in the  $\text{Cl}_2/\text{Ar}/\text{O}_2$  plasma than in the Ar plasma.

### 3.5 Future work

In the present experimental set-up, difference spectra for Cl emission can't be obtained because bias-off intensity is too large. Reducing the bias-off signal will possibly help in detecting Cl emissions and increase O difference signal as well. Thus, installing a black anodized aluminum sheet just above the electrode and optical fiber can block the light coming from source. Further calibration standards can be used to improve the quantification of signals to obtain atomic concentration of species in the adsorbed layers.

This technique can be extended to determine sputtering threshold of various yttrium containing chamber wall coating materials.  $Y_2O_3$ , YOF and  $YF_3$  coatings are widely used in industrial etching chambers. With GD-OES technique at minimum possible coupon bias, various Y peaks can be observed at higher exposure time and large spectrometer slit width. Measured values of sputtering threshold will help to determine the durability of these coating materials in industrial chambers.

## Chapter 4 – Chlorine Recombination Coefficients

### 4.1 Literature Review

Chlorine plasmas are widely used for etching poly-Si and other materials for integrated circuit manufacturing<sup>124</sup>. In plasma etching processes at lower pressures (typically 0.01 - 0.1 Torr), radicals typically undergo on the order of a hundred collisions with walls before being pumped from the chamber. Heterogeneous reactions on the walls therefore play an important role in determining radical species number densities, which in turn can affect plasma parameters such as electron density, electron temperature and the electron energy distribution function (EEDF)<sup>125</sup>.

The rates at which these reactions occur is a function of the plasma-facing material (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ , polymers, etc.) and can vary over a wide range. For a given material, rates can also change dramatically, due to changing surface conditions caused by exposure to the plasma radicals and energetic ions, as well as etching products. Chamber cleaning processes can also alter reaction rates. These effects lead to both short and long term drift in plasma etching metrics such as etching rate uniformity and selectivity.

For chlorine plasmas, Cl atoms and positive ions are the most important species in determining etching rates and uniformities. Cl is lost at the surface by reactions with  $\text{SiCl}_x$  to form  $\text{SiCl}_{x+1}$ , as well as by recombination reactions with Cl to form  $\text{Cl}_2$ . The recombination probability,  $\gamma_{\text{Cl}}$ , for Cl is generally reported to be first order with Cl flux to the surface. Many values have been reported for  $\gamma_{\text{Cl}}$ , spanning a wide range. Meeks et al., reported a value of 0.15 for chlorinated anodized aluminum (nominally  $\text{Al}_2\text{O}_3$ ), a common coating for plasma chambers<sup>126</sup>. Ashida and Lieberman calculated  $\gamma_{\text{Cl}} = 0.15$  through global

model in a pulsed chlorine plasma<sup>127</sup>. Kota et al. measured recombination coefficients for Cl on a variety of surfaces in a molecular beam experiment<sup>128, 129</sup>. Values for  $\gamma_{\text{Cl}}$  ranged from 0.01 for crystalline silicon to  $\sim 0.85$  for stainless steel.

Aydil and co-workers investigated surface chemistry dependent kinetics in  $\text{Cl}_2$  plasma by OES in conjunction with actinometry, while the state of the reactor walls was monitored using multiple total internal reflection-fourier transform infrared (MTIR-FTIR) spectroscopy to monitor the composition of the surface films and absorbates *in situ*<sup>130, 131</sup>. They reported a wall recombination probability of Cl atoms on the  $\text{SiO}_2$  covered walls of  $\gamma_{\text{Cl}} = 0.03$ <sup>132</sup>, an order magnitude lower than that reported for anodized aluminum<sup>128</sup>. Cunge et al. measured Cl recombination probabilities in chlorine-containing plasmas on various plasma-treated surfaces, including plasma-cleaned  $\text{Al}_2\text{O}_3$  ( $\gamma_{\text{Cl}} = 0.3$ ) and a  $\text{SiO}_x\text{Cl}_y$  coating ( $\gamma_{\text{Cl}} \sim 0.005$ ) formed by exposure to etching products in a  $\text{Cl}_2/\text{O}_2$  plasma<sup>133, 134</sup>. Corr et al., used 2-photon laser-induced fluorescence (LIF) to measure absolute atomic chlorine densities for comparisons with 2D fluid simulations. The best agreement between model and experiment was obtained for  $\gamma_{\text{Cl}} = 0.02$  on plasma modified stainless steel<sup>135</sup>. Using the spinning wall method, Guha, et al., found that recombination coefficients on  $\text{Cl}_2$  plasma-conditioned anodized Al surfaces increased from about 0.01 to 0.1 with increasing Cl-to- $\text{Cl}_2$  number density ratio<sup>136</sup>. Using the same technique, Stafford et al., studied  $\text{Cl}_2$  plasma-conditioned stainless steel and found similar increases in  $\gamma_{\text{Cl}}$  over the same range of Cl-to- $\text{Cl}_2$  number density ratios, but the absolute values (0.004 to 0.03) were about half of what they were for  $\text{Al}_2\text{O}_3$ <sup>137</sup>. In a follow-up study, Khare et al., found  $\gamma_{\text{Cl}} = 0.03$  on an oxygen plasma-conditioned surface and  $< 0.001$  on silicon-chloride-rich layer formed by etching Si in a  $\text{Cl}_2/\text{O}_2$  plasma<sup>138</sup>.

Kinetic parameters are difficult to measure *in situ* in plasma processing due to the complexity of the plasma. Various experimental and computational methods have been used to obtain the *in situ* recombination coefficients briefly described above. One of those methods is power-modulated plasmas. Donnelly and Flamm modulated a 14 MHz SiF<sub>4</sub> plasma at 1 kHz and used time resolved optical emission spectroscopy (OES) to study the reactions of F<sub>2</sub> and F with SiF<sub>2</sub> that produce broadband chemiluminescence, accompanying Si etching in fluorine-containing plasmas<sup>139</sup>. Olesik and Bradley used power modulation to gain insights into mechanisms for excitation and relaxation processes in an Ar inductively coupled plasma used for elemental analysis<sup>140</sup>. The plasma processes associated with excitation of Ca and Li emissions was determined by measuring time delay between an abrupt increase/decrease in power and changes in the emission intensities. A similar method was employed by Wanger and Veprek to study deposition of amorphous and micro-crystalline silicon in a SiH<sub>4</sub>/H<sub>2</sub> plasma<sup>141</sup>. Hansen, et al., used a pulsed direct current (DC) plasma to study kinetics of CF<sub>4</sub>/O<sub>2</sub>/Ar plasmas<sup>142</sup>. CF and CF<sub>2</sub> were monitored by laser-induced fluorescence. They concluded that under their conditions, it appeared that CF, CF<sub>2</sub>, and excited F were formed primarily by electron impact on CF<sub>4</sub>.

Following this work, Hancock introduced time-resolved actinometry to investigate the kinetics of F and CF<sub>2</sub> in CF<sub>4</sub> and CF<sub>4</sub>/O<sub>2</sub> plasmas<sup>143</sup>. Relative number densities were determined as a function of varying delays between the extinction and re-initiation of power. Bouchoule and Ransom<sup>144</sup> modulated the power to a H<sub>2</sub>/Ar plasma and used time-resolved emission and laser-induced fluorescence to derive recombination rate constants and probabilities for heterogeneous H recombination as a function of chamber conditioning time. Booth and Sadeghi<sup>145</sup> also used time-resolved actinometry to investigate O and F

reactions on stainless steel. They found that sticking coefficients (equated with recombination or other reactions) for O decreased from 0.5 to 0.09 when F was introduced into O<sub>2</sub> plasmas, but F values remained at 0.06, independent of O addition.

Kiss and Sawin used power modulation to study the kinetic rates and mechanisms of CF<sub>4</sub>, CF<sub>3</sub>Cl and C<sub>2</sub>F<sub>6</sub>/Cl<sub>2</sub> plasmas<sup>147,148</sup>. The modulation in electron density caused by power modulation induced a periodic perturbation in the kinetics of F and Cl, measured by Ar actinometry. By coupling experiments with kinetic models, they deduced reaction mechanisms and recombination probabilities of 0.15 and 0.05 for Cl and CF<sub>3</sub>, respectively, on anodized Al<sup>148</sup>. Cunge and coworkers investigated surface loss kinetics by measuring species densities using absorption spectroscopy in the afterglow of BCl<sub>3</sub>/Cl<sub>2</sub> and Cl<sub>2</sub> pulsed plasmas<sup>149, 150</sup>. They derived heterogeneous loss coefficients of  $\gamma = 0.3 \pm 0.1$  for BCl on Al<sub>2</sub>O<sub>3</sub>,  $0.1 \pm 0.03$  for Cl atom on AlF<sub>3</sub>, and  $0.007 \pm 0.004$  for Cl atom on SiO<sub>x</sub>Cl<sub>y</sub> surfaces. In previous studies for a mostly yttria-coated reactor, during repeated etching of Si in a Cl<sub>2</sub> inductively-coupled plasma (ICP), alternating with waferless chamber cleaning in a NF<sub>3</sub> ICP, we found time-dependent increases in Cl and Si-containing radical species concentrations as the chamber walls in transition from a F-enriched to Cl-enriched surface. This effect was ascribed to decreasing probabilities for heterogeneous reactions that produce Cl<sub>2</sub> and SiCl<sub>4</sub><sup>125, 151</sup>. Finally, Curley et al.,<sup>152</sup> studied Cl and H heterogeneous loss rates on unanodized aluminum in Cl<sub>2</sub>/H<sub>2</sub> ICPs, using actinometry and pulsed power. They report low H recombination coefficients, varying from 0.006 to 0.023 as conditions were varied, and a more constant value of 0.03-0.06 for Cl.

## 4.2 Experimental

Time-resolved optical emission spectra were recorded with one spectrometer (Ocean Optics HR4000 with 0.17 nm resolution) that covered the 740–920 nm region. Spectra integration and averaging times were adjusted based on the intensity levels and rise and decay times of the species of interest. Line-integrated optical emission was collected using an optical fiber cable, equipped with a collimating lens on the input side. The fiber cable leading to the spectrometer was positioned behind the chopper, as shown in Fig. 4.1.

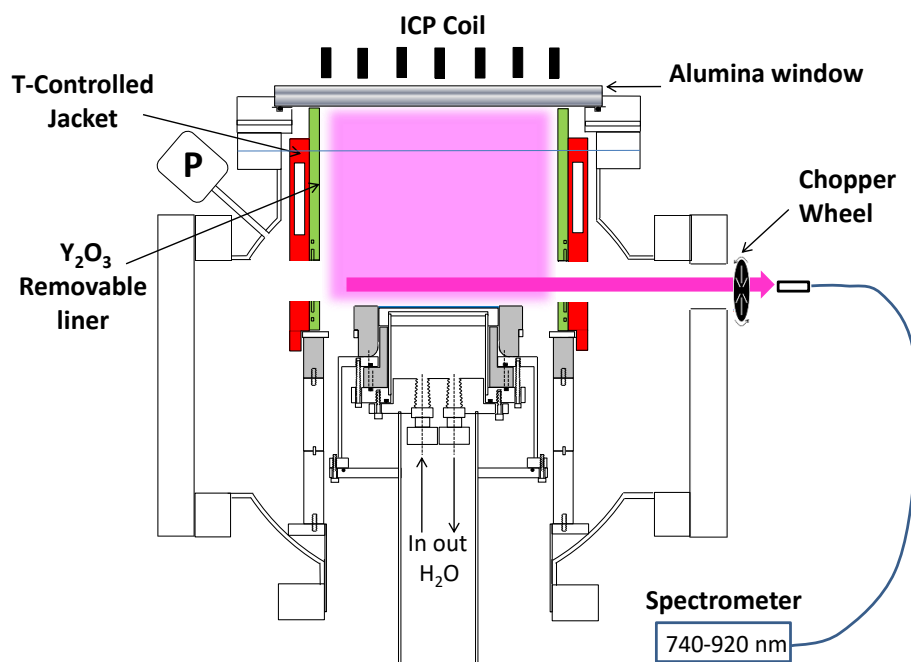


FIG. 4.1. Schematic of the inductively-coupled plasma reactor chamber.

The time-resolved optical emission as a function of phase in the power modulation period was simply achieved with a mechanical chopper wheel (SCITEC 300C), as described in Fig. 4.2. The setup is similar to that used by Wang, et al.,<sup>153</sup>. A sync out pulse

from the chopper triggered a pulse generator (BNC 505) that produced an adjustable delay pulse to amplitude modulate (AM) a function generator that was configured to deliver a 13.56 MHz sinusoidal wave. The modulated output of the function generator was amplified and delivered to the plasma through an impedance matching network. The degree of modulation was determined by the amplitude of the adjustable delay pulse, while the duration of a particular level of power delivery and time relative to the beginning of the current sampling window of the chopper wheel were determined by the width and delay time of the pulse. Therefore, for a given delay time, the sampling window was always open to the spectrometer at the same phase of the power modulation period for all cycles. The power modulation period was determined by the rotation speed and number of slots on the chopper blade. The time resolution of this optical detection system was determined by the open time of the chopper blade. This resulted in a time resolution (defined as the time for a step function signal to rise and fall by  $1/e$ ) of 50  $\mu\text{s}$  for the 2 ms modulation period. Since the Cl number density rise and fall times are on the order of 1 ms, this resolution is more than adequate.

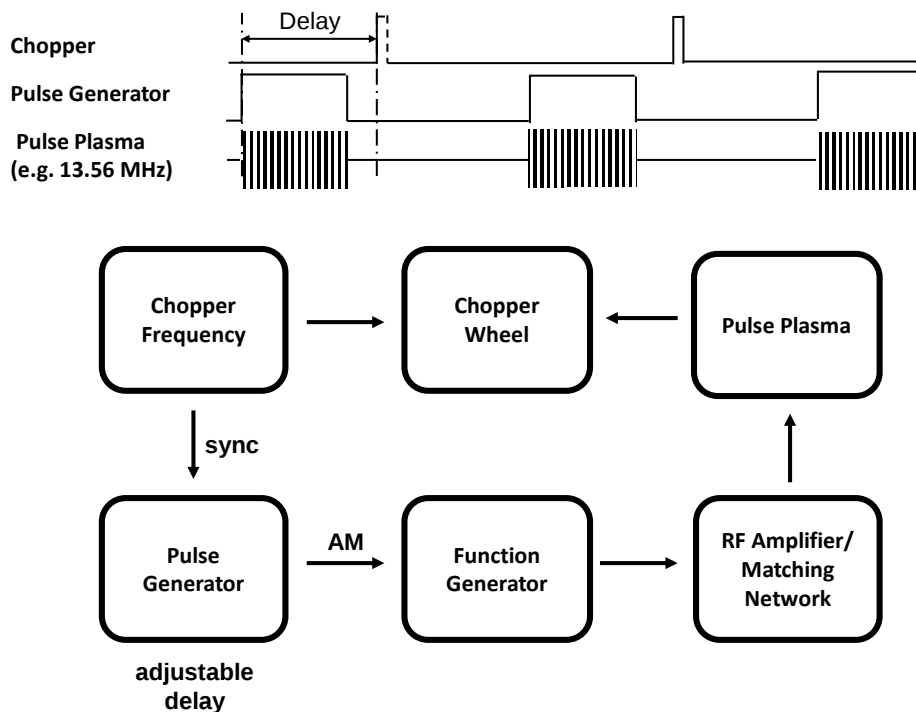


FIG. 4.2. Diagram of time resolved system for optical emission measurements.

The plasma was operated with a 20 standard cubic centimeters per minute (sccm) flow rate. A 2 sccm flow of a trace rare gases (TRG) mix of 40% Ne, 20% Ar, 20% Kr and 20% Xe was added to the  $\text{Cl}_2$  flow for actinometry measurements. In some cases, 1 sccm of  $\text{O}_2$  was added to the feed gas. In a few experiments, the TRG flow was replaced with 2 sccm  $\text{N}_2$  for determining gas temperature by rotational analysis of  $\text{N}_2 \text{ C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$  optical emission<sup>154-156</sup>. The total pressure was kept at 20 mTorr for all experiments. Modulation frequencies of 500 Hz, with corresponding duty cycles of 50% were used. Power was modulated between 320W and 0 W. The substrate stage holding a 3 inch diameter un-patterned p-type Si wafer was either grounded, or biased with 15 W of radio frequency (rf) power (18 MHz, -80V<sub>DC</sub> self-bias). Bias was pulsed on in sync with pulsed power to the coil.

After  $\text{NF}_3$  plasma cleaning, time-resolved measurements were recorded in  $\text{Cl}_2/\text{TRG}$  or  $\text{Cl}_2/\text{O}_2/\text{TRG}$  power modulated plasmas: 1) before the application of substrate bias, 2) during Si etching with rf bias on the substrate stage, and 3) after rf bias was turned off. A reduced global model was used to extract the single variable,  $\gamma_{\text{Cl}}$ , the Cl heterogeneous loss coefficients.  $\gamma_{\text{Cl}}$  was determined from Cl-to-Xe number density measurements<sup>146</sup>.

## 4.3 Results

### 4.3.1 – Gas temperature measurements and effects of gas heating on determination of $\gamma_{\text{Cl}}$

Gas heating can complicate extraction of heterogeneous reaction probabilities such as  $\gamma_{\text{Cl}}$  through several effects. First, at constant pressure, species number densities scale inversely with gas temperature ( $T_g$ ). Some modulation in  $T_g$  will occur in pulsed plasmas when the modulation period is longer than or comparable to the time for gas cooling. If the species number density is determined by a method such as absorption spectroscopy or laser-induced fluorescence, then this must be corrected for. The correction is particularly difficult for absorption spectroscopy, since temperature and hence number density varies by as much as a factor of five across the optical path length over which the line-integrated absorption measurement is made. If on the other hand, species number density is determined from actinometry, and the relative number density ratio of the species to the actinometry gas (e.g., Cl-to-Xe ratio in the present case) is used, then this temperature effect cancels out and can be ignored. Second, temperature affects the rate of diffusion of species to the walls. The loss rate for Cl due to diffusion to the walls increases with  $T_g$  by between  $T_g^{1/2}$  and  $\sim T_g^{3/2}$  depending on pressure. As shown below, the effect is relatively

small in the experiments described in this study, but is nonetheless corrected for in determining the loss probability for Cl at the walls.

To incorporate the effects of transient gas heating into the derivation of  $\gamma_{Cl}$ , neutral gas temperature was measured through N<sub>2</sub> (C<sup>3</sup>Π<sub>u</sub> → B<sup>3</sup>Π<sub>g</sub>) rotational spectroscopy. A small amount (10%) of N<sub>2</sub> was added to the discharge and the rotational temperature of the C<sup>3</sup>Π<sub>u</sub> state was determined from the emission band at 337.1 nm<sup>154-156</sup>. This temperature has been shown by others to be equal to the rotational temperature of ground-state N<sub>2</sub>, which is thermally equilibrated with the (translational and rotational) gas temperature<sup>154, 155</sup>.  $T_g$  measurements, derived from line-integrated N<sub>2</sub> emission 2 cm above the wafer, are shown in Fig. 4.3 (solid squares) for power modulated plasmas.  $T_g$  increased during the powered period from about 580K at 100 μs to 810K at 1000 μs. An exponential rising and falling function was fit to the measurements (line in Fig. 4.3) to provide an expression for  $T_g$  as a function of time in both the active glow and afterglow periods. This is used in the global model for determination of  $\gamma_{Cl}$ .

#### 4.3.2 – Modulated Cl-to-Xe Optical Emission and Number Density Ratios

Time-resolved Cl number densities were extracted from the actinometry expression<sup>157</sup>,

$$\frac{n_X}{n_A} = a_{X,A} \frac{I_X}{I_A} \frac{\gamma_A}{\gamma_X}, \quad (4.1)$$

where  $I_A$  is the intensity of the line chosen for the rare gas, A (Xe 828.0 nm), to best match the energy of the emitting species of interest, X (Cl 792.4 nm) and  $\gamma_A$  and  $\gamma_X$  are the spectrometer relative sensitivities at the emitting wavelength of the selected transitions. The proportionality constant,  $a_{X,A} = a_{Cl,Xe} = 10$  at 20 mTorr was taken from previous studies

<sup>158</sup>. Cl emission from dissociative excitation of Cl<sub>2</sub> was neglected, since it was found in previous studies<sup>158</sup> to be undetectable at the pressure and degree of dissociation in the present work. Excitation via dissociation of SiCl<sub>x</sub> is even less likely, since the Si-Cl bonds are stronger than the Cl<sub>2</sub> bond.

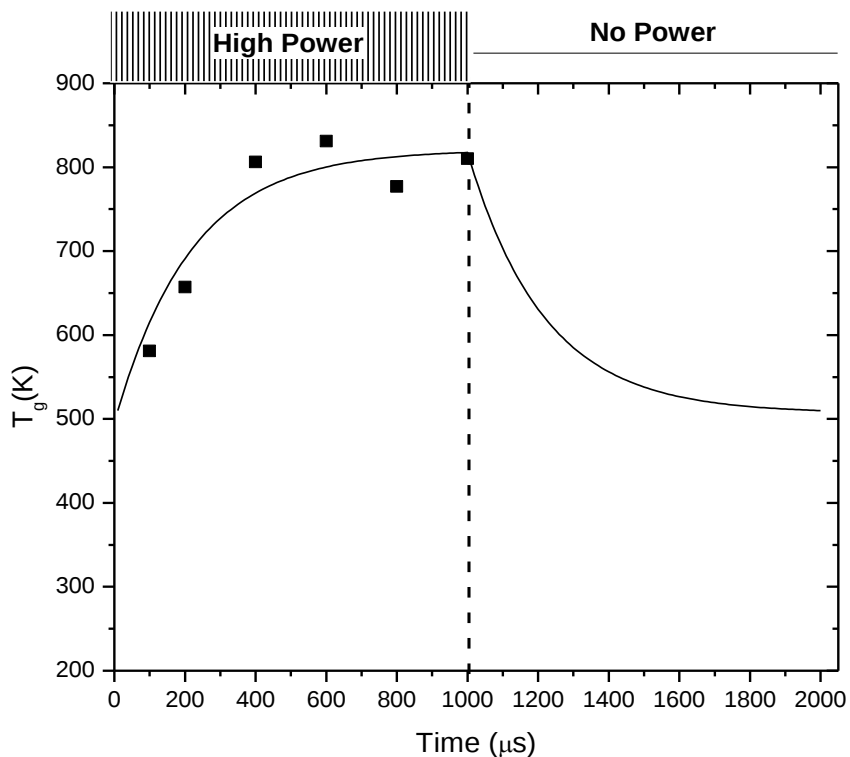


FIG. 4.3. Time resolved gas temperature measurements (solid squares) in a Cl<sub>2</sub>/O<sub>2</sub> plasma (20/2 sccm, respectively) at 20 mTorr pressure. Pulsing frequency = 500 Hz, 50% duty cycle, 320W (ON) to 0W (OFF). Squares are experimental results and line is exponential fitting.

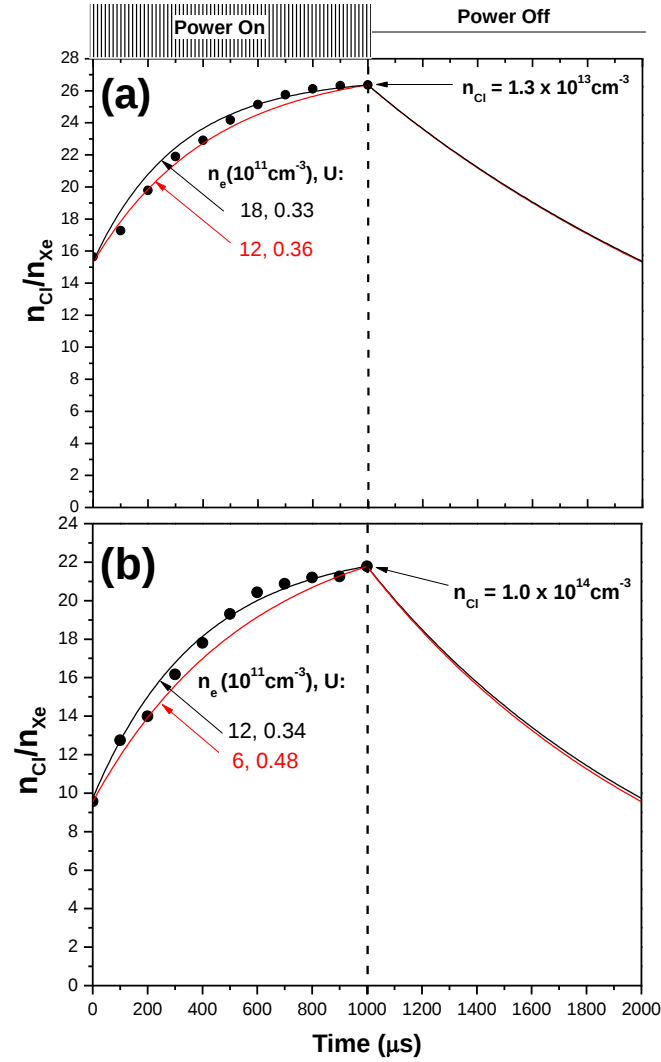


FIG. 4.4. Solid circles: Time-resolved  $n_{Cl}/n_{Xe}$  number density ratios as a function of time during the powered interval. The lines are simulation from the global model described below. Pulsing frequency = 500 Hz, Duty cycle = 50%, ICP power = 320 W (ON), 0 W (OFF), pressure = 20 mTorr, (a)  $Cl_2/TRG$  plasma. (b)  $Cl_2/O_2/TRG$  plasma.

Time-resolved intensities of Cl and Xe during the power portion of the modulation period were recorded as a function of plasma conditions over long time spans (up to 1 hr). Sample results are shown in Fig. 4.4 for **a)** after Si etching and then conditioning the chamber in a  $Cl_2$  plasma without substrate bias, and **b)** after similar conditioning in a  $Cl_2/O_2$  plasma, in the absence of etching of the Si substrate. Reaction probabilities of 0.11 and

0.17 for loss of Cl at the walls in Cl<sub>2</sub> and Cl<sub>2</sub>/O<sub>2</sub> plasmas, respectively, were determined from a model fit to the measured  $n_{Cl}/n_{Xe}$  values, as discussed in detail below.

### 4.3.3 – Surface reaction probability calculation

Surface reaction probabilities,  $\gamma_{Cl}$ , can be generally defined as the total loss probability for Cl at the walls due to formation of products including Cl<sub>2</sub> and SiCl<sub>x=1-4</sub>. If we first ignore heterogeneous reaction products other than Cl<sub>2</sub>, (justified below), then the following mechanism can be considered for the time-dependent global plasma chemistry:



where  $f_{Cl_2}$  in (4.2) is Cl<sub>2</sub> gas injection flux into the reactor,  $k_{dis}$  and  $k_{at}$  are rate constants for electron impact dissociation and attachment reactions (4.3) and (4.4). Recombination of Cl at the walls occurs by a two-step process, with reaction (4.6) being rate limiting. SiCl<sub>2</sub> is assumed to be the Si etching product desorbing. (SiCl is rapidly converted to SiCl<sub>2</sub> by the gas phase reaction with Cl<sub>2</sub>, which has a rate constant<sup>150</sup> of  $5.3 \times 10^{-11} \text{cm}^3$ ; SiCl<sub>3</sub> is expected to be a minor primary product, and the expected primary production of SiCl<sub>4</sub> etching product reduces the effect we are concerned with below.) The flow of SiCl<sub>2</sub> into the gas phase,  $f_{SiCl_2}$ , in (4.7), was computed from the Si etching rate ( $\sim 1820 \text{ \AA}/\text{min}$ , based

on average power scaling of rates found in a previous studies in a continuous  $\text{Cl}_2$  plasma in the same system <sup>125</sup>). Subsequent reactions (4.8) and (4.9) with  $\text{Cl}_2$  produce  $\text{SiCl}_4$  as a major or dominant Si-containing product in the gas phase. Electron impact dissociation of  $\text{SiCl}_x$  species is ignored, consequently  $\text{SiCl}_4$  is lost from the system by pumping in reaction (4.10). All other species are assumed to have the same pumping speed as  $\text{SiCl}_4$ , but since the loss rate for these species through reactions (4.3) – (4.6), (4.8), 4.9) are fast compared with the pumping speed, this assumption is irrelevant. Langmuir probe and Xe optical emission measurements are used to estimate the other time-dependent parameters ( $n_e$ ,  $T_e$ ,  $k_{dis}$  and  $k_{at}$ ). While we do include predictions of Cl-to-Xe number density ratios throughout the entire modulation period, we will use only the comparison of measured and predicted relative Cl-to-Xe number density ratios at the beginning and end of the afterglow period, determined solely by diffusion of Cl to the walls followed by its recombination to  $\text{Cl}_2$ , to derive  $\gamma_{Cl}$  values.

### ***i. Without Etching Products***

In the absence of etching products (i.e., the no-bias condition before or long after etching with bias), chlorine is present as either  $\text{Cl}_2$  or Cl. Because the gas residence time in the reactor ( $\sim 200$  ms) is much longer than the modulation period, loss of  $\text{Cl}_2$  and Cl due to pumping was negligible, relative to dissociation and recombination reaction rates. The pumping speed does, however, affect the total number density and the number density of Xe and  $\text{SiCl}_4$ , as well as the total gas number density. Ignoring any differences in pumping speeds, the time dependence of Cl was determined from the analytical or numerical solution of the time-rate of change and mass balance equations

$$\frac{dn_{Cl}}{dt} = 2k_d n_e n_{Cl_2} - k_{loss} n_{Cl} \quad (4.11)$$

and

$$\frac{n_{Cl_2}^0}{n_{Xe}^0} = \frac{n_{Cl_2}}{n_{Xe}} + \frac{n_{Cl}}{2n_{Xe}}, \quad (4.12)$$

where  $n_{Xe}$  is the Xe number density and the superscript 0 refers to number density with no plasma.  $\frac{n_{Cl_2}^0}{n_{Xe}^0}$  is simply equal to the feed gas flow rate ratio. The rate constant  $k_d$  ( $\text{cm}^3\text{s}^{-1}$ ) in Eq. (4.11) is the sum of the electron impact dissociation and dissociative attachment rate constants,  $k_{dis} = 4.52 \times 10^{-8} \exp(-7.3/T_e)$  and  $k_{at} = 6.2 \times 10^{-10} T_e^{-0.189} \exp(-1.04/T_e)$ , respectively.<sup>158</sup> It is assumed that  $\text{Cl}^-$  quickly recombines with  $\text{Cl}_2^+$ . At the measured  $T_e = 2.0$  eV (Fig. 4.4), electron impact dissociation is responsible for 67% of the generation of Cl. When power is turned off and  $T_e$  drops precipitously,  $k_{dis}$  becomes negligibly small, and  $k_{at}$  increases slightly, but because electrons are no longer being generated, dissociation of  $\text{Cl}_2$  during this period produces very little Cl.

For cylindrical shaped reactors, the rate constant,  $k_{loss}$ , for loss of species A at the walls can be obtained from Eqs. (4.13) – (4.16)<sup>159</sup>

$$\frac{1}{k_{loss}} = \frac{1}{k_D} + \frac{1}{k_W}, \quad (4.13)$$

$$k_D = \frac{D_{AB}}{\Lambda_0^2}, \quad (4.14)$$

and

$$k_W = \frac{\gamma_A}{2(2-\gamma_A)} \frac{\bar{v}_{AB} S}{V}, \quad (4.15)$$

where  $k_D$  is the diffusion rate for transport of A to the walls,  $k_W$  is the loss rate at the walls,  $\gamma_A$  is the probability for loss at the walls, S is the surface area exposed to the plasma and V is the reactor volume.  $\Lambda_0$  is characteristic length given by

$$\frac{1}{\Lambda_0^2} = \left(\frac{\pi}{l}\right)^2 + \left(\frac{2.405}{r}\right)^2, \quad (4.16)$$

where  $l$  and  $r$  are the plasma length (13.97 cm) and radius (7.62 cm).  $\tilde{v}_{AB}$  is the mean thermal speed for the gas impinging on the walls, corresponding to the reduced mass,  $M_A M_B / (M_A + M_B)$ , where A is Cl and B is Cl<sub>2</sub>. The temperature of the gas at the walls should be used to compute  $\tilde{v}_{AB}$ . This temperature,  $T_{gw}$ , was estimated to be 447K. It was obtained from the average temperature  $T_{ave} = 662K$ , measured 2 cm from the nearest surface (actually the substrate), and an estimate of temperature jump of  $\sim 134K$  between the gas and the wall at temperature  $T_w = 313K$  (using expressions given by Pan, *et al.*<sup>160</sup> and assuming the same values for C and  $\sigma_T$  as they found for O<sub>2</sub>).

The binary diffusion coefficient  $D_{AB}$  (cm<sup>2</sup>s<sup>-1</sup>) is given by the expression:

$$D_{AB} = 0.0018583 \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p \sigma_{AB}^2 \Omega_{D,AB}(T_{AB}^*)}}, \quad (4.17)$$

where  $M_A$  and  $M_B$  are the atomic and molecular masses (g/mol.) of Cl and Cl<sub>2</sub>,  $p$  is pressure (atm) and  $T$  is gas temperature (K). The dimensionless quantity,  $\Omega_{D,AB}(T_{AB}^*)$ , is the collisional integral for diffusion and is a function of the dimensionless temperature  $T_{AB}^* = kT/\varepsilon_{AB}$ .<sup>161</sup> The parameters  $\sigma_{AB} = (\sigma_{Cl} + \sigma_{Cl_2})/2$  and  $\varepsilon_{AB} = (\varepsilon_{Cl}\varepsilon_{Cl_2})^{1/2}$  are those appearing in the Lennard-Jones potential between Cl and Cl<sub>2</sub> ( $\sigma_{Cl} = 3.548$ ,  $\sigma_{Cl_2} = 4.115$ ,  $\varepsilon_{Cl}/k = 75$ ,  $\varepsilon_{Cl_2}/k = 357$ ).<sup>161, 162</sup>  $\Omega_{D,AB}(T_{AB}^*) = 1.11$  at  $T = 300$  K, 0.95 at 500 K and 0.845 at 800 K.  $D_{AB} = 5921 \text{ cm}^2 \text{ s}^{-1}$  at 300 K and 20 mTorr. Finally,  $D_{Cl,Cl_2} = 1.25 D_{AB}$ . (Multiplying by 1.25 brings the room temperature value computed from the above expressions into agreement with the reported measured value<sup>162</sup>.)

In Eq. 4.17, the temperature dependence is due to 3 causes: a  $T^{1/2}$  dependence of the thermal speed, a relatively small dependence of the collision integral, and a  $T^1$  dependence caused by the  $1/T$  dependence of the number density at constant pressure for an open vessel. Because the pulsed plasma period ( $\sim 2\text{ms}$ ) is much smaller than gas

residence time ( $\sim 200\text{ms}$ ), the plasma reactor can be treated as a sealed chamber within one pulsed cycle. Assuming ideal gas behavior, this leads to a cancelling out of the  $T^1$  dependence of  $D_{AB}$  for rapid changes above and below the average temperature,  $T_{ave}$ , where the average pressure is  $p_{ave}$  ( $= 20 \text{ mTorr}$ ), the average total number density is  $n_{ave}$ , and the diffusion coefficient is  $D_{ave}$ . Hence the time-dependent diffusion coefficient during the modulation period is given

$$D_{AB} = D_{ave} \sqrt{\frac{T_g}{T_{ave}}} \frac{n_{ave} \Omega_{D,AB}(T_{ave}^*)}{n_{tot} \Omega_{D,AB}(T_{AB}^*)}. \quad (4.18)$$

The time-dependence during the modulation period of the total number density,  $n_{tot}$ , is caused by the rising and falling generation of Cl from dissociation of  $\text{Cl}_2$ . (If no dissociation were occurring, then  $n_{tot}$  would be equal to  $n_{ave}$  throughout the cycle.)

We can determine  $\gamma_{Cl}$ , Cl atom loss coefficients, which in the absence of etching products is equivalent to the Cl recombination probability on the walls, by matching Cl number densities computed from a solution to Eqs. (4.11) and (4.12) to the measured Cl number densities as a function of time, with  $\gamma_{Cl}$  as the only adjustable parameter. Before reaching a periodic steady state, the Cl number densities in powered and unpowered periods are given by

$$\text{Power on: } n_{Cl} = \frac{a}{b} [1 - e^{-bt}] + n_{Cl_0} e^{-bt} \quad (4.19a)$$

and

$$\text{Power off: } n_{Cl} = n_{Cl_1} e^{-k_{loss}(t - t_1)}, \quad (4.19b)$$

where  $t$  is time within the entire period ( $t = 0$  at the beginning of the period),  $t_1$  is the time when power is switched off ( $t_1 = 1000 \mu\text{s}$  in the examples shown here), and  $n_{Cl_0}$  and  $n_{Cl_1}$  are the Cl number densities at beginning and end of a powered period. The constants are

defined as  $a = 2k_d n_e n_{Cl2}^0$  and  $b = k_d n_e + k_{loss}$ .  $n_{Cl}$  and  $n_{Cl0}$  will continue to increase until reaching their constant, periodic steady-state values.

Since  $n_e$  does not rise to an instantly constant value at the beginning of the power period, and  $T_g$  rises and falls during the modulation period, more accurate simulations of  $n_{Cl}$  as a function of time were obtained by numerically integrating Eqs. (4.11) and (4.12), with time-dependent  $T_g$ , and relative  $k_d n_e$  that was assumed to be proportional to Xe emission intensity.

If the entire powered period is used to extract  $\gamma_{Cl}$ , then the absolute  $k_d n_e$  must be known.  $k_d$  is a function of  $T_e$  for an assumed Maxwellian electron energy distribution. The rate coefficient,  $k_{dis}$ , for the dominant electron impact dissociation process is based on a single set of measurements of the cross section as a function of electron energy, where the lowest measured values were at 8 and 10 eV<sup>163</sup>.  $T_e$  is not a strong function of position in most of the plasma, nor is it a strong function of time during the powered period, after the first  $\sim 10$   $\mu$ s. A value of  $T_e = 2.0$  eV was obtained from Langmuir probe measurements. Given the small population of electrons above 8 eV at  $T_e = 2$  eV, measured deviations from a Maxwellian distribution that suppress high energy electrons at higher pressures (i.e., 20 mTorr in this study), the stated  $\sim 50\%$  uncertainty in measured cross sections, and lack of cross sections below 8 eV,  $k_{dis}$  is, unfortunately, likely to be uncertain by an order of magnitude.

Unlike  $T_e$ ,  $n_e$  is a strong function of position in the discharge. Langmuir probe measurements were not recorded as a function of axial position in the present study, however, electron densities at 20 mTorr are expected to be much lower near the substrate than the peak density closer to the coil, due to localized power deposition, slow diffusion

and changes in electronegativity<sup>164-167</sup>. Consequently, the average  $n_e$  to be used in the model should be much larger than the measured value of  $\sim 3 \times 10^{10} \text{ cm}^3$  recorded 2 cm above the substrate.

Finally, if  $\gamma_{Cl}$  is extracted from the best fit of the predicted *absolute* Cl number densities to the measured values, then accurate absolute Cl number densities are required. It is difficult to estimate the accuracy of the calibration of the actinometry method for determining  $n_{Cl}$ , but it is likely no better than a factor of 2. In addition, since  $n_{Cl}$  is measured away from the region of most intense power deposition, the values are lower than the average  $n_{Cl}$  in the chamber. There is much less uncertainty in the measured time-dependent *relative*  $n_{Cl}$  values, however.

To circumvent the problems with a lack of accuracy in  $k_d n_e$  and  $n_{Cl}$ ,  $\gamma_{Cl}$  was determined without the need to know  $k_e n_e$  by computing the *relative*  $n_{Cl}$  for the power-off portions of the modulation period, using eq. (4.19b). Of course, the plasma does not emit light during this period, so the only measured Cl number densities available for comparison with model predictions are  $n_{Cl1}$  and  $n_{Cl2}$ , with  $n_{Cl2}$  ( $= n_{Cl0}$ ) being the Cl atom density at the end of the power-off interval (= beginning of the power-on period), at time  $t_2$  ( $= t_0$ ). All the  $\gamma_{Cl}$  values given below were obtained in this manner. In most cases, optical emission measurements were only recorded at the beginning and end of the powered cycle to obtain  $n_{Cl0}$  and  $n_{Cl1}$ .

In other cases, such as shown in Fig. 4.4, measurements were made at intermediate times during the powered period. Model predictions (curves in Fig. 4.4) were computed for a range of  $n_e$  values (assuming the value for  $k_d$  is correct) and “pinned” to the measurements at  $n_{Cl0}$  and  $n_{Cl1}$  by introducing an uncertainty factor,  $U$  (defined as the measured-to-

computed  $n_{Cl}$ ). The examples of the  $Cl_2/TRG$  and  $Cl_2/O_2/TRG$  plasmas are shown in Fig. 4.4(a) and 4.4(b), respectively. The solid symbols are experimental data and the lines are global model predictions with different  $n_e$  and  $U$  factors. In  $Cl_2/TRG$  plasmas, from the power-off region,  $k_{loss}$  (at  $T_{ave} = 662K$ ) is  $\sim 718 s^{-1}$  and the corresponding  $\gamma_{Cl}$  is 0.11. A reasonable fit to the full powered region is achieved at  $1.2-1.8 \times 10^{12} cm^{-3}$  and  $U = 0.33-0.36$ . Similar procedures were conducted in  $Cl_2/O_2/TRG$  plasmas and a reasonable fit is achieved at  $n_e = 0.6-1.2 \times 10^{12} cm^{-3}$  and  $U = 0.34-0.48$  with corresponding  $\gamma_{Cl}$  is 0.17. The relatively high  $n_e$  can easily be attributed to the uncertainty in  $k_d$  and the axially non-uniform  $n_e$ , as discussed above, while the overestimation of absolute  $n_{Cl}$  in the model (i.e.,  $U < 1$ ) is likely due to the accuracy and spatial dependence issues, also discussed above.

As with pure  $Cl_2$  plasmas,  $Cl$  heterogeneous loss coefficients in  $Cl_2/O_2$  plasmas can also be ascribed solely to  $Cl$  recombination to form  $Cl_2$ . In the gas phase,  $Cl + O_2 \rightarrow ClO_2$  is a three body reaction and can be ignored. The rate constant for the only possible two body reaction ( $Cl_2 + O \rightarrow ClO + Cl$ ) is about  $5e-14 cm^3s^{-1}$ <sup>168</sup>. Consequently, at a  $Cl_2$  number density of  $2 \times 10^{14} cm^{-3}$ , the time for this reaction to occur is about 0.1s, i.e., much longer than the pulse period. Also, the  $O$  number density is  $< 10^{12}$  (assuming  $< 10\%$  dissociation of  $O_2$ ), hence the amount of  $Cl$  produced by this reaction, over 50 periods, is 100-fold smaller than the  $Cl$  number density. We have previously studied heterogeneous reactions that form  $ClO$  and  $ClO_2$  on alumina/silica surfaces exposed to a plasma<sup>169</sup>. At 5%  $O_2$ , the yields of  $ClO$  and  $ClO_2$  are negligible relative to  $Cl_2$ , hence this is an insignificant reaction under the present conditions.

## ii. With Etching Products

Time-resolved measurements of  $n_{Cl}$  were also recorded with bias applied to the substrate. Sample results are shown in Fig. 4.5. In previous studies an etching rate of 4550 Å/min was measured in this reactor with a similar rf bias and a continuous power of 400 W<sup>125</sup>. If we assume that the etching rate scales with power averaged over the period when bias is on, then an etching rate of 1820 Å/min would correspond to the pulsed-power conditions used here. Using the measured  $n_{Cl}/n_{Xe}$  in Fig. 6.5 and the expressions above,  $\gamma_{Cl}$  values of 0.07 and 0.03 were determined for  $Cl_2$ /TRG and  $Cl_2$  / $O_2$ /TRG plasmas, respectively.

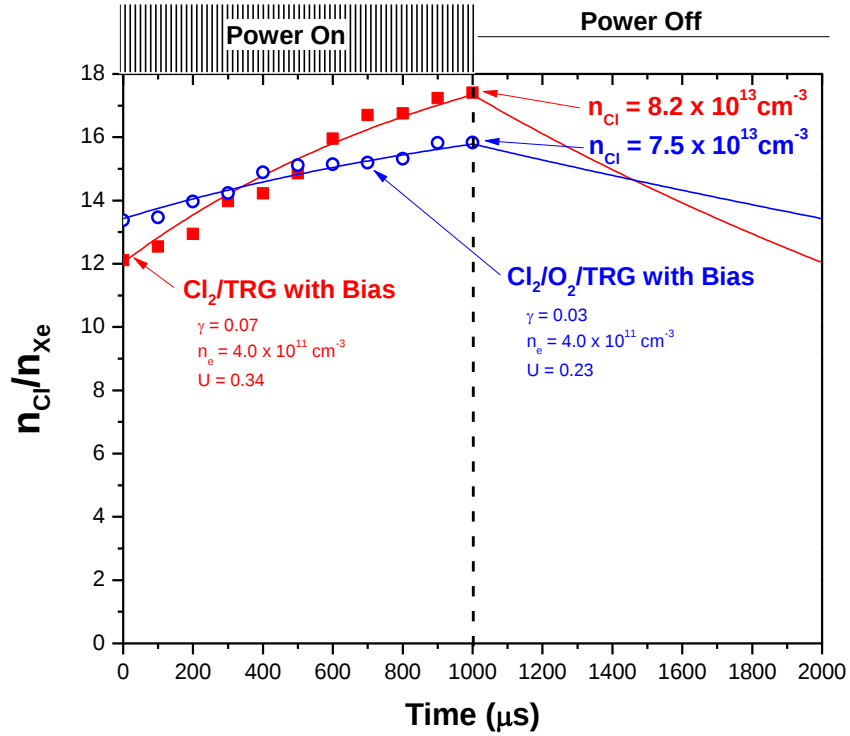


FIG. 4.5. Time-resolved number densities of  $n_{Cl}$  (792.4 nm) divided by  $n_{Xe}$  (828.0 nm) line ( $n_{Cl}/n_{Xe}$ ) in a  $Cl_2$ /trace rare gases (TRG) and  $Cl_2/O_2$ /TRG pulsed plasma. Symbols are experimental data ( $n_{Cl}/n_{Xe}$ ) determined from calibrated actinometry and lines are simulation results.

In the presence of etching products (i.e., with rf bias on the stage), chlorine is also present as  $\text{SiCl}_{x=1-4}$  products. Consequently, reactions (4.7) through (4.10) need to be considered. If  $\text{O}_2$  is present in the feed gas, then  $\text{SiOCl}_{x=1-2}$  could also be formed. Cl is formed by electron impact or dissociative attachment of these species, and additionally by Cl-abstraction reactions of Si-containing radicals with  $\text{Cl}_2$ <sup>150, 170</sup>. During power-off periods, formation of Cl by electron impact or attachment will be negligible, but formation of Cl by fast gas-phase  $\text{Cl}_2$  abstraction reactions must be considered. This complicates the extraction and interpretation of  $\gamma_{\text{Cl}}$ , which in addition now can also include loss of Cl at the walls due to heterogeneous reactions with  $\text{SiCl}_{x=0-3}$  species.

For the 3" diam. Si wafer, the estimated etching rate of 1820 Å/min corresponds to a flow rate of 1.6 sccm of Si entering the plasma. With the feed gas flow rate of 22 sccm, a pressure of 20 mTorr, and a gas temperature of 662K, this corresponds to a total Si-containing species number density (assuming no  $\text{Si}_2$ , or higher species) of  $2 \times 10^{13} \text{cm}^{-3}$ . Preliminary, time-resolved ultraviolet absorption measurements in this reactor indicate that the number densities at the end of the power-on period are  $<1 \times 10^{11} \text{cm}^{-3}$  and  $3 \times 10^{12} \text{cm}^{-3}$  and for SiCl and SiCl<sub>2</sub>, respectively<sup>171</sup>. If SiCl<sub>3</sub> is present at a similar number density to SiCl<sub>2</sub>, as found by Cunge et al<sup>133</sup> at 20 mTorr, then ~70% of the Si-containing products is SiCl<sub>4</sub>. It is likely that SiCl<sub>3</sub> is present at levels less than those of Cunge et al, since at the lower average powers in the present study, more  $\text{Cl}_2$  will be available to quickly convert SiCl<sub>3</sub> to SiCl<sub>4</sub>, which would then increase to ~85% of the total Si-containing products. (In fact, SiCl<sub>3</sub> number density decreased to a low value relative to SiCl<sub>2</sub> when the pressure in the study by Cunge et al. was raised from 20 to 68 mTorr.) In either case, the present study is in reasonable agreement with the finding by Cunge et al.,<sup>150</sup> that for similar conditions,

about 89% of the Si-containing products were  $\text{SiCl}_4$  during etching in a Si-containing  $\text{Cl}_2$  ICP.

If all of the  $\text{SiCl}$  in the plasma were to react with excess  $\text{Cl}_2$  in the afterglow to generate  $\text{Cl}$ , this would produce at most an additional  $\sim 1 \times 10^{11} \text{cm}^{-3}$ , which is negligible compared to the measured  $n_{\text{Cl}}$  (Fig. 4.5, solid squares).  $\text{SiCl}_2$  apparently reacts slowly if at all with  $\text{Cl}_2$  in the gas phase to produce  $\text{Cl}$  and  $\text{SiCl}_3$ <sup>150</sup>. This would produce at most  $3 \times 10^{12} \text{cm}^{-3}$   $\text{Cl}$  that would be modulated in the same manner as  $\text{Cl}$  produced mainly by  $\text{Cl}_2$  electron impact dissociation and consumed by loss at the walls. Since the  $\text{Cl}$  number density is much larger than this ( $\sim 8 \times 10^{13} \text{cm}^{-3}$ ), this causes a negligible effect on the measured  $\gamma_{\text{Cl}}$ .  $\text{Cl}$  could be lost at the surface by reactions with  $\text{SiCl}_x$ . Since  $\text{SiCl}_4$  is not expected to stick to the surface, and  $\text{SiCl}$  and  $\text{SiCl}_3$  are present at about three orders of magnitude less than  $\text{Cl}$ , the only species needing to be considered is  $\text{SiCl}_2$ . Chang et. al., found that the sticking coefficient of  $\text{SiCl}_2$  is very low (0.05) in the presence of chlorine impingement by a beam of  $\text{Cl}^+$  and  $\text{Cl}$ <sup>172</sup>. Since the  $\text{Cl}$  flux to the surface is at least twenty times larger than that of  $\text{SiCl}_2$ , the contribution of a heterogeneous reaction between  $\text{Cl}$  and  $\text{SiCl}_2$  to  $\gamma_{\text{Cl}}$  can be neglected compared with the production of  $\text{Cl}_2$ .

For  $\text{Cl}_2/\text{O}_2$  plasmas, it is likely that the  $\text{SiCl}_x$  number density is higher than in the  $\text{Cl}_2$  plasma. The etching rate is 1.4-fold higher, and emissions from  $\text{SiCl}_{x \leq 3}$  are higher (typically 4 $\times$ , 1.8 $\times$  and 1.8 $\times$  higher for  $\text{SiCl}$ ,  $\text{SiCl}_2$  and  $\text{SiCl}_3$ , respectively).<sup>125</sup> This is also consistent with the findings Cunge et al.,<sup>150</sup> for etching in a  $\text{Cl}_2/\text{O}_2$  plasma, where they found that 40% of the products were  $\text{SiCl}_{x \leq 3}$  radicals. If half of the products in the present study were  $\text{SiCl}_{x \leq 3}$  radicals (i.e.,  $\sim 1.5 \times 10^{13} \text{cm}^{-3}$ ) that generate one  $\text{Cl}$  per  $\text{SiCl}_{x \leq 3}$  in the afterglow period, then they could produce an additional modulation of similar magnitude to that

observed drop in  $n_{Cl}/n_{Xe}$  in Fig. 4.5. This could cause the value for  $\gamma_{Cl}$  to be about half that determined from the data in Fig. 4.5. By the same token, the a surface reaction between Cl and  $SiCl_2$  could contribute to the total heterogeneous loss of Cl, though still likely less than Cl recombination, given the low  $SiCl_2$  sticking coefficient and at least several times lower flux to the surface, relative to Cl.

Though it is not necessary to fit the entire power-on period to extract  $\gamma_{Cl}$ , this was done for the measurements in Fig. 4.5 for both  $Cl_2$  and  $Cl_2/O_2$  plasmas during Si etching. The curves represent the best fit conditions. The consistency in the values for  $n_e$  and  $U$  with those obtained in the absence of bias (Fig. 4.4) are a good indication that, at least for  $Cl_2$  plasma etching of Si, secondary reactions of  $SiCl_x$  radicals with Cl at the walls and  $Cl_2$  in the gas phase cause minor alteration in the kinetics for Cl that are dominated by generation of Cl from  $Cl_2$  dissociation by mainly electron impact, and loss of Cl at the walls to form  $Cl_2$ .

#### **4.3.4 – Measurements of $\gamma_{Cl}$ during Si etching as function of processing conditions and times**

Following a long period (~70 mins) of Si etching, the wafer was removed from the chamber and transferred under vacuum to the load lock chamber before performing a  $NF_3$  plasma chamber cleaning process. After cleaning, the Si substrate was transferred back to the stage. Flows of the processing gas ( $Cl_2$  or  $Cl_2/O_2$ ) and the rare gas mixture were introduced to the chamber and a pulsed plasma was ignited. Figs. 4.6 and 4.7 present  $\gamma_{Cl}$  measurements (green squares) extracted from the model fits to the measured  $n_{Cl0}/n_{Cl1}$

quantities, at several times during the first few minutes of plasma operation. The black triangles and red circles in Figs. 4.6 and 4.7 represent  $n_{Cl0}$  and  $n_{Cl1}$ , respectively.

### i. After $NF_3$ Plasma Cleaning

In both  $Cl_2$  and  $Cl_2/O_2$  plasmas (Figs. 4.6 and Fig. 4.7),  $\gamma_{Cl}$  is about 0.30 after the  $NF_3$  plasma conditioned the surface. Previously, we attributed the low Cl number density immediately after cleaning the chamber with a  $NF_3$  plasma to a high recombination probability on this highly fluorinated surface, caused by the low electron density at Y sites due to ionic bonding of multiple F atoms to Y. This leads to a relatively weak bond between Y and Cl, hence a high rate of heterogeneous reactions of Cl and  $SiCl_x$  with the weakly bound Cl. An initially high recombination coefficient for Cl is borne out by the current experiments.  $\gamma_{Cl}$  in this case is very large  $0.20 \pm 0.02$  in  $Cl_2/TRG$  plasmas and  $0.30 \pm 0.08$  in  $Cl_2/O_2/TRG$  plasmas, as shown in Fig. 4.6 and 4.7 (before first dashed lines).

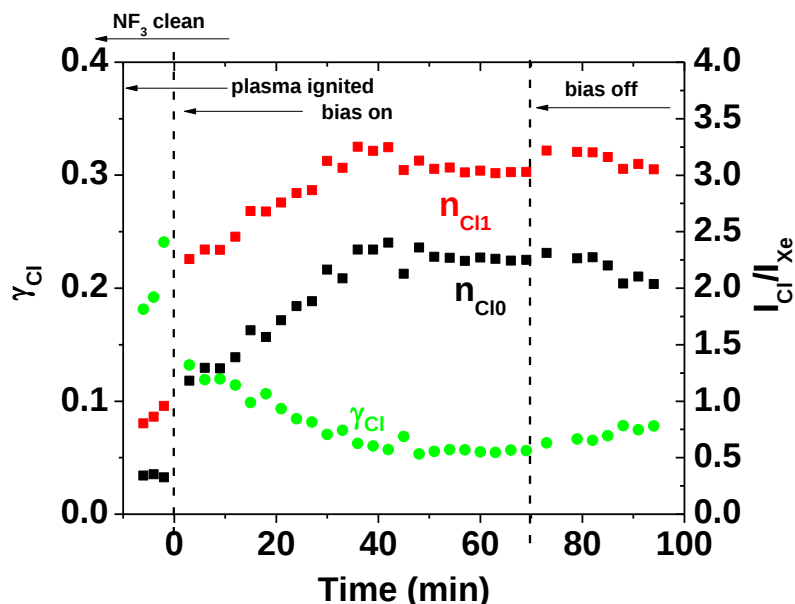


FIG. 4.6. Recombination coefficients and optical emission intensities from Cl divided by the intensity of the Xe, as a function of time. Pulsing frequency = 500 Hz, Duty cycle = 50%, Pressure = 20 mTorr; flow rates = 20 sccm  $Cl_2$ , 2 sccm TRG; ICP power = 320 W (ON), 0 W (OFF) and  $V_{DC}$  = -80 V.

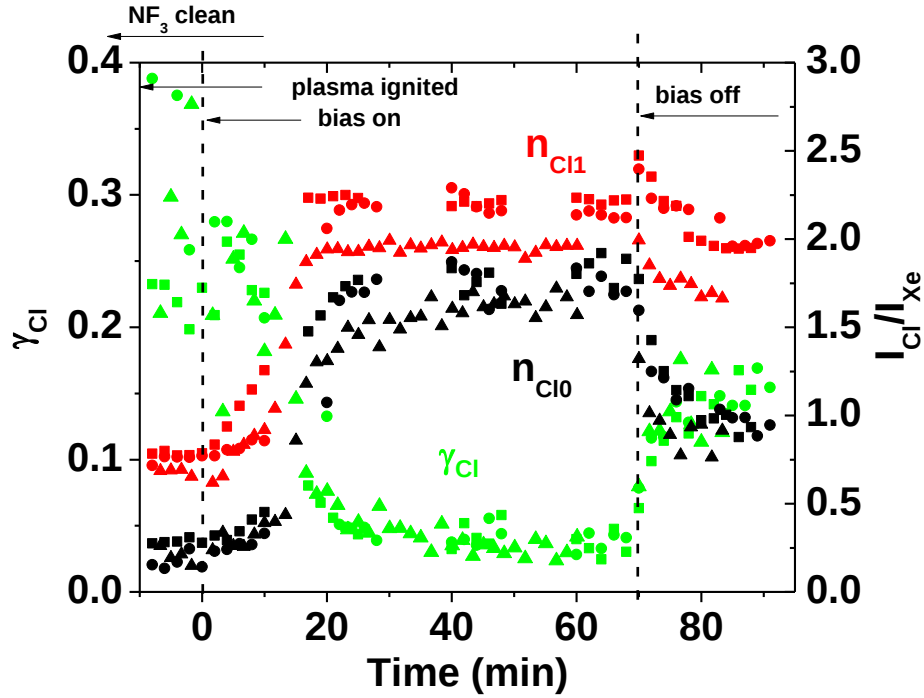


FIG. 4.7. Recombination coefficients and optical emission intensities from Cl divided by the intensity of the Xe, as a function of time with 1 sccm  $O_2$  addition pulsed plasma. Experiments were repeated three times, corresponding to the different symbols (squares, circles and triangles).

## ii. During Si Etching

RF bias power was then applied to the Si substrate, in sync with the pulsed power to the ICP, resulting in an etching rate of about 1820 Å/min in  $Cl_2$ /TRG plasmas and slightly higher in  $Cl_2/O_2$ /TRG plasmas.  $\gamma_{Cl}$  drops as a function of time in the presence of etching products and eventually reaches a steady value of  $0.06 \pm 0.01$  in  $Cl_2$ /TRG plasmas and  $0.03 \pm 0.01$  in  $Cl_2/O_2$ /TRG plasmas. Some of the drop is ascribed to the removal of F from the surface by reactions of  $SiCl_x$  to form volatile  $SiCl_xF$  products (presumably  $SiClF$  and  $SiCl_3F$ ).<sup>125, 151</sup> In  $Cl_2/O_2$ /TRG plasma, silicon oxychloride film is deposited through oxidation of  $SiCl_x$  molecules adsorbed on reactor walls, further lowering  $\gamma_{Cl}$ <sup>173, 174</sup>.

### iii. *After RF Bias to the Si substrate is turned off*

After bias was turned off, the recombination coefficient in the  $\text{Cl}_2/\text{TRG}$  plasma increased slightly from 0.055 to a constant 0.08 over the next 20 minutes (Fig. 4.6). One explanation for the small rise in  $\gamma_{\text{Cl}}$  is that during etching,  $\text{SiCl}_x$  competes with Cl for binding at sites  $-\text{W}$  that are active for either Cl recombination in reactions (4.5) and (4.6), or formation of  $\text{SiCl}_{x+1}$  in reactions (4.20) and (4.21),



If reaction (4.21) has a lower probability than reaction (4.6), then when bias is extinguished and  $\text{SiCl}_x$  number densities drop, the total heterogeneous loss coefficient for Cl will increase. It is also possible that a small drop in  $\text{SiCl}_x$  coverage frees added recombination sites.

In  $\text{Cl}_2/\text{O}_2/\text{TRG}$  plasmas shown in Fig. 4.7, the rise in  $\gamma_{\text{Cl}}$  from 0.03 to 0.14 after bias is turned off is more dramatic. The very low  $\gamma_{\text{Cl}}$  during etching in the  $\text{Cl}_2/\text{O}_2/\text{TRG}$  plasma can be attributed to the  $\text{SiO}_x\text{Cl}_y$  layer that forms<sup>173, 174</sup>. After bias is turned off, the  $\text{SiO}_x\text{Cl}_y$  layer is etched away. After long exposure to the  $\text{Cl}_2/\text{O}_2/\text{TRG}$  plasma, this surface differs from that formed after long exposure to the  $\text{Cl}_2/\text{TRG}$  plasma in that it contains more O dangling bond sites that are active for recombination<sup>174</sup>.

### 4.3.5 – Temperature dependence

The recombination probabilities presented in Fig. 4.8 were determined from  $n_{\text{Cl}0}$  and  $n_{\text{Cl}1}$  measurements as a function of wall temperature. The different symbols represent

experiment starting at different initial temperatures. Since it was more convenient to increase temperature during the measurements, the overlap between data sets indicates no systematic errors occur as a function of time. Within the scatter in the measurements, there appears to be at most a slight temperature dependence for  $\gamma_{Cl}$ , with a broad minimum near room temperature. Macko et al.,<sup>175</sup> found a similar nearly-temperature-independent broad minimum for recombination of O atoms on pyrex and ascribed it to a gradual transition from Langmuir-Hinshelwood kinetics at low temperature to Eley-Rideal kinetics at higher temperatures. A similar transition could be occurring in the present case.

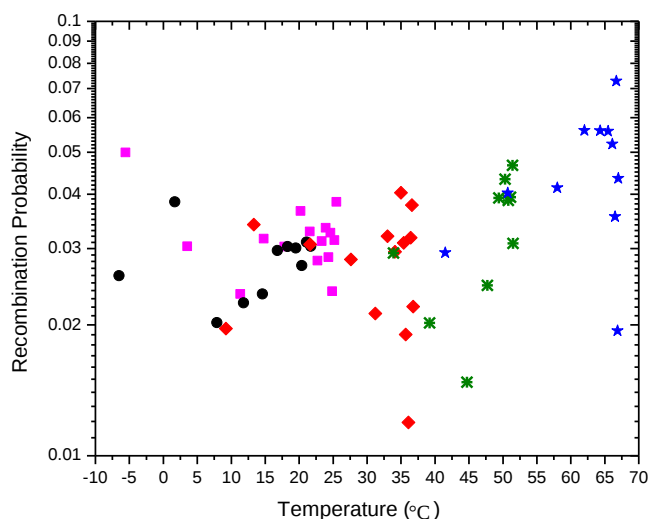


FIG. 4.8. Recombination coefficients in  $Cl_2/O_2/TRG$  pulsed plasmas. Different symbols represent experiment starting at different initial temperatures. Pulsing frequency = 500 Hz, Duty cycle = 50%, Pressure = 20 mTorr; flow rates = 20 sccm  $Cl_2$ , 2 sccm TRG, 1 sccm  $O_2$ ; ICP power = 320 W (ON), 0 W (OFF) and  $V_{DC} = -80$  V.

## 4.4 Discussion

In previous studies in the same  $\text{Y}_2\text{O}_3$ -coated reactor during repeated  $\text{Cl}_2$  plasma etching and  $\text{NF}_3$  plasma cleaning steps, we found time-dependent increases in Cl number density, as well as in emission from Si and  $\text{SiCl}_{x=1-3}$  as the chamber walls transition from a F-enriched to Cl-enriched surface<sup>125, 151</sup>. The somewhat surprising increase in  $n_{\text{Cl}}$  upon the initiation of rf bias and etching of the Si substrate was ascribed to a decreasing heterogeneous recombination probability.

After exposure to the  $\text{NF}_3$  plasma cleaning process, the  $\text{Y}_2\text{O}_3$ -coated walls are heavily fluorinated and free of Si<sup>125</sup>.  $\gamma_{\text{Cl}}$  for this surface is high ( $\sim 0.2$  to  $0.3$  in Fig. 4.6 and Fig. 4.7). When the walls are exposed to etching products, F is slowly removed over  $\sim 10$  min and  $\gamma_{\text{Cl}}$  drops to  $0.06$  and  $0.03$  in  $\text{Cl}_2$  and  $\text{Cl}_2/\text{O}_2$  plasmas, respectively, matching well with increases in Cl/Xe emission intensity ratios, as recently reported<sup>125</sup>. This phenomena was previously attributed to displacement of F by less electronegative Cl at Y sites, allowing impinging Cl to be bound more strongly at Y sites than when Y is coordinated with multiple strongly electron withdrawing F. This increased bond strength between Cl and Y lowers the probability that impinging Cl will abstract this Cl, hence  $\gamma_{\text{Cl}}$  decreases.

After the bias is turned off,  $\gamma_{\text{Cl}}$  in  $\text{Cl}_2$  plasmas increases only slightly to  $0.08$ , while in  $\text{Cl}_2/\text{O}_2/\text{TRG}$  plasmas, a higher  $0.14$  is found.  $\gamma_{\text{Cl}}$  increases because the Si containing film is etched away and the surface is modified by plasma exposure. The relationship between recombination coefficient and oxygen content in  $\text{Cl}_2$  plasmas has been discussed by Khare et al.,<sup>174</sup> These “spinning wall” experiments revealed that Cl Langmuir-Hinshelwood recombination increases with increasing oxygen coverage from  $\gamma_{\text{Cl}} < 0.001$  on a *lightly*

oxidized surface (~21% O surface coverage), to  $\gamma_{\text{Cl}} = 0.03$  on oxidized surface by  $\text{Cl}_2/5\%$   $\text{O}_2$  pretreatment (~50% O surface coverage), to  $\gamma_{\text{Cl}} = 0.07$  on a heavily oxidized anodized Al surface (~64% O surface coverage). This trend is consistent with the present study, where the highest  $\gamma_{\text{Cl}}$  (apart from the initially fluorinated surface) of 0.14 for the  $\text{Cl}_2/\text{O}_2$  plasma after etching was found for conditions where the surface is expected to be most heavily oxidized. As argued previously, some O will be in a configuration where it can bond to only one metal atom on the oxide surface ( $\text{AlO}_2$  in prior work<sup>174</sup> and  $\text{YO}_2$  here<sup>125, 151</sup>), resulting in some O-dangling bond sites ( $-\text{O}$ ) that are expected to catalytically recombine Cl in the two-step process:



and



## 4.5 Conclusions

A combination of power modulation experiments and simulations was used to measure Cl heterogeneous reaction coefficients,  $\gamma_{Cl}$ , on plasma-conditioned yttria walls during Si etching. Time-resolved optical emission spectroscopy with actinometry was carried out to record absolute Cl number densities,  $n_{Cl}$ , during the powered portion of the modulation period. A simple global model was used to predict the periodic modulation in  $n_{Cl}$  for comparison with measurements. By using only those values for  $n_{Cl}$  measured at the beginning and end of the powered period, and only matching the measured and computed *relative* change in  $n_{Cl}$  over the unpowered period, the model no longer requires a knowledge of  $n_e$ ,  $T_e$ , and absolute  $n_{Cl}$ , hence most of the uncertainty is removed in the extraction of sole adjustable parameter,  $\gamma_{Cl}$ .

After waferless chamber cleaning in an  $NF_3$  plasma, the fluorinated surface was active for Cl recombination in a  $Cl_2$  plasma, with  $\gamma_{Cl} = 0.2$  to  $0.3$ . This initially high  $\gamma_{Cl}$  was ascribed to the ionic bonding of multiple F atoms to Y, reducing the bond strength of Cl on Y and thereby enhancing Cl recombination. As soon as bias was applied to the Si substrate and etching began, F is believed to be removed as a result of reactions with  $SiCl_x$ , and  $\gamma_{Cl}$  decreased to  $0.05$ - $0.07$ . If biased was extinguished,  $\gamma_{Cl}$  increased slightly to  $0.08$ . The addition of a small amount of  $O_2$  to the  $Cl_2$  plasma during Si etching lead to a relatively slow reduction in  $\gamma_{Cl}$  to  $0.03$ , due to the presence of an  $SiO_xCl_y$  layer. When substrate bias was turned off in the  $Cl_2/O_2$  plasma, the apparently relatively thin  $SiO_xCl_y$  layer was etched within a  $\sim 3$  min, and  $\gamma_{Cl}$  increased to a constant  $0.14$ . The higher  $\gamma_{Cl}$  in  $Cl_2/O_2$  plasmas after etching is ascribed to the presence of extra O dangling bonds on the surface, which catalytically recombine Cl.

## Chapter 5 – Complex Transients in Power Modulated Inductively-Coupled Chlorine Plasmas

### 5.1 Ignition delay problems in pulsed plasmas

Power modulation (i.e., rapid switching between high and low power) can have advantages over more commonly studied pulsed plasmas<sup>176</sup>. Power modulation can affect not only the relative concentration of radicals, but also their spatial distribution in the plasma reactor. Gas flowing through the plasma is dissociated by electron-impact, and the resulting radical consumed by etching or deposition. As a result, processing rates can vary greatly along the flow path of the gas<sup>177</sup>. Power modulation has the potential to reduce these rate variations and therefore improve uniformity<sup>177</sup>. Power modulation also provides a method for studying plasma reaction kinetics, using optical emission spectroscopy (OES). For example, Kiss and Sawin used power modulated plasmas to investigate kinetics for various fluorocarbon and halogen gases and determine dominant reaction pathways<sup>178-180</sup>.

Plasma instabilities, often characterized by capacitive-to-inductive (E-H) transitions, have been seen under various electronegative plasmas condition<sup>182-184</sup>. This type of instability has often been ascribed to the effects of electron attachment<sup>182</sup>, and the time-dependent changes in the loss and generation rates of charged particles as a function of electron number density and inductive currents for electronegative plasmas<sup>183</sup>.

Pulsed electronegative plasmas can be difficult to re-ignite during each cycle, since  $n_e$  rapidly decays in the afterglow (when power is off) due to attachment<sup>185</sup>. In most instances, the capacitive-coupling is sufficient to re-ignite the plasma, initially exciting the few remaining electrons to very high energy and causing a rapidly increasing rate of ionization. Hence, an instability can be produced by the E–H mode transition<sup>183, 186, 187</sup>. In

reactors with purely inductive antenna designs, or where capacitive coupling is suppressed with Faraday shielding, ignition during an E-mode is not possible. To operate pulsed chlorine-containing plasmas under these conditions, Liu et al., used a tandem plasma configuration, in which a continuously powered plasma was injected into the pulsed plasma to provide a low density of “seed” electrons to aid in re-ignition<sup>185</sup>. This approach did not produce the desired result of prompt ignition. It was found that the plasma would not ignite until the number density of positive ions left from the last power pulse had decayed to the value supplied by the seed plasma. This behaviour is reminiscent of a type of E-H mode transition (actually H-E) that was previously found in a pulsed Cl<sub>2</sub> plasma operating in the presence of continuous substrate bias<sup>181</sup>. After the ICP power was switched off,  $T_e$  and  $n_e$  rapidly decayed to very low values until late in the afterglow, when the positive ion density decayed to the level sustained by the bias power, at which time the electron density increased to the level also sustained by this low density, capacitively-coupled plasma (CCP).

The objective of the present study is to determine whether such ignition problems occur during power modulation between high and low power Cl<sub>2</sub> ICPs without Faraday shields<sup>181</sup>. Time resolved OES, broadband emission detected with a photomultiplier tube (PMT), Langmuir probe (LP) measurements, and power delivery measurements revealed that two cases can be obtained, one in which no delay occurs and one with a substantial pre-ignition period in the transition from high power to low power, or less commonly from low to high power. This latter mode can have many forms with complex dynamics that can even have periods corresponding to two modulation periods.

## 5.2 Experimental

A detailed schematic of the experimental reactor including matching network is shown in Fig. 5.1.

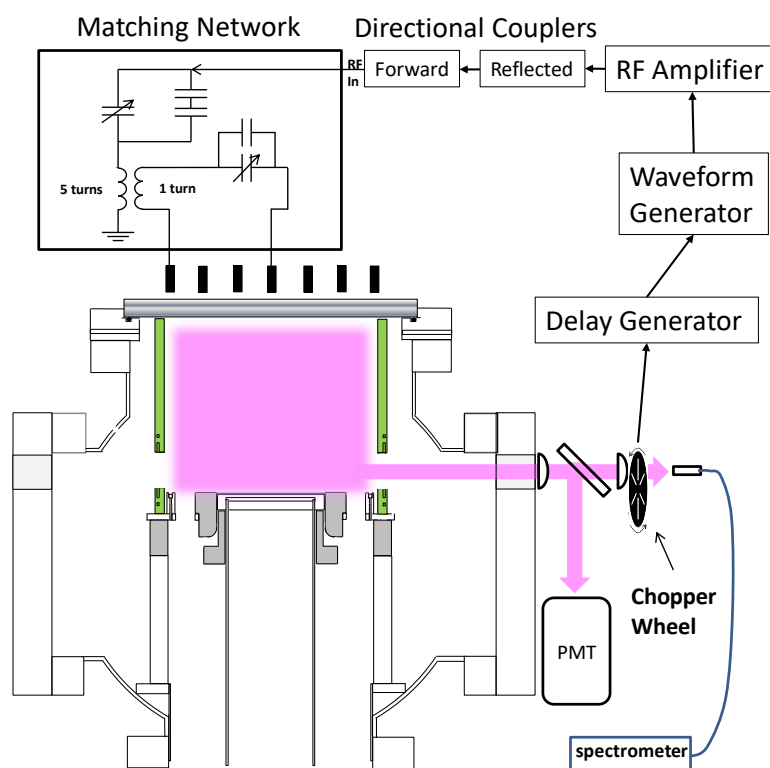


FIG. 5.1. Schematic of the inductively-coupled plasma reactor.

Power was delivered to the plasma using a modulated 13.56 MHz sine wave generator (HP 3325A), a broadband amplifier (ENI A500, 0.3-35 MHz) and an L-C impedance-matching network. No Faraday shield was used, hence, capacitive-coupling also occurs. Average powers were measured with Bird power meters and time-resolved forward and reflected powers were recorded with calibrated directional coupler elements

(Bird RF 400-50). The directional coupler elements were terminated in series with a 15 MHz low-pass filter (Mini-Circuits BLP-15+) to allow for accurate phase angle measurement between forward and reflected power waveforms without complications due to harmonic content in the waveforms. The stated “called-for” low power-to-high power ratios is defined as being equal to the ratio of the peak-to-peak voltage supplied by the sine wave generator. The actual delivered ratios deviate somewhat (or sometimes substantially) from these values. Typical conditions used unless otherwise stated were 500 Hz pulse frequency, 50% duty cycle (defined as the percentage of time at the high power), with a low power to high power ratio of 60%. Standard flow rates were 20 sccm Cl<sub>2</sub> and 2 sccm Ar at 10 mTorr total pressure, measured during plasma operation.

The directional couplers measure the time-resolved forward and reflected voltages passing through the cable. Calibration of the amplitude was obtained by placing both elements in the forward direction and delivering known powers to a 50 ohm dummy load. This allows the elements to then measure forward and reflected power from the calibration constant for the elements under matched conditions. During plasma operation, the phase difference between the two waves was also determined. The phase is a function of both the plasma and matching network settings, and enables (along with the reflection coefficient magnitude) measurement of the complex impedance of the system measured at the match input. This relative phase provides an indicator of when no power is being delivered to the plasma. Under this condition the phase shift is equal to that recorded when the feed gas is off and the pressure is below 10<sup>-5</sup> Torr at the prescribed match conditions for plasma operation. Since this “vacuum” phase is an arbitrary function of the settings of the capacitor and inductor in the matching network, it therefore must be measured for each plasma

experiment. Time-resolved powers measured by the directional couplers are increasingly inaccurate as reflected power increases and the load increasingly differs from  $50 \Omega$ <sup>188</sup>.

Optical emission spectra were recorded with four spectrometers (Ocean Optics HR4000 with 0.17 nm resolution) that covered the 200–900 nm region. Emission was collected using optical fibers equipped with collimating lenses on the input side. Time-resolved intensity measurements were achieved with a mechanical chopper that was synchronized with the pulsing frequency of the plasma, as describe in detail elsewhere<sup>189</sup>. The resolution of time-resolved OES was 7% of the pulsed plasma period. A photomultiplier tube (PMT) was also used to routinely monitor time-resolved, broadband optical emission. A red sharp cut filter (Corning 2-64) was used to block all light below ~650 nm. The region between this wavelength and the PMT cutoff near 900 nm is dominated by emission from Cl. Because of the better time resolution (~1  $\mu$ s), the PMT was used throughout to monitor the relative presence or absence of energetic electrons during the pulse period.

Langmuir probe (Scientific Systems Smart Probe) measurements were carried out to obtain positive ion and electron densities ( $n_+$  and  $n_e$ ), plasma potentials ( $V_p$ ), and electron energy probability functions,  $f(\varepsilon)$  (EPPF)<sup>190</sup>. Measurements were performed 2 cm above Si substrate in the center of plasma chamber, where the electron density was relatively low, because it was far away from the ICP coil. Electron temperature ( $T_e$ ) was calculated from the slope of semi-log plot of the EPPF. Electron density was derived from integration of the EPPF as

$$n_e = \int_0^\infty \varepsilon^{\frac{1}{2}} f(\varepsilon) d\varepsilon . \quad (4.1)$$

Positive ion densities,  $n_+$  were determined from the ion saturation current region using Laframboise theory<sup>191</sup>.

$$n_+ = 0.6\zeta\left(\frac{r_p}{\lambda_D}, \frac{V-V_p}{T_e}\right) \frac{I_i^+}{eA} \sqrt{\frac{2\pi M_i}{kT_e}}, \quad (4.2)$$

where  $r_p$  and  $A$  are the probe tip radius and area,  $\lambda_D$  is the Debye length,  $I_i^+$  is the ion current,  $e$  is the elemental charge and  $\zeta$  is a correction factor that depends on the probe radius-to-length ratio and  $e(V-V_p)/kT_e$ .<sup>191</sup> The positive ion mass,  $M_i$ , was assumed to be a constant 85 amu (the average of  $\text{Cl}^+$ ,  $\text{Cl}_2^+$ ,  $\text{SiCl}_2^+$  and  $\text{SiCl}_3^+$ , the most likely ions present) during the entire period. The negative ion density (assumed to be  $\text{Cl}^-$ ) is taken to be  $n_- = n_+ - n_e$ .

## 5.3 Results

### 5.3.1 – Power modulated Ar ICP

Time-resolved optical emission spectroscopy was conducted for power-modulated Ar ICPs. The called-for low power was 60% of the high power level. Emission intensity of Ar 750.4 nm is shown in Fig. 5.2. As the plasma entered the high power state, Ar emission intensity increased smoothly to steady state within 400  $\mu\text{s}$ . When the plasma switched to the low power state, emission intensity dropped within 150  $\mu\text{s}$  to a value that is about 54% of the high power intensity. (The decay time could be shorter due to the rather low time resolution of the chopper system, but Langmuir probe measurements in Fig. 5.3 indicate a similar decay time for  $n_e$ .) This drop in intensity is close to the expected drop in called-for power, meaning that for these conditions, the fraction of power delivered to the Ar pulsed ICP is about the same at high and low power.

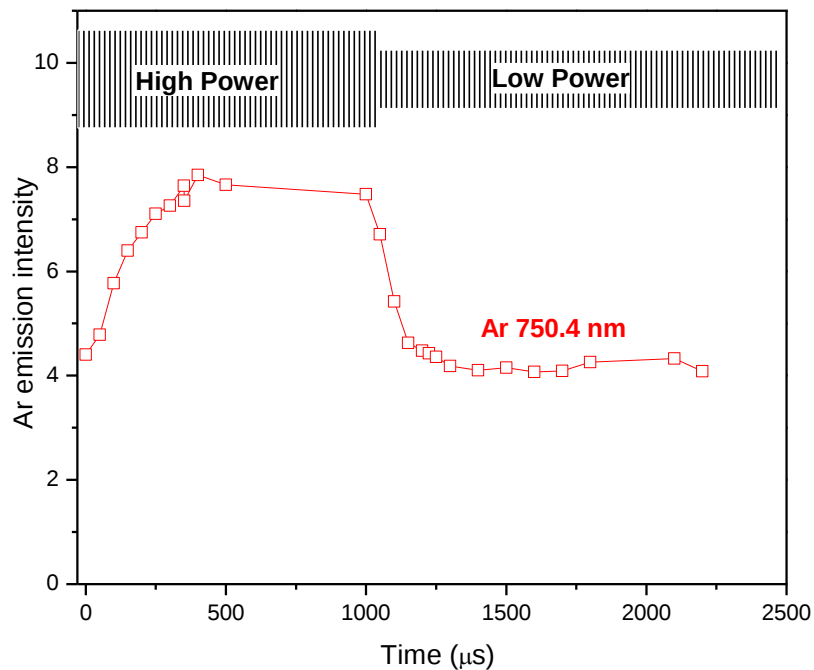


FIG. 5.2. Ar optical emission intensity at 750.4 nm as a function of time during a 400 Hz pulse for 40% duty cycle at 20 mTorr pressure and 220 W ICP average power. The called-for ratio of low to high power is 60%.

Langmuir probe measurements were also performed for Ar ICPs as a function of time. Measurements of  $n_e$ ,  $T_e$  and  $V_p$  are presented in Fig. 5.3.  $T_e$  and  $V_p$  were constant throughout the period, while  $n_e$  rose and fell monotonically during transitions between low and high power. Hence, the behavior of power-modulated Ar ICPs, as indicated by optical and electrical measurements, was as expected. Unlike  $\text{Cl}_2$ -containing plasmas, under no circumstances was any anomalous behavior observed as a result of power modulation in 100% Ar plasmas.

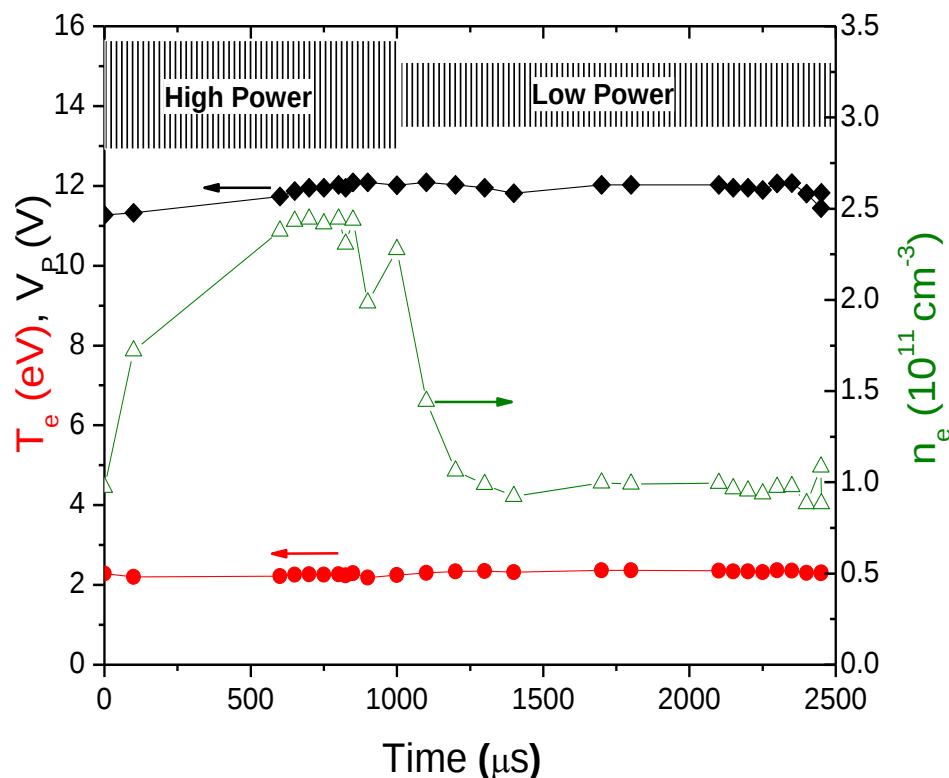


FIG. 5.3. Electron density, electron temperature and plasma potential as a function of time during a 400Hz pulse of Ar plasma at 20 mTorr Pressure. Average power = 182 W. The called-for ratio of low to high power is 60% with duty cycle of 40%.

### 5.3.2 – Power modulated $\text{Cl}_2$ /TRG ICP

Chlorine plasmas were modulated under the same conditions as those for the Ar ICP described above. Pressure was 10mTorr with flow rates of 20 sccm  $\text{Cl}_2$  and 2 sccm Ar. Two distinct steady-states were found, as shown in Figs. 5.4 and 5.5. In a “normal mode” (Fig. 5.4), there was a stable transition between high and low power, much like Ar ICPs, while in an “abnormal mode” (Fig. 5.5), after switching from low to high power, the plasma extinguished and there was a substantial delay before the plasma re-ignited and stabilized

at the expected lower density. The delay observed when power switched from high to low was reflected in a drop in emission intensity and electron density. For consistency, the plasma was first matched to minimum average reflected power, which was a nearly identical matching state for the two conditions. Small adjustments were made in the position of the tunable inductor in the matching network to cause the ignition delay to appear or disappear. Figs. 5.4 and 5.5 also show the behavior of the directional couplers that captured the envelope of the time-dependent forward and reflected powers. When no delay occurred (Fig. 5.3), the reflected power remained well below the forward power. When a delay in plasma ignition was found (Fig. 5.5), reflected power spikes to  $\sim 100$  W with the directional coupler still measuring  $\sim 120$  W net power into the plasma.

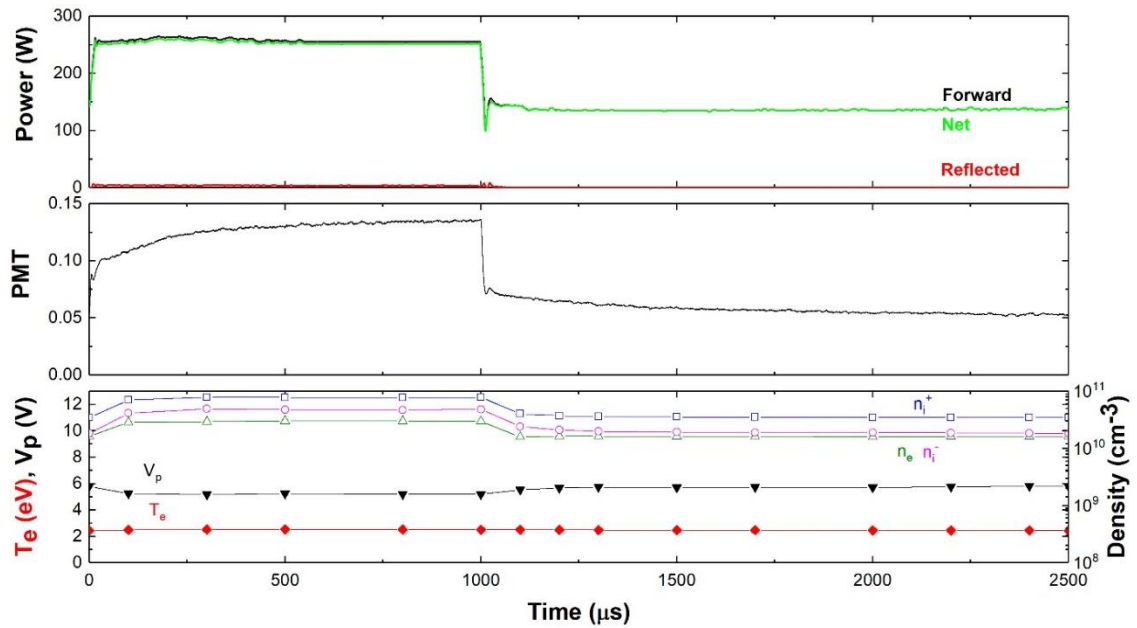


FIG. 5.4. Condition resulting in no ignition delay for a 10 mTorr  $\text{Cl}_2/\text{Ar}$  plasma. Upper: forward, reflected, and net power from calibrated directional coupler measurements. Middle: PMT intensity measurement. Bottom: Langmuir probe measurement. The ratio of low power to high power is 60%.

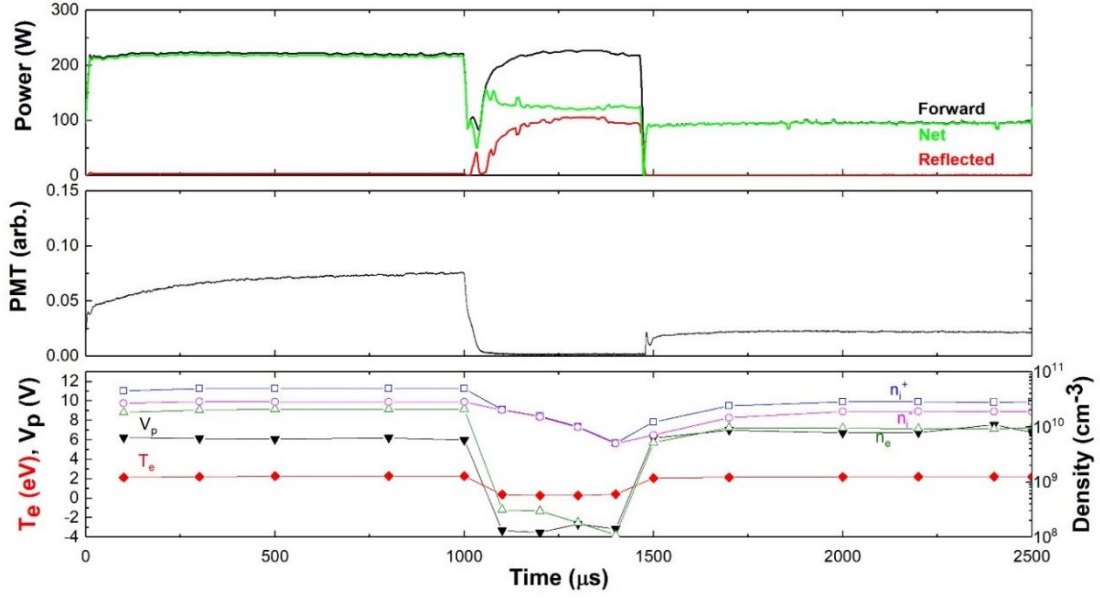


FIG. 5.5. Condition resulting in an ignition delay for a 10 mTorr  $\text{Cl}_2/\text{Ar}$  plasma. Upper: forward, reflected, and net power from calibrated directional coupler measurements. Middle: PMT intensity. Bottom: Langmuir probe measurement. The ratio of low power to high power is 60% with a duty cycle of 40%.

Ignition delay as a function of pulse duty cycle is shown in Fig. 5.6. At low duty cycle, the ignition delay is at a low value with a sudden transition to a high delay time between 30% and 40% duty cycle. At 20% and 30% duty cycle, both the lower and higher delay time states occur, and can be reached by slight changes in matching network settings. The dependence on pulse frequency was investigated at a constant 50% duty cycle.

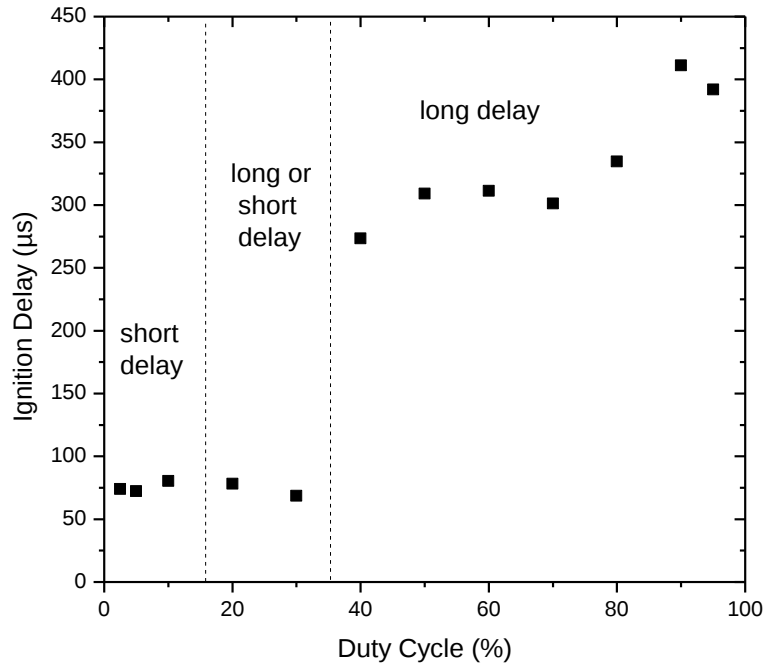


FIG. 5.6. Ignition delay as a function of the duty cycle for 400Hz pulse frequency at 10 mTorr. For 20% and 30% duty cycle, two states with either a short, or less common long ignition delay modes are found. Average power = 227 W at 60% duty cycle. The ratio of low power to high power is 60%.

As shown in Fig. 5.7, the ignition delay decreased with increasing pressure from 2500  $\mu\text{s}$  at 3 mTorr to 70  $\mu\text{s}$  at 13 mTorr, and then remained nearly constant at 50-75  $\mu\text{s}$  at higher pressures. The shorter ignition delay time above 13 mTorr also corresponded with the pressure at which the early afterglow exhibited weak emission, indicative of a weakly capacitively coupled plasma.

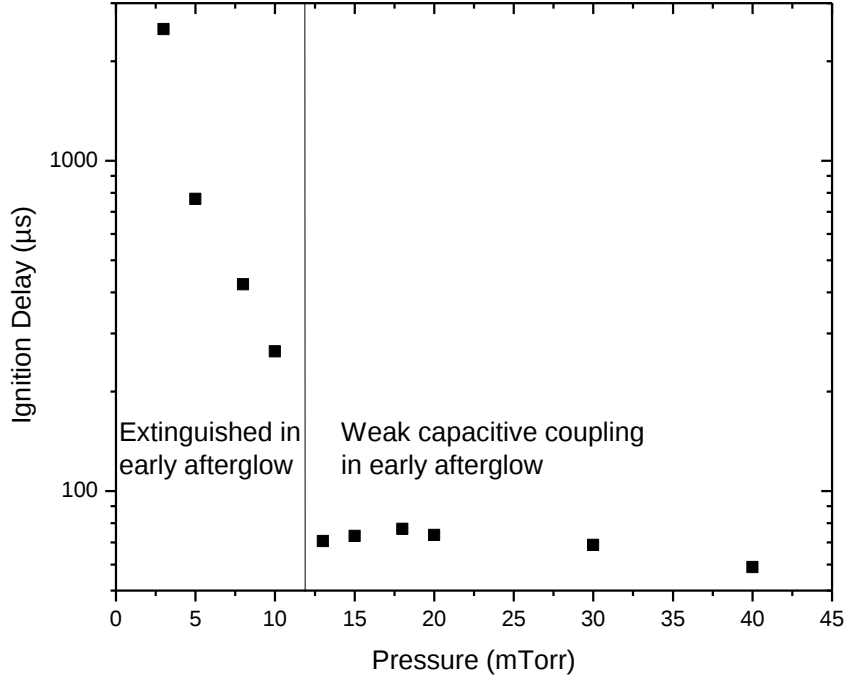


FIG. 5.7. Ignition delay time as a function of pressure. Average power = 203 W at 5 mTorr and 201 at 30 mTorr, 500Hz pulse frequency, 50% duty cycle. The called-for ratio of low power to high power is 60%.

Langmuir probe measurements for 5 and 10 mTorr pressures are shown in Figs. 5.8 and 5.9. For both pressures,  $T_e$  and  $V_p$  rapidly dropped to values near zero after the called-for power was dropped to the low power state. The plasma became an ion-ion plasma within  $<100 \mu s$  and then  $n_+$  and  $n_-$  dropped smoothly at the same rate. When  $n_+$  decayed to  $2 \times 10^9 \text{cm}^{-3}$  at 5 mTorr or  $5 \times 10^9$  at 10 mTorr, the plasma ignited, and  $n_+$  increased to a stable value of  $3 \times 10^{10} \text{cm}^{-3}$  at both pressures. Between 1000 and 2000  $\mu s$ , the ion density dropped well below the value reached at the end of the low power plasma. This is counter to previous observations where the plasma “turns on” when the ion density reaches to low power state ion density<sup>181,185</sup>. This could be due to the fact that Langmuir probe

measurements were taken far from the power delivery region (away from the coil), unlike prior studies, where probe measurements were made close to the power deposition regions<sup>181, 185</sup>.

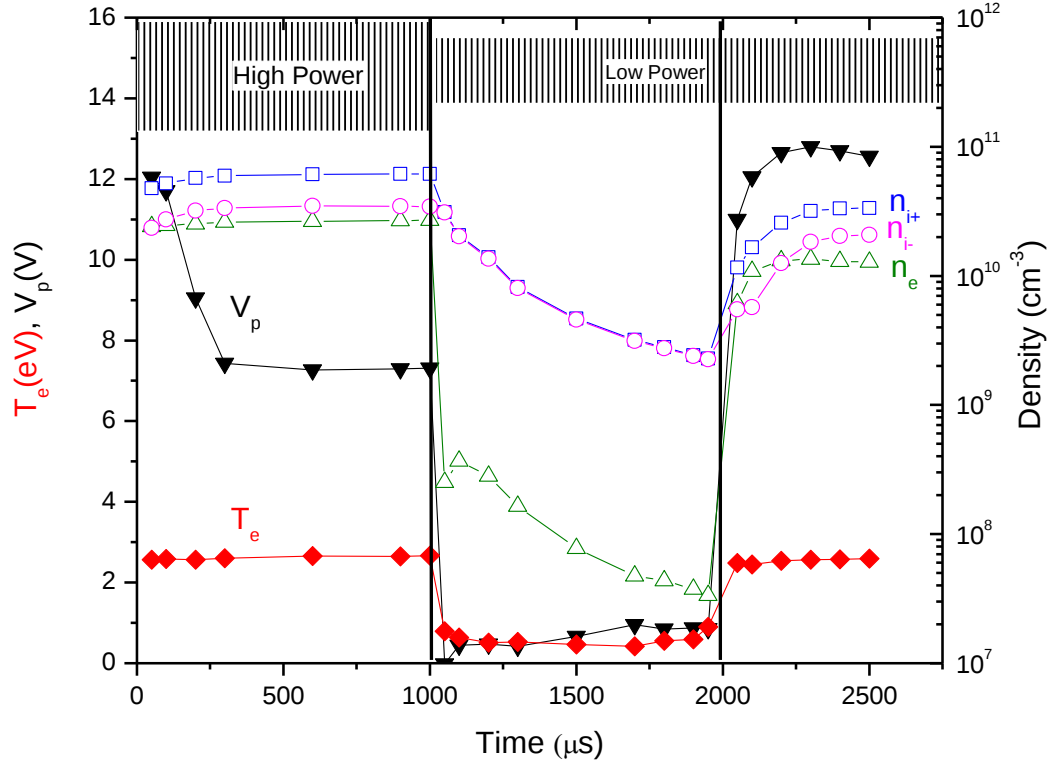


FIG. 5.8. Langmuir probe measurements for a 5 mTorr, 400 Hz pulse frequency, 40% duty cycle plasma. Average power = 176W. Called-for low to high power ratio of 60%.

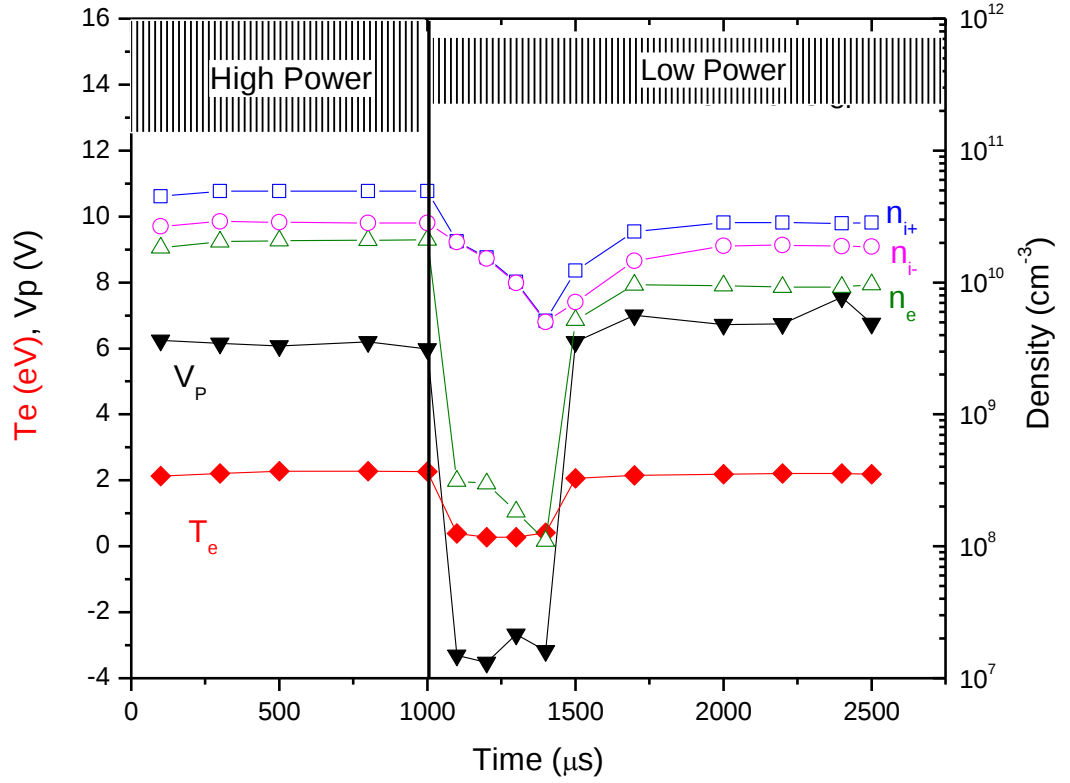


FIG. 5.9. Langmuir probe measurements for a 10 mTorr, 400 Hz pulse frequency, 40% duty cycle plasma. Average power = 180 W. Called-for low to high power ratio of 60%.

There is a change in the characteristics of the ignition delay at 20 mTorr (Fig. 5.10), with a spike in  $V_p$  and a drop to a stable electron density in the afterglow region, before fully turning on at the anticipated lower plasma density. The EEPF in the early afterglow at 20 mTorr (Fig. 5.11) exhibits a two-temperature distribution. The high energy tail is quite pronounced and combined with the characteristic of PMT measurements (Fig. 5.12) and the current-voltage (IV) curves confirm the existence of a low-density plasma in early afterglow. During the transition from high to low power, the emission intensity decayed rapidly to a low but non-zero value before reigniting into the expected low power state.

This low but non-zero emission intensity is presumably from a weak capacitively-coupled plasma. (These PMT measurements were done in another run at the same pressure; apparently the time at which the signal was at a stable, non-zero low value was somewhat shorter than during the Langmuir probe measurements in Fig. 5.10.)

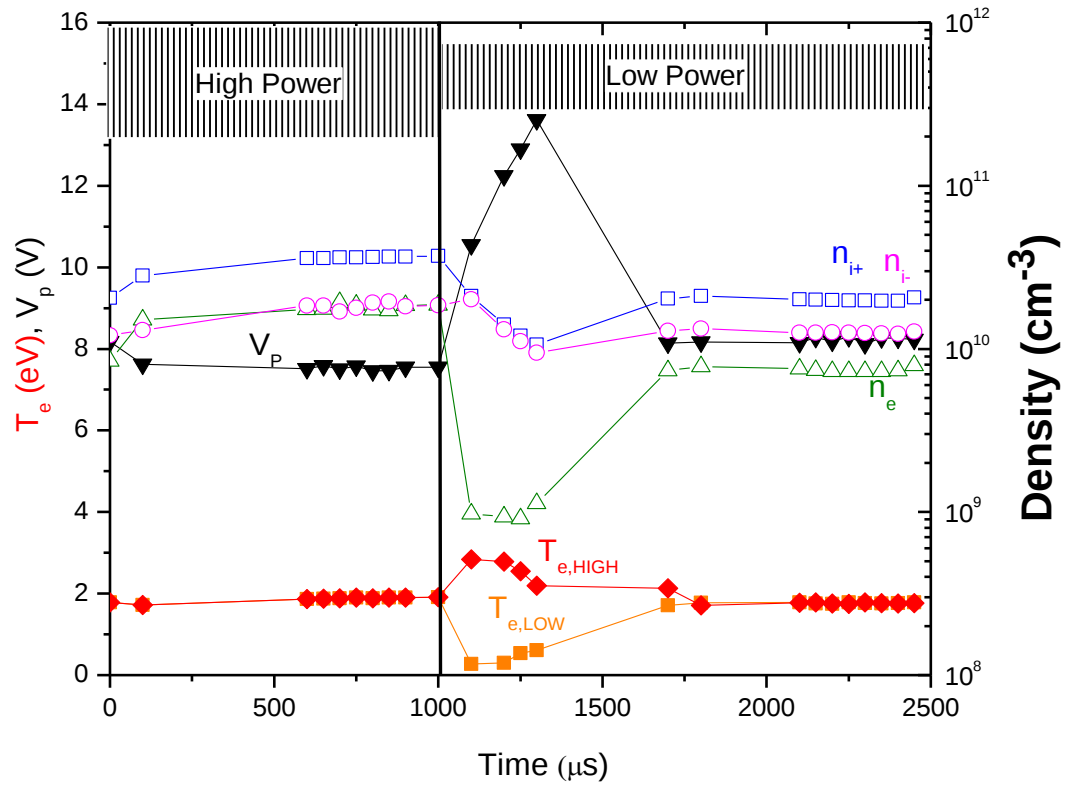


FIG. 5.10. Langmuir probe measurements for 20 mTorr, 400 Hz pulse frequency, 40% duty cycle. Called-for low to high power ratio of 60%. Average power = 168 W.

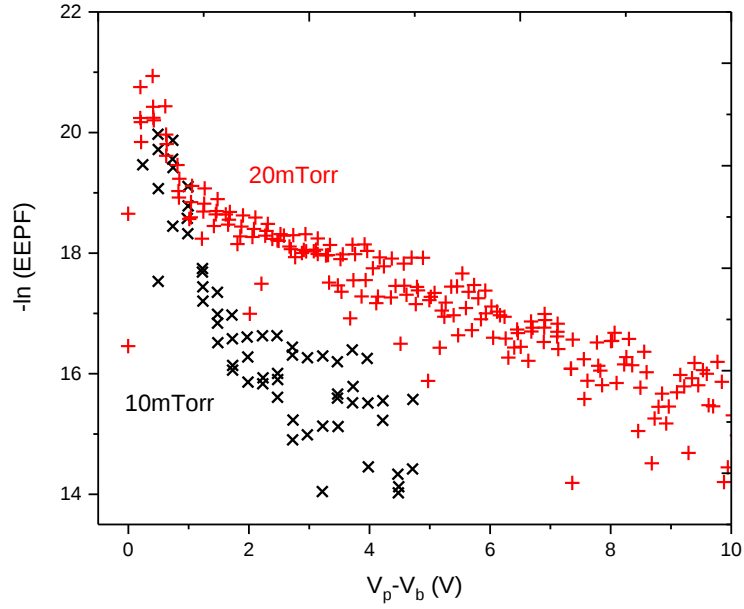


FIG. 5.11. EEPFs ( $-\ln(\text{EEPF} \text{ (eV}^{-3/2}\text{m}^{-3}\text{)})$ ) during the “ignition delay” region ( $1200 \mu\text{s}$  – see Figs. 4.7 and 4.8) for both 10 mTorr and 20 mTorr. 400Hz pulse frequency, duty cycle = 50%. called-for low to high power ratio = 60%. Average power = 180 W and 168 W for 10 and 20 mTorr respectively.

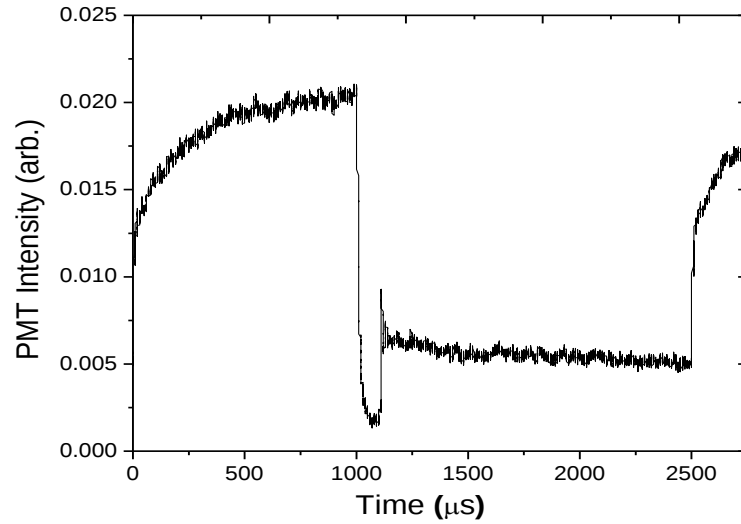


FIG. 5.12. Photomultiplier tube measurement for 20 mTorr. 400 Hz pulse frequency, 40% duty cycle  $\text{Cl}_2/\text{Ar}$  pulsed plasma. Average power = 212 W. The called-for ratio of low power to high power is 60%.

## 5.4 Discussion

The high-to-low power transition for conditions that produce an ignition delay is characterized by a short term initial decrease in both forward and reflected power. As the low-to-high power ratio is decreased, the optimal matching conditions at low and high power increasingly differ, raising the likelihood that an ignition delay will occur. Similar ignition delays have previously been found in chlorine plasmas<sup>181, 185</sup>. When a pulsed ICP was operated with continuous rf bias on a substrate stage immersed in the plasma,  $n_e$  and  $n_+$  decayed by typically 4 and 2 orders of magnitude in the afterglow period<sup>181</sup>. At the point when  $n_+$  decayed to the level sustained by the stage power, a capacitively-coupled plasma ignited. At this time,  $n_e$ , which had decayed to a level well below the steady-state CCP value, abruptly increased and stabilized at the value commensurate with the CCP.

This phenomena of the plasma not igniting until the positive ion density decayed to the value corresponding to the low power state was also found in an ICP with a Faraday shield to eliminate any capacitive coupling<sup>185</sup>. In this case, the lower plasma density state was obtained by injecting ions and electrons through a grid separating the pulsed ICP from an “ignition source” ICP. This tandem plasma arrangement was needed to continuously ignite the pulsed ICP (albeit with a delay) since there was no capacitive coupling to invoke an E-to-H transition.

In the present study, the ion density drops well below the steady state low power ion density before re-ignition occurs. As mentioned above, this is likely because the Langmuir probe measurements were taken near (2 cm from) the substrate and far away (11 cm) from where power is delivered, near the coil. In the two prior studies, the Langmuir

probe measurements were made closer to the coil<sup>185</sup>, or close to the capacitively-coupled, powered electrode<sup>181</sup>. Hence, in the present study it is likely that the low power period plasma ignites near the time when the ion density near the coil decays to the low power level.

This inability for the plasma to re-ignite until the positive ion density decayed to that sustained by the low power state caused the previously observed ignition delay to increase as the magnitude of the high power increased or that of the low power decreased<sup>185</sup>. In the present study, it was found that the delay time was nearly independent of duty cycle (i.e., percentage of time in the high power state) up to 20% and then increased with increasing duty cycle. This is understandable, in light of the prior studies. At low duty cycles, the plasma density is mainly sustained by the low power and  $n_e$  in the high power state is nearly constant at low duty cycle, hence the delay is not expected to change. As duty cycle increases beyond 20%,  $n_e$  in the high power state increases and so does the delay in re-ignition, as it takes longer for the positive and negative ion density to decay to the low power state value.

As shown in Fig. 5.4, it is possible to obtain “normal” behavior when switching from high-to-low power, with constant electron temperatures, and charge densities that quickly rise and fall to near-constant levels expected from the called-for power ratio. In the majority of cases, however, “abnormal” re-ignition was found. Of these, the anomalies were usually observed in the low power period, but it is also possible to produce delays in ignition during the high power intervals. Several types of abnormalities were found in the low-power period: **(A)** The plasma is off for part of this period, followed by a capacitively-coupled plasma. **(B)** The inductive plasma is sustained immediately upon dropping to low

power. **(C)** An inductive plasma forms after a very brief dip in optical emission. **(D)** A capacitively-coupled plasma jumps to inductive mode (i.e., E-to-H mode transition).

The behavior in power modulated chlorine inductively-coupled plasmas is reminiscent of instabilities that have been widely reported for electronegative gases<sup>181-185, 192, 193</sup>. The ignition delay effect is similar to the self-oscillations found in continuously-powered electronegative gas plasmas, due to back and forth transitions between inductive and capacitive modes<sup>183, 184</sup>. The frequency of oscillation found in those studies varied from ~100 to 1 kHz, and tended to increase with increasing pressure<sup>183, 184</sup>. The half periods of these oscillations (5 to 500  $\mu$ s) overlap the range of ignition delay times in the present study (~60 to 2000  $\mu$ s) that similarly decrease with increasing pressure up to about 13 mTorr, but then became independent of pressure at higher pressure.

The transition from high to low applied power in the present study is similar to the H-to-E mode transition described by Chabert *et al.*,<sup>183</sup> This instability-triggered self-modulation of electronegative SF<sub>6</sub> and SF<sub>6</sub>/Ar plasmas has been explained with a global model that considers the dynamics of power balance. For  $\alpha_0 = n_i/n_e \gg 1$  throughout the cycle, the loss of power,  $P_{loss}$ , is through electron inelastic processes in the bulk plasma and flux of charged species to the walls, given by

$$P_{loss} = en_e V \sum_i k_i n_{g,i} \varepsilon_i + A[\Gamma_e(\Phi + 2T_e) + \Gamma_-(\Phi + 2T_-)], \quad (5.3)$$

where  $V$ ,  $A$ , and  $\Phi$  are the plasma volume, bounded area, and potential,  $T_-$  is the negative ion temperature, and  $\Gamma_e$  and  $\Gamma_-$  are the electron and negative ion flux to the walls. ( $\Gamma_-$  is actually the positive ion flux since  $n_+ = n_-$ , and no negative ions reach the walls, provided  $n_e$  has not decayed to the point where an ion-ion plasma forms.) The summation is over all

electron reactions with  $\text{Cl}_2$  and  $\text{Cl}$  that cause the loss of electron energy,  $\varepsilon_i$ . Equation (5.3) predicts a linear dependence on  $n_e$  if  $T_e$  and  $\Phi$  remain constant. In fact, when transitioning from high to low power, these parameters can remain constant (Figs. 5.3 and 5.4), decrease (Figs. 5.5 and 5.8), or increase (Fig. 5.10 at higher energies). The EEPF can also become highly non-Maxwellian (Fig. 5.11), affecting the rate constants  $k_i$ .

At  $n_e > 10^9 \text{cm}^{-3}$ , most power is absorbed by electrons.<sup>183</sup> This can be expressed as the sum of capacitive and inductive components,

$$P_{abs} = \frac{1}{2} I_{rf}^2 R_{abs} \left( \frac{n_{ind} n_e}{n_{ind}^2 + n_e^2} + \frac{n_{cap}}{n_{cap} + n_e} \right), \quad (5.4)$$

where  $I_{rf}^2 R_{abs}$  term determines the power at some settings of the matching network, incorporated in the parameters  $n_{ind}$  and  $n_{cap}$ .

Electron number densities can change much faster than can positive and negative ion densities. This is believed to be the cause of the oscillations in light intensity and plasma density observed in  $\text{SF}_6$ -containing plasmas.<sup>183</sup> Near the end of a high-density phase, the negative ion density builds up to the point where  $P_{loss}$  exceeds  $P_{abs}$ . Electron density rapidly drops, and the plasma enters a capacitively-coupled phase. Negative ion density then decays until  $P_{abs}$  exceeds  $P_{loss}$ , whereupon  $n_e$  increases rapidly and the plasma becomes inductively-couple, repeating the cycle.

The  $P_{abs}$  curves in Fig. 5.13 were generated from equation (5.4), using arbitrary values for  $n_{cap}$  and  $n_{ind}$  that produced curves of similar shape to those for  $\text{SF}_6$  plasmas, computed by Chabert *et al.*,<sup>183</sup> and Lieberman and Lichtenberg.<sup>28</sup> The upper and lower dashed lines represent  $P_{loss}$  that varies linearly with  $n_e$ , with higher and lower  $n$ -levels. The

points where  $P_{abs}$  and  $P_{loss}$  intersect represent short term, or stable long term plasma operation.

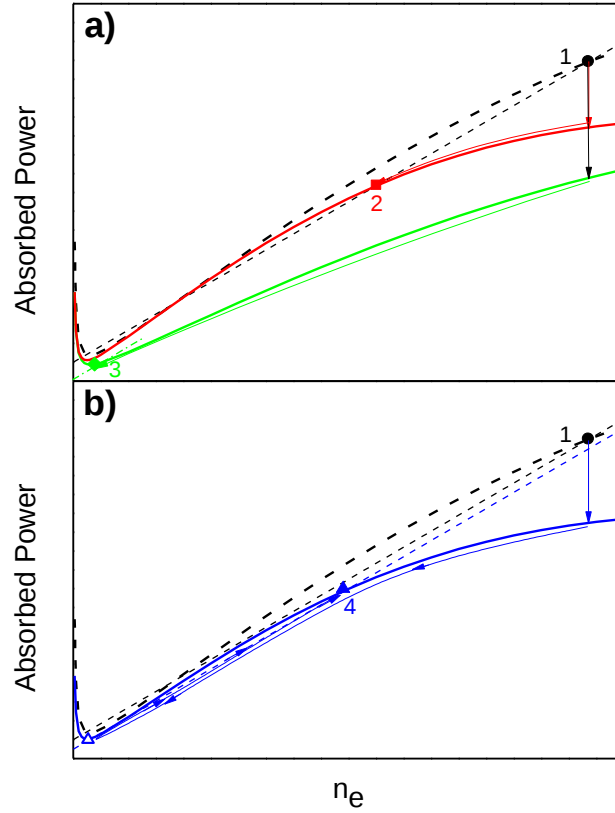


FIG. 5.13. Qualitative  $P_{abs}$  and  $P_{loss}$  values vs  $n_e$ , predicted from equations (5.3) and (5.4). The thick dashed black line represents the high power state, operating at a density corresponding to the black circle. **a)** The power was switched to a lower value. **b)** The blue curve is a slightly lower power.

While ignition delays can generally be minimized by tuning the impedance matching network to minimize reflected power during the low power state, dynamic matching, with its added complexity and technical challenges, can provide optimum power delivery to the plasma throughout the modulation cycle. This can be accomplished by tuning the frequency applied to the plasma or by varying capacitance and/or inductance values in the matching network, requiring that the time response of the matching system is

sufficient to capture these transient modes. The inductive and capacitive reactance can be matched with a frequency matching control scheme at a much faster rate than it can be by modifying the capacitance or inductance<sup>194</sup>.

Similarly, incorporation of “load levelling” power delivery where the generator output power is increased to compensate for impedance mismatch induced power reflection may provide more predictable delay time response with respect to the two power levels. Careful consideration must be taken when operating in a power modulated plasma with a low/high power ratio under fixed match conditions such that those used in this study, as the matching condition chosen will produce reflected power in either the low power state, the high power state, or both depending on the chosen matching condition.

## 5.5 Conclusions

We have shown experimentally an abnormal plasma mode in a chlorine power modulated plasma which is analogous to instabilities that have been reported usually under electronegative continuous power conditions<sup>183, 184</sup>. Depending on slight changes in the matching network capacitor and inductor settings, two modes of operation have been observed: one in which the plasma makes a stable transition from high to low power, and one in which the plasma extinguishes at the beginning of the low power period, then reignites after 60 to 2000  $\mu$ s, depending on pressure and duty cycle. At low pressure (<5 mTorr) and larger duty cycle, a complex frequency halving mode was also seen, where the plasma extinguishes for the entirety of the low power cycle and continues to be

extinguished for the entire next high power cycle, before re-igniting shortly after dropping to low power.

Most of the transient behavior can be qualitatively explained by considering the dependence of the power absorbed and lost as a function of both the electron and ion densities. As soon as the shift from high to low power occurs,  $P_{abs}$  can exceed  $P_{loss}$ , causing the plasma to stay in an inductively-coupled mode, or  $P_{abs} < P_{loss}$ , resulting in a rapid loss in electron density that causes the plasma to be extinguished until reaching a low enough negative ion density that the plasma re-ignites into either a capacitively-coupled state, or a capacitive to inductive mode. The re-ignition time is a function of the decay time of positive and negative ions as well as the steady state electron density at the new power state.

## **Chapter 6 – Time-Resolved Measurements of Absolute Number Densities of Products During Etching of Si in Chlorine Plasmas, and Si and SiO<sub>2</sub> in Fluorocarbon Plasmas, Using Ultraviolet Absorption Spectroscopy**

### **6.1 Introduction**

Optical diagnostics have the advantage that they are non-invasive to the plasma<sup>44</sup>. Optical emission spectroscopy (OES) has been used widely for plasma diagnostics. A disadvantage of OES is that the absolute number density of species cannot be easily obtained. Another optical diagnostic is broad-band UV absorption, which has the advantage of direct measurement of number density. The downside to UV absorption is that it requires an optical path across the reactor and is generally not as sensitive as OES.

Time-resolved absorption has been reported for the afterglow of halogen based<sup>195-198</sup> and fluorocarbon based plasmas. Cunge *et al.*, used a monochromator to scan over the wavelengths of the desired band, and measured the intensity with a photomultiplier tube<sup>196</sup>. With this setup, Cunge and colleagues were able to measure stable baseline noise levels of  $<5 \times 10^{-5}$  with the use of UV LEDs<sup>195</sup>, and  $\sim 1 \times 10^{-4}$  with a Xe arc lamp<sup>199</sup>.

Optical techniques such as those described above are a bit more involved in a pulsed plasma, as the plasma is not at steady-state. Time-resolved optical emission is also not viable in the off period of a pulsed plasma as the electron temperature quickly decays to values below the excitation threshold. One way to avoid this issue is use of a pulsed plasma with non-zero power applied in what would have been the afterglow.

### 6.1.1 – Ultraviolet (UV) absorption

In UV absorption spectroscopy, a UV light source is used to promote atomic and molecular species to excited electronic states, and changes in the amount of transmitted light through the plasma are recorded. UV absorption has been used extensively for both halogen based ( $\text{Cl}_2$  and  $\text{HBr}$ )<sup>196, 197, 199-204</sup> and fluorocarbon based<sup>198, 205-212</sup> plasmas.  $\text{Cl}_2$  plasmas have been studied during Si etching while measuring Si,  $\text{SiCl}$ ,  $\text{SiCl}_2$  and  $\text{Cl}_2$  number densities<sup>199</sup>. UV absorption has also been used in conjunction with vacuum UV (VUV) absorption and mass spectrometry to do a nearly complete mass balance of Cl,  $\text{Cl}_2$  and  $\text{SiCl}_{0-4}$  during Si etching (Fig. 6.1)<sup>196</sup>.

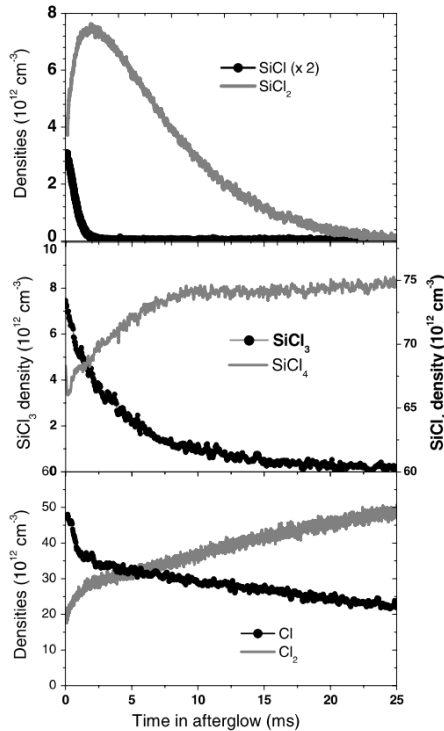


FIG. 6.1. Time variation of (upper)  $\text{SiCl}$  and  $\text{SiCl}_2$  by UV absorption spectroscopy (middle)  $\text{SiCl}_3$  and  $\text{SiCl}_4$  by mass spectrometry and VUV absorption (lower)  $\text{Cl}$  and  $\text{Cl}_2$  by mass spectrometry and VUV absorption spectroscopy. Ar (100 sccm),  $\text{Cl}_2$  (50 sccm),  $\text{SiCl}_4$  (60 sccm) at 10mTorr with 800 W source power at 30 Hz with 15% duty cycle<sup>196</sup>.

Booth *et al.*, measured CF, CF<sub>2</sub>, and SiF<sub>2</sub> absorbance in C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> plasmas<sup>206</sup>. For CF<sub>2</sub>, absolute number densities were measured using reported absorption cross-sections<sup>207</sup>. Luque *et al.*, used broadband absorption as well as *ab initio* calculations to deduce CF concentrations, transition probabilities, and gas temperatures<sup>209, 210</sup>.

UV absorption is often carried out with a Xe-arc lamp. The Xe-arc is inherently unstable, however, as discussed by Booth *et al.*,<sup>199</sup>. As an alternative to the Xe-arc lamp, they showed that UV light emitting diodes (UV LEDs) had superior stability<sup>195</sup>. Figure 5.2 shows typical unabsorbed baselines for both a Xe arc lamp and a UV LED. The curved shape and non-zero slope for the lamp are an indication of very small changes in the spectrum between the times spectra were recorded with and without the absorbing species being present. The nearly straight line and value of 1.0 for the ratio of the UV LED intensity at different times shows that it is more stable than the Xe arc lamp.

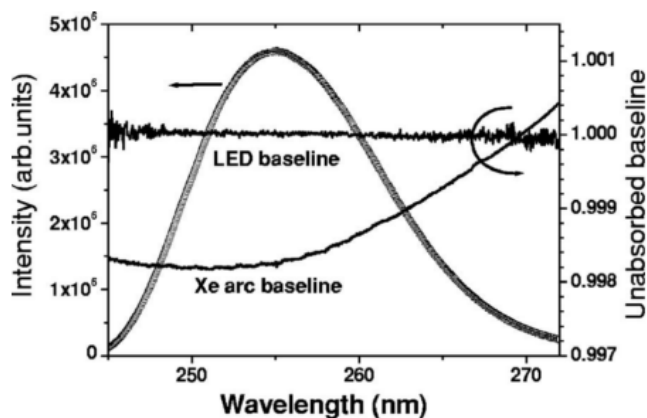


FIG. 6.2. Emission spectrum from a 255 nm LED and baseline obtained from the ratio of two spectra acquired with 5 min interval and a similar baseline obtained with a 150 W Xe arc source<sup>195</sup>.

Because UV LEDs cover only a small range of wavelengths, they are generally not practical for general detection of various species by UV absorption spectroscopy. Hence it was decided to use a Xe arc lamp and deal with the instability issue by repeatedly making four separate measurements over a short time:

1. Lamp with plasma ( $L_p$ )
2. Plasma with no lamp ( $P$ )
3. Lamp without plasma ( $L_0$ )
4. Background ( $B$ )

The absorption of light through the gas is governed by the Beer-Lambert law,

$$\frac{I_T}{I_0} = e^{-A} \text{ and } A = nl\sigma, \quad (6.3)$$

where  $I_0$  is the incident light, and the transmitted light ( $I_T$ ) depends on the absorption cross section ( $\sigma$ ), path length ( $l$ ) and number density of the species ( $n$ ). The transmitted intensity can also be written in terms of the measured data,

$$\frac{I_T(\lambda)}{I_0(\lambda)} = \frac{L_p(\lambda) - P(\lambda)}{L_0(\lambda) - B(\lambda)}. \quad (6.4)$$

The density of some species ( $A$ ) can then be determined by combining equations (6.3) and (6.4),

$$n(A) = \frac{-1}{\sigma(A) l} \ln \frac{L_p(\lambda) - P(\lambda)}{L_0(\lambda) - B(\lambda)}. \quad (6.5)$$

For molecular species, the absorption spectrum is composed of many lines with little spacing, often making it difficult to resolve individual peaks within the total band.

Under these situations it is often more convenient to extract number densities from the integrated absorption. The following equation is then used instead of equation (6.4)

$$W \cong nl \int \sigma(\lambda, T) d\lambda, \quad (6.6)$$

where  $W$  is the integrated absorbance for a given wavelength range and  $\int \sigma(\lambda, T) d\lambda$  is the wavelength integrated cross-section for that same wavelength range. Tabulated cross-sections for SiCl and SiCl<sub>2</sub> are computed using this wavelength integrated cross-section formulation therefore, the area underneath the absorbance band with a straight baseline instead of peak absorbance will be used for SiCl and SiCl<sub>2</sub>.

### 6.1.2 – Time-resolved UV absorption

Typical absorption of Si-etch products in a chlorine plasma ranges from 0.0005-0.01.<sup>199</sup> Therefore the fractional drift in absorbance, background including plasma emission intensity, and lamp intensity must be less than this to detect the true absorbed intensity.

The detailed procedure for steps 1-4 defined above is as follows. First, the UV lamp intensity plus plasma emission intensity are recorded by the spectrometer ( $L_P$ ). Next, the shutter is closed, blocking the UV light so that light from just the plasma is detected ( $P$ ). Finally, the shutter is opened, the plasma is switched off, and the spectrum of just the lamp is recorded ( $L$ ). This sequence is repeated approximately every second, using LabView code to control the shutter, plasma power, and collect the measured intensities. In this way, drifts in  $L_P$ ,  $P$ , and  $L_0$  signals are greatly reduced. At the end of the experiment a long background (BG) is taken. The background is not included in the iterative technique as it

is not expected to be time dependent (provided that the spectrometer has had sufficient time to warm up), so removing its determination from the iterations allows for faster cycling. The result is a relatively inexpensive, compact, highly sensitivity UV absorption measurement system.

The “UV only” spectrum was recorded while the processing feed gas is still flowing, hence absorption of the feed gas needs to be considered.  $\text{CF}_4$  and  $\text{C}_4\text{F}_8$  do not absorb in the UV region of interest, but  $\text{Cl}_2$  does, beginning around 280 nm, peaking weakly near 330 nm, and falling to near-zero absorbance at about 380 nm. When the plasma is ignited,  $\text{Cl}_2$  is consumed and its absorbance is lessened. Therefore, the lamp spectrum recorded with the plasma off differs slightly from the  $L_0$  values required in equation (6.5). Turning the  $\text{Cl}_2$  feed gas off would allow the unabsorbed lamp spectrum to be obtained and then to determine the  $\text{Cl}_2$  number density in addition to the number densities of the Si-containing species. This would, however, add a large amount of plasma-off time to the experiment. In addition, the absorbance from  $\text{Cl}_2$  is quite low (0.003 at 10 mTorr and 600 K), so accurate measurements of  $\text{Cl}_2$  number densities would be difficult for continuously-powered plasmas, not to mention pulsed plasmas. Since Si and  $\text{SiCl}$  absorption lines and bands are sharp compared to the  $\text{Cl}_2$  absorption, the only effect of a changing  $\text{Cl}_2$  absorption is a slight shift in the baseline, which can easily be accounted for. For  $\text{SiCl}_2$ , the absorption dwarfs that of  $\text{Cl}_2$  and so a negligible error (<10%) is introduced by simply ignoring it.

Finally, the maximum signal-to-noise is obtained when the intensity of the lamp plus plasma emission is just below the value at which the detector saturates. Therefore, integration times need to be minimized near intense emission/absorption wavelengths (250, 288, and  $\sim 325$  nm). Consequently, when broader scans extending to longer wavelengths

are recorded, it is necessary to make multiple measurements with different integration times, scans to average, and repetition cycles. The raw UV intensity was checked before each experiment to determine the valid wavelength range in which absorption would occur and this expectation was checked against the raw data to determine the acceptable spectral range of absorption.

## **6.2 Results**

### **6.2.1 – Absorption of silicon etch byproducts in chlorine plasma**

Individual lamp with plasma ( $L_P$ ), plasma only (P), and lamp only spectra are shown in Figure 6.3. Flows of  $\text{Cl}_2$  (20 sccm) and Ar (2 sccm) were used with a source power of 360 W, substrate bias of -90 V, and pressure of 20 mTorr. At ~310 nm, the UV and UV with plasma spectrum saturate, which will invalidate absorption above the saturation wavelength.

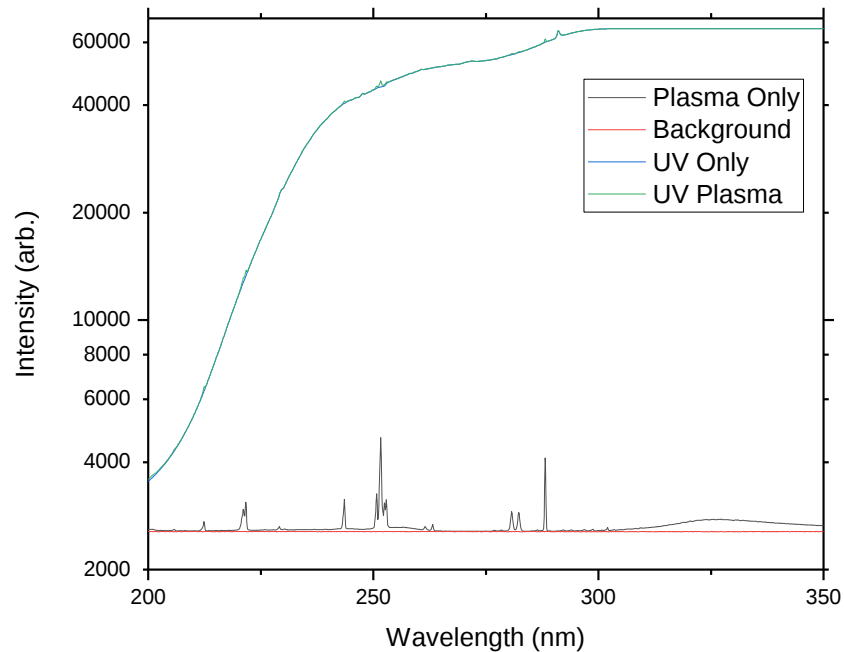


FIG. 6.3 An example of the four spectral scans needed to compose an absorption spectrum. Conditions: 8 ms integration time, 25 scans to average, and 2000 repetition cycles were used. 20 sccm  $\text{Cl}_2$ /2 sccm Ar at 20 mTorr, 360 W source power, with -90 V substrate bias.

The resulting time-resolved absorbance using the procedure described above is shown in Figure 6.4. Plotted is the absorbance, which is the negative natural log of transmittance, where transmittance is described in equation (6.5). Absorption by  $\text{SiCl}$  (280 nm, 282 nm),  $\text{SiCl}$  (290 - 300nm), and  $\text{Si}$  (288.16 nm) can be seen.  $\text{SiCl}_2$  (300-360 nm) also absorbs but most of the band was saturated under these conditions.

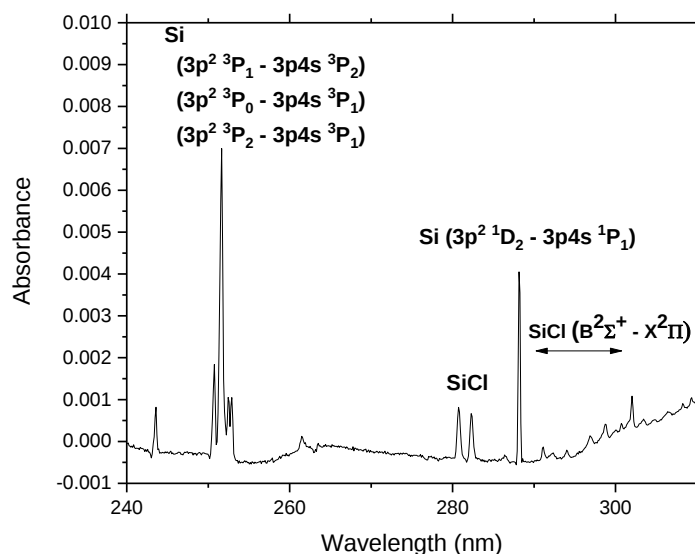


FIG. 6.4. Absorption of Si and SiCl in a continuous wave chlorine plasma. 8 ms integration time, 25 scans to average, and 2000 repetition cycles was used. 20 sccm Cl<sub>2</sub>/2 sccm Ar at 20 mTorr, 360 W source power, with -90V substrate bias.

Integrated absorption was determined by measuring the area under the absorption peaks, choosing baselines on either side of the band. SiCl number density can be calculated from equation (6.7). Wavelength integrated cross sections of  $1.75 \times 10^{-29} \text{m}^{-3}$  for SiCl ( $v', v''$ ) = (0,0) at 290-295 nm and  $1.9 \times 10^{-29} \text{m}^{-3}$  for SiCl ( $v', v''$ ) = (0,1) at 295-300 nm with a beam path length (L) of 15.24 cm were used. SiCl  $v''=0$  number density (determined from the 0,0 band) is  $1.08 \times 10^{11} \text{cm}^{-3}$ , and the SiCl  $v''=1$  number density (determined from the 0,1 band) is  $8.63 \times 10^{10} \text{cm}^{-3}$ . The total SiCl number density of  $v''=0$  plus  $v''=1$  of  $1.94 \times 10^{11} \text{cm}^{-3}$  agrees well with experiments done under similar conditions<sup>199</sup>.

The Si atom absorption cross-section can be estimated using a procedure similar to that by Kogelschatz *et al.*,<sup>199</sup>

$$\sigma(\lambda, T) = \lambda_0^2 \frac{e^2}{4\epsilon_0 m c^2} f_{12} \frac{\sqrt{2}}{\sqrt{\pi} \delta\lambda(T)} \text{ and} \quad (6.8)$$

$$\delta\lambda(T) = \frac{\lambda_0}{\sqrt{2 \ln 2}} \times 10^{-20} \times \sqrt{\frac{T}{M}}, \quad (6.9)$$

where  $\lambda_0$  is the peak wavelength of the transition in meters,  $f_{12}$  is the oscillator strength of the transition, T the gas temperature in Kelvin,  $m$  the electron mass in kilograms, and M the mass of the atom in kilograms. The Si atom density is taken as the sum of the triplet ground state sublevels ( $^3P_0$ ,  $^3P_1$ , and  $^3P_2$ ) and singlet metastable states ( $^1D_2$  and  $^1S_0$ ). An estimated gas temperature of 500K was used for the calculation. Table 6.1 shows the transition, peak wavelength, oscillator strength, and estimated cross-section (in  $\text{cm}^2$ ).

Table 6.1 Estimated absorption cross section, oscillator strength, and peak wavelengths, used to estimate number density for a given Si sublevel.

| Lower level | $\lambda_0$ (nm) | $f_{12}^{213, 214}$ | $\sigma$ ( $\text{cm}^2$ ) |
|-------------|------------------|---------------------|----------------------------|
| $^3P_0$     | 251.43           | 0.21                | $1.27 \times 10^{-12}$     |
| $^3P_1$     | 250.69           | 0.1                 | $6.00 \times 10^{-13}$     |
| $^3P_2$     | 252.85           | 0.053               | $3.23 \times 10^{-13}$     |
| $^1D_2$     | 288.16           | 0.17                | $1.35 \times 10^{-12}$     |
| $^1S_0$     | 263.1            | 0.355               | $2.35 \times 10^{-12}$     |

Using the estimated cross-sections, the total triplet ground state silicon atom density can be estimated as  $9.38 \times 10^8 \text{cm}^{-3}$  with a sub-state distribution ( $^3P_0 : ^3P_1 : ^3P_2$ ) of (0.41 : 0.27 : 0.32). The measured  $^1D_2$  metastable concentration is  $1.72 \times 10^8 \text{cm}^{-3}$  for a total silicon density of  $1.12 \times 10^9 \text{cm}^{-3}$ . No silicon in the  $^1S_0$  was detected under these conditions.

An example of  $\text{SiCl}_2$  absorption can be seen in Figure 6.5. The baseline differed slightly from zero and was often negative due to drift and changing  $\text{Cl}_2$  number density with the plasma on and off, as discussed above. A straight baseline for calculating  $\text{SiCl}_2$  number density was taken between 305 nm and 336 nm and the area was calculated to be 0.00335 nm. Path length of 15.24 cm and wavelength integrated cross section of  $1.74 \times 10^{-29} \text{ m}^3$  were used. A number density of  $1.26 \times 10^{12} \text{ cm}^{-3}$  was found using equation (6.7),

$$n = \frac{W}{l \int \lambda d\lambda} = \frac{0.00335 \text{ nm}}{15.24 \text{ cm} * 1.74 \times 10^{-29} \text{ m}^3} = 1.26 \times 10^{12} \text{ cm}^{-3}. \quad (6.10)$$

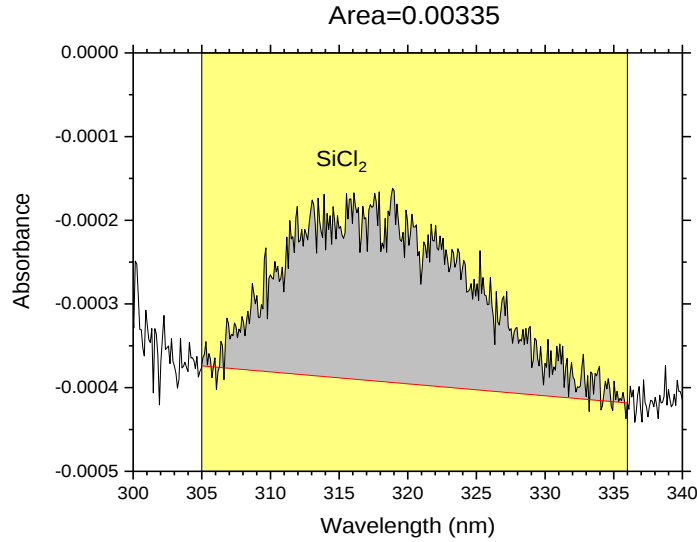


FIG. 6.5. Absorption of  $\text{SiCl}_2$  (300-360 nm) in a continuous wave chlorine plasma. Conditions: 8 ms integration time, 25 scans to average, and 3000 repetition cycles were used. 20 sccm  $\text{Cl}_2$ /2 sccm Ar at 10 mTorr. 280 W source power, -70 V substrate bias.

Absorption was measured continuously for 60 minutes for a CW plasma at 280 W source power, -70 V substrate bias, and 10 mTorr pressure. The absorption results were then calculated for different segments of time (Fig. 6.6). Si (251 and 288 nm) and  $\text{SiCl}$  (280 and 282 nm) absorbance measurements could be made every 6 minutes with

reasonable signal-to-noise levels. This time could be reduced depending on the required resolution of each peak and the desired accuracy of number densities. Absorption (open symbols, dotted lines) agree fairly well qualitatively with emission intensities (solid symbols, solid lines) for both Si and SiCl, indicating that at least in this case, OES tracks relative number densities measured by absorption.

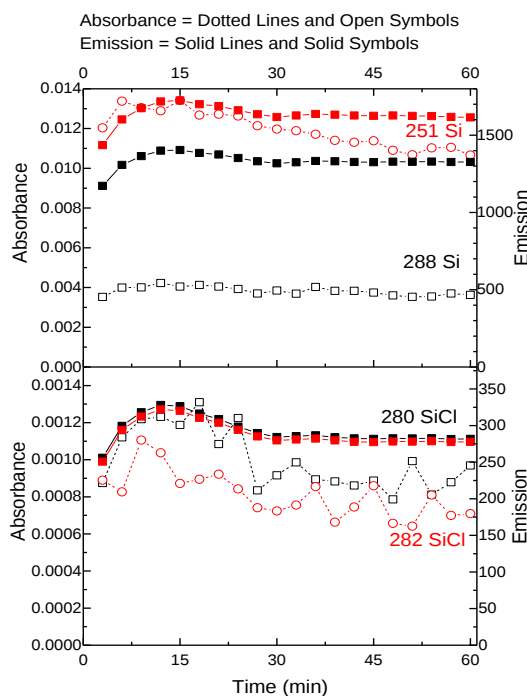


FIG. 6.6. Time-variation of absorption and optical emission of Si and SiCl. 20 sccm  $\text{Cl}_2$ /2 sccm Ar at 10 mTorr. 280 W source power, -70 V substrate bias. Dotted lines and open symbols correspond with absorption and solid lines and solid symbols correspond with emission. (upper) Si (lower) SiCl.

Time-resolved absorption measurements in a pulsed plasma were done at high source and bias powers to maximize absorption (Fig. 6.7). The experiment was carried out with a 400 Hz pulsed plasma with a duty cycle of 40%, average ICP power of 176 W, average substrate bias voltage of -40 V, and 20 mTorr pressure. The chopper was set to 800  $\mu\text{s}$  to maximum etching product number densities, at the end of the active glow. Figure

6.7 shows the absorption spectrum for Si and SiCl under these conditions. As the bias power was high relative to previous experiments<sup>199</sup>, absorption, by Si at 251.43nm, is almost six times as large as that reported by Kogelschatz *et al.*,<sup>199</sup>.

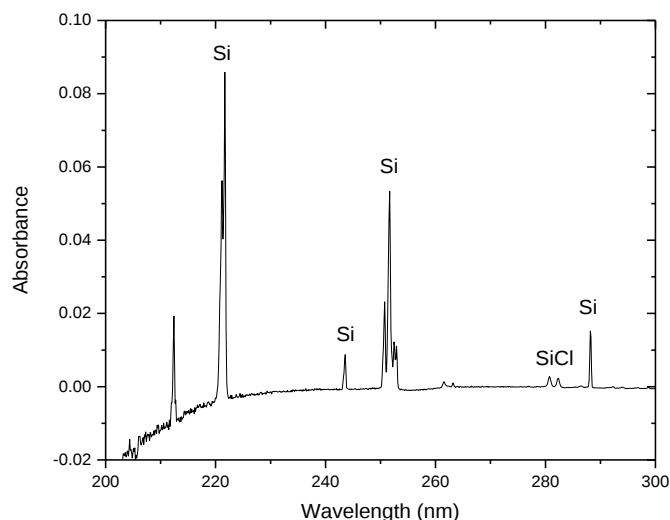


FIG. 6.7. Time-resolved absorption for Si, and SiCl. 80 ms integration time, 25 scans to average, and 500 repetition cycles were used. 20 sccm Cl<sub>2</sub>/2 sccm Ar at 20 mTorr, 176 W source power, with -40 V substrate bias. 400 Hz pulse plasma with spectra taken at 800  $\mu$ s (near the end of the activeglow).

Absorption measurements were taken over a full pulse cycle at 160 W average power, 500 Hz pulsed frequency, 50% duty cycle and 10 mTorr pressure. The delay between the optical chopper and the plasma signal was changed to measure Si, SiCl, and SiCl<sub>2</sub> relative densities during the activeglow and afterglow (Fig. 6.8). SiCl<sub>2</sub> absolute number density can be calculated with the band area from 300-360 nm and using the wavelength integrated cross section of  $1.75 \times 10^{-29} \text{m}^3$  as was done for Figure 5.5<sup>199</sup>. The maximum SiCl<sub>2</sub> number density, at the end of the activeglow was  $3.1 \times 10^{12} \text{cm}^{-3}$ . The 251 and 288 nm absorbance peaks for Si and 280 and 282 nm peaks for SiCl were averaged together to increase signal to noise. Si, SiCl, and SiCl<sub>2</sub> rise and nearly reach steady state

within the activeglow period (1000  $\mu\text{s}$ ). At the beginning of the afterglow, the Si drops most rapidly to near zero within 200  $\mu\text{s}$ , followed by SiCl. SiCl<sub>2</sub> on the other hand, drops slower. For Si and SiCl, the drop in number density is likely due to the fast gas phase reaction of  $\text{SiCl}_{x-1} + \text{Cl}_2 \rightarrow \text{SiCl}_x + \text{Cl}$ . For SiCl, there will therefore be a loss and gain during the time Si is dropping. SiCl<sub>2</sub> on the other hand, is not believed to react nearly as rapidly with Cl<sub>2</sub> in the gas phase, hence loss at the surface may be more likely.

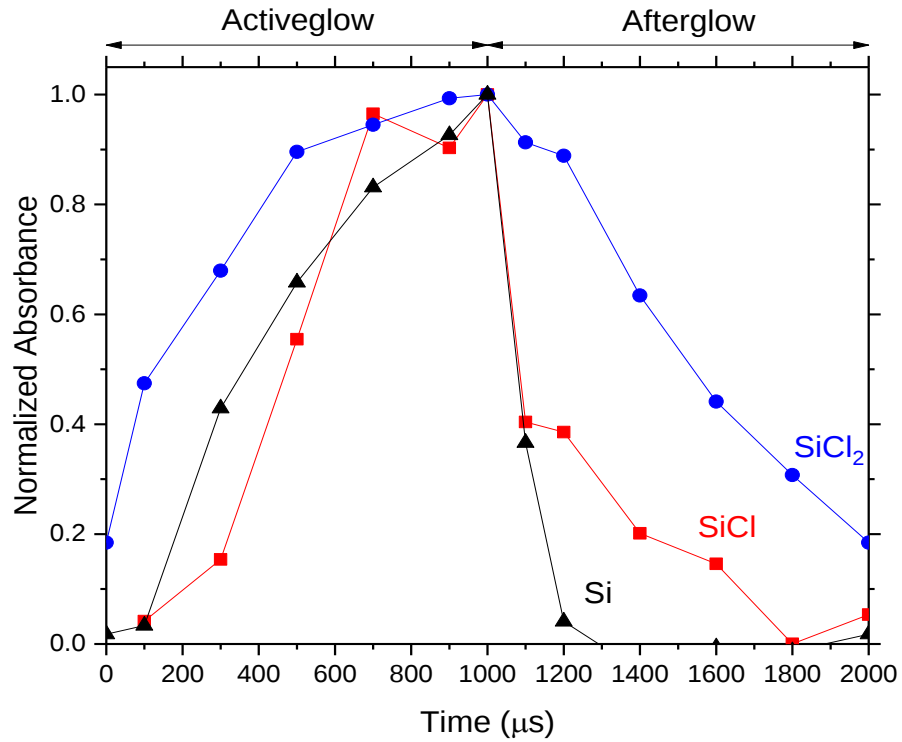


FIG. 6.8. Time-resolved absorption of (black) Si, (red) SiCl, and (blue) SiCl<sub>2</sub>. 500 Hz pulsed plasma with 50% duty cycle. 20 sccm Cl<sub>2</sub>/2 sccm Ar at 10 mTorr, 160 W average source power, with -44 V average substrate bias. SiCl<sub>2</sub> number density =  $3.1 \times 10^{12} \text{cm}^{-3}$  at 1000  $\mu\text{s}$ .

### 6.2.2 – CF<sub>x</sub> absorption in CF<sub>4</sub> and C<sub>4</sub>F<sub>8</sub> plasmas

Absorption of CF<sub>x</sub> in a CF<sub>4</sub> plasma is expected to be much weaker than in a C<sub>4</sub>F<sub>8</sub> plasma, as the primary dissociation products of CF<sub>4</sub> are CF<sub>3</sub> and F atoms<sup>206, 215</sup>. Time-averaged absorption of a 10 kHz pulsed CF<sub>4</sub> plasma is shown in Figure 5.9. The experiment was conducted with 20 sccm CF<sub>4</sub>, 2 sccm Ar, at an average power of 192 W and 20 mTorr pressure. Spectrometer integration time of 100 ms, with 10 scans averaged, and 1000 repetition cycles were used, resulting in a total experiment time of 50 minutes. The absorbance by CF<sub>2</sub> ( $2 \times 10^{-4}$ ) is near the detection limit of this setup. Also, a baseline drift is seen from 220-240 nm, causing negative apparent absorbance.

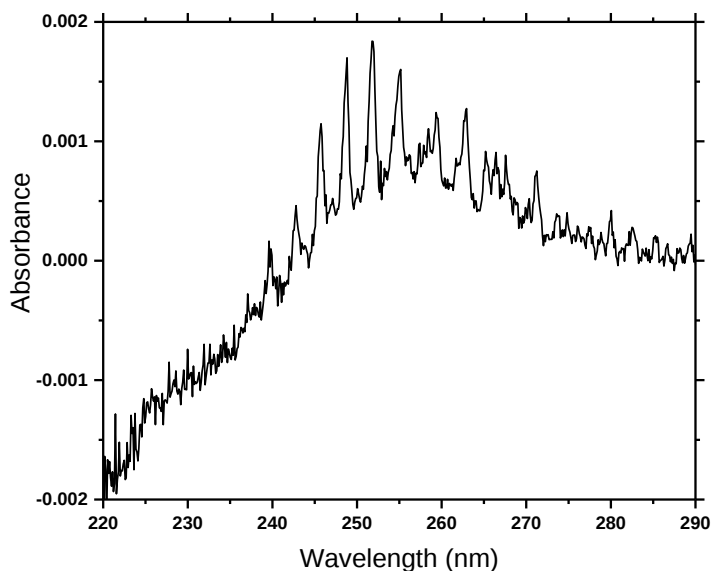


FIG. 6.9. Time-averaged absorption of CF<sub>2</sub> in pulsed CF<sub>4</sub> plasma. 20 sccm CF<sub>4</sub>/2 sccm Ar at 20mTorr. 192 W average power, 10 kHz pulse frequency, 50% duty cycle. 100 ms integration time, 10 scans to average, and 1000 repetition cycles.

Time-resolved absorption of  $\text{CF}_2$ , both late in the activeglow and late in the afterglow, in a pulsed  $\text{C}_4\text{F}_8$  plasma at an average power of 160 W and 10 mTorr pressure is shown in Figure 5.10. Absorption intensity of  $\text{CF}_2$  is nearly two orders of magnitude larger than seen in  $\text{CF}_4$  as  $\text{C}_4\text{F}_8$  will more readily dissociate into  $\text{CF}_2$ .  $\text{CF}_2$  number density of  $3 \times 10^{14} \text{ cm}^{-3}$  is found by using a  $\text{CF}_2$  absorption cross section of  $2.91 \times 10^{-17} \text{ cm}^2$  at 249 nm with the same path length that was used for  $\text{SiCl}$  and  $\text{SiCl}_2$ .  $\text{CF}_2$  does not decrease in the afterglow of a 500Hz 50% duty cycle pulsed plasma, and in fact increases slightly. This behavior is typical for  $\text{C}_4\text{F}_8$  and has been reported before<sup>215</sup>. Gas phase reactions that consume  $\text{CF}_2$  are very slow, and its sticking coefficient on surfaces is low, so heterogeneous loss rates are also slow. Broadening of the individual  $\text{CF}_2$  peaks in the activeglow compared with the afterglow is indicative of a higher rotational temperature in the activeglow compared with afterglow. This cooling of the gas in the afterglow raises the total number density and hence the  $\text{CF}_2$  number density, and could explain its small rise in the afterglow. The increase in  $\text{CF}_2$  number density in the afterglow could also be attributed in part to the surface reaction  $\text{CF}(\text{g}) + \text{F}(\text{s}) \rightarrow \text{CF}_2(\text{g})$ <sup>215</sup>.

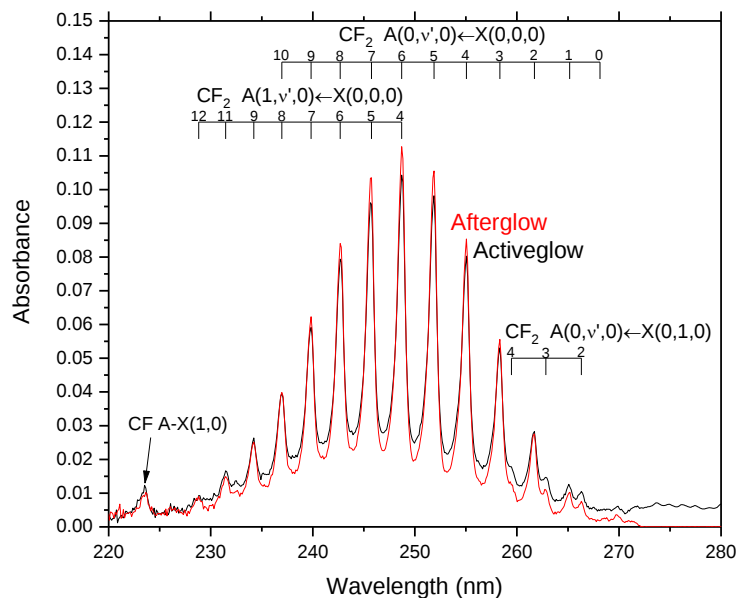


FIG. 6.10. Time-resolved  $\text{CF}_2$  absorption in  $\text{C}_4\text{F}_8$  pulsed plasma. 10 sccm  $\text{C}_4\text{F}_8$ /2 sccm Ar at 20 mTorr. (black) late in the activeglow, (red) late in the afterglow. 160 W average source power, 500 Hz, 50% duty cycle. 300 ms integration time, 3 scans to average, with 100 repetition cycles.

$\text{CF}_2$  was monitored for a full pulse period cycle in both 100Hz and 500Hz pulse frequency (Fig. 6.11 and Fig. 6.12). Calculated number densities for  $\text{CF}_2$  of  $\sim 3 \times 10^{14} \text{cm}^{-3}$  agree with experiments done under similar conditions<sup>215, 216</sup>.

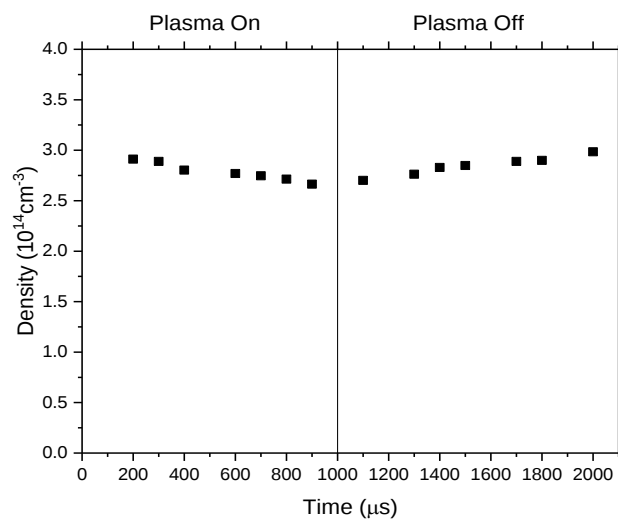


FIG. 6.11. Time-resolved  $\text{CF}_2$  absorption in 10 sccm  $\text{C}_4\text{F}_8$ /2 sccm Ar plasma at 20 mTorr, 160 W average power, 500 Hz pulse frequency, 50% duty cycle.

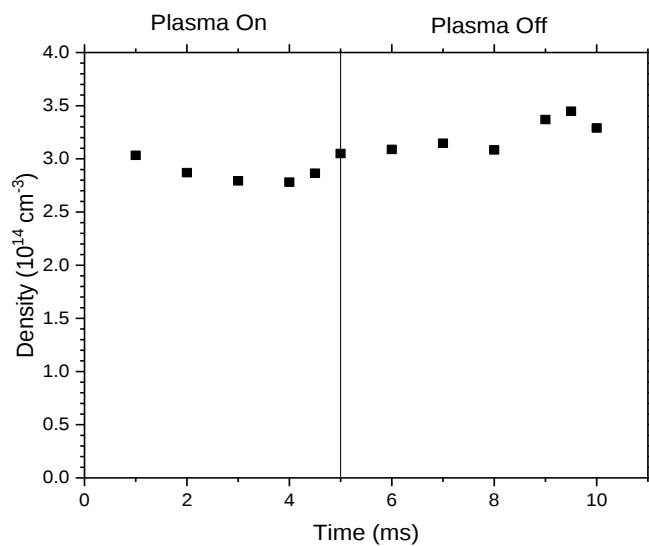


FIG. 6.12. Time-resolved  $\text{CF}_2$  absorption in 10 sccm  $\text{C}_4\text{F}_8$ /2 sccm Ar plasma at 20 mTorr, 160 W average power, 100 Hz pulse frequency, 50% duty cycle.

### 6.2.3 – CF<sub>x</sub> absorption and emission in CHF<sub>3</sub> and C<sub>4</sub>F<sub>8</sub> plasmas

Typical emission spectra of CHF<sub>3</sub>/Ar/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma are shown in Fig. 6.13. Emitting species included CF(B→X) at 202.38 nm, CF<sub>2</sub>(A→X) at 251.77 nm, CO(b<sup>3</sup>Σ<sup>+</sup> → a<sup>3</sup>Π) at 282.5 , 296.42, and C<sub>3</sub> (A<sup>1</sup>Π<sub>u</sub> → X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) between 380 to 405 nm<sup>217</sup>,<sup>218</sup>. A summary of emitting species, energies above the ground state, emission transitions, and selected wavelengths are given in table 6.2.

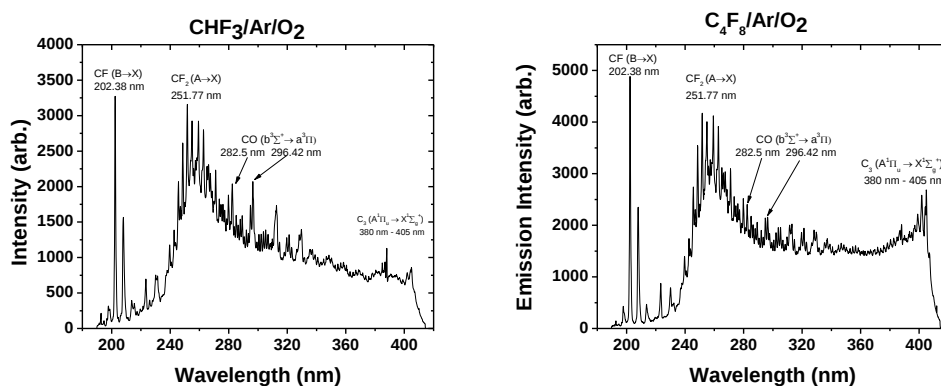


FIG. 6.13. Optical emission spectrum of CHF<sub>3</sub>/Ar/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasmas. ICP power=300W at 13.56 MHz, V<sub>DC</sub> = -100 V at 18 MHz, pressure= 20 mTorr, flow rates (sccm) were CHF<sub>3</sub> or C<sub>4</sub>F<sub>8</sub>:Ar:O<sub>2</sub>=10:2:1

Table 6.2 Emitting species, energy above the ground state, emission transitions, and peak wavelengths, for CHF<sub>3</sub>/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub> plasmas.

| Emitters        | Energy above the ground state (eV) | Transitions                                                                                                                                                                                                         | $\lambda$ (nm)                                                               |
|-----------------|------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| CF              | 6.09                               | $(B^2\Delta_r \rightarrow X^2\Pi_r)$<br>$(A^2\Sigma^+ \rightarrow X^2\Pi_r)$                                                                                                                                        | 202.38<br>207.99                                                             |
| CF <sub>2</sub> | 4.93                               | $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$<br>(1,7,0) – (0,0,0)<br>(1,6,0) – (0,0,0)<br>(1,5,0) – (0,0,0)<br>(1,4,0) – (0,0,0)<br>(0,5,0) – (0,0,0)<br>(0,4,0) – (0,0,0)<br>(0,3,0) – (0,0,0)<br>(0,3,0) – (0,1,0) | 239.71<br>242.68<br>245.64<br>248.59<br>251.77<br>254.94<br>259.34<br>262.72 |
| CO              | 10.34                              | $(b^3\Sigma^+ \rightarrow a^3\Pi)$<br>(1,0)<br>(0,0)<br>(0,1)<br>(0,2)<br>(1,4)<br>(0,3)<br>(1,5)<br>(0,4)                                                                                                          | 265.8<br>282.7<br>296.65<br>312.5<br>321.27<br>329.67<br>337.17<br>354.79    |
| C <sub>3</sub>  | 3.07                               | $(A^1\Pi_u \rightarrow X^1\Sigma_g^+)$                                                                                                                                                                              | 405.01                                                                       |
| F               | 14.74                              | $3p [3/2]^o \rightarrow 3s [3/2]$                                                                                                                                                                                   | 703.6                                                                        |
| Ar              | 13.48                              | $4p [1/2]_o \rightarrow 4s [1/2]^o$                                                                                                                                                                                 | 750.34                                                                       |

### *i. ICP power dependence*

For CHF<sub>3</sub>/Ar/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma, emission intensity of Ar (750.4 nm) is plotted as a function of ICP power in Fig. 6.14(a) and Fig. 6.15(a), respectively. The Ar 750.4 nm line is a good match for the energy of emitting levels of F, but not the lower

energy emitters  $\text{CF}_2$ ,  $\text{CF}$ ,  $\text{CO}$ , and  $\text{C}_3$ . Argon intensity increases for both  $\text{CHF}_3$  and  $\text{C}_4\text{F}_8$  plasma as ICP power goes up. The measured emission intensity ratios  $\frac{I_{\text{CF}_2}}{I_{\text{Ar}}}, \frac{I_{\text{CF}}}{I_{\text{Ar}}}, \frac{I_{\text{CO}}}{I_{\text{Ar}}}, \frac{I_{\text{C}_3}}{I_{\text{Ar}}}, \frac{I_{\text{F}}}{I_{\text{Ar}}}$  for  $\text{CF}_2$ ,  $\text{CF}$ ,  $\text{CO}$ ,  $\text{C}$ ,  $\text{F}$  relative to  $\text{Ar}$  as a function of ICP power, are presented in Fig. 6.14(a) and Fig. 6.15(a) for  $\text{CHF}_3/\text{Ar}/\text{O}_2$  and  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasma, respectively. For  $\text{CHF}_3/\text{Ar}/\text{O}_2$  plasma, we can see that ICP power has insignificant dependence on  $\text{CF}_2$ . But  $\text{CF}$  and  $\text{F}$  keep increasing as ICP power increases.

The absolute number densities of  $\text{CF}_2$  using UV absorption are plotted as a black symbols and the  $\frac{I_{\text{CF}_2}}{I_{\text{Ar}}}$  ratios obtained from optical emission are plotted as red symbols and a line in Fig.6.14(b). Within the scatter of the measurements, there is no apparent dependence of  $\text{CF}_2$  absolute number density on the ICP power.

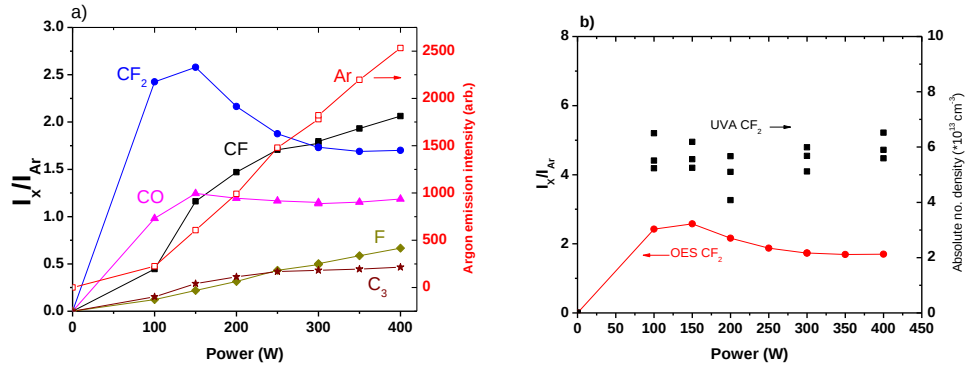


FIG. 6.14. a)  $\frac{I_{\text{CF}_2}}{I_{\text{Ar}}}, \frac{I_{\text{CF}}}{I_{\text{Ar}}}, \frac{I_{\text{CO}}}{I_{\text{Ar}}}, \frac{I_{\text{C}_3}}{I_{\text{Ar}}}, \frac{I_{\text{F}}}{I_{\text{Ar}}}$  for  $\text{CHF}_3/\text{Ar}/\text{O}_2$  plasma. Pressure=20mTorr,  $V_{\text{DC}}=-100\text{V}$  at 18 MHz. Flow rates (sccm) were  $\text{CHF}_3:\text{Ar}:\text{O}_2=10:2:1$ , ICP power variation (0-400W) b) ICP power effect on  $\text{CF}_2$  density in  $\text{CHF}_3/\text{Ar}/\text{O}_2$  plasma using UV absorption and OES. Pressure constant at 20mTorr.

For  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasma (Fig. 6.15a), the number density of  $\text{CF}_2$  and  $\text{CO}$  increase when the ICP power increase from 100W to 200W and sharply decrease after 200W. The number density of  $\text{CF}$  and  $\text{F}$  keep increasing with ICP power. At higher ICP power,  $e^-$

density increases and dissociation of  $\text{CF}_2$  generates CF and F ( $\text{CF}_2 + e^- \rightarrow \text{CF} + \text{F} + e^-$ ), explaining the sharp decrease of  $\text{CF}_2$  and increase of CF. Furthermore, CF undergoes electron impact reactions at higher ICP power that leads to increases in C and F number densities. C emission is not observed however,  $\text{C}_3$  emission is detected. CO could be dissociating to C and O at higher ICP power.

The absolute number density of  $\text{CF}_2$  using UV absorption and relative density using OES is plotted in Fig. 6.15(b). From 100W to 200W, the absolute number density of  $\text{CF}_2$  using UV absorption increase to  $3.2 \times 10^{14} \text{ cm}^{-3}$  at 200W. As ICP power becomes double from 200W to 400W,  $\text{CF}_2$  number density drops by a factor of  $\sim 1.5$ . The relative number density of  $\text{CF}_2$  using OES has a similar trend to UV absorption.

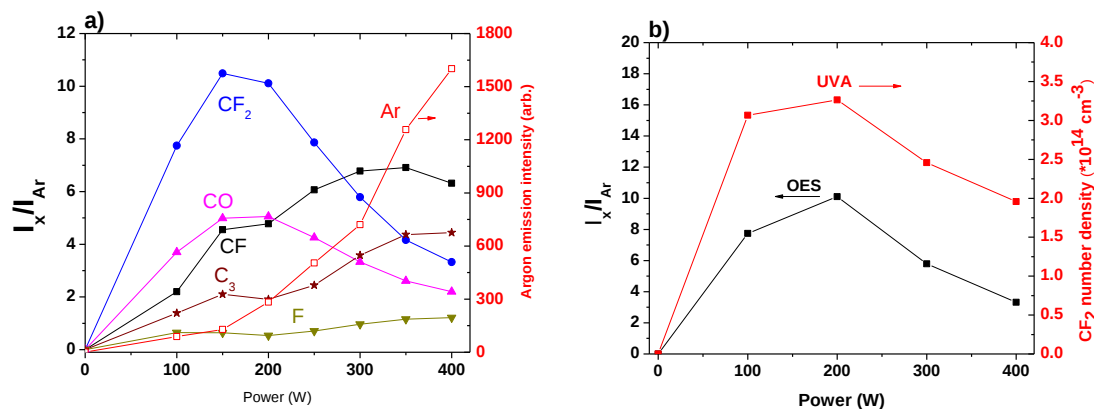


FIG. 6.15. a)  $\frac{I_{\text{CF}_2}}{I_{\text{Ar}}}, \frac{I_{\text{CF}}}{I_{\text{Ar}}}, \frac{I_{\text{CO}}}{I_{\text{Ar}}}, \frac{I_{\text{C}_3}}{I_{\text{Ar}}}, \frac{I_{\text{F}}}{I_{\text{Ar}}}$  for  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasma. Pressure=20mTorr,  $V_{\text{DC}}=-100\text{V}$  at 18 MHz. Flow rates (sccm) were  $\text{C}_4\text{F}_8:\text{Ar}:\text{O}_2=10:2:1$ , ICP power variation (0-400W) at 13.56MHz. b) ICP power effect on  $\text{CF}_2$  density in  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasma using UV absorption and OES.

Clearly, it can be seen from Fig. 6.14 (b) and 6.15 (b) that  $\text{CF}_2$  number density is independent of source power in  $\text{CHF}_3$  plasma, but decays at higher power in  $\text{C}_4\text{F}_8$  plasmas. These trends are similar to the trends of  $\text{CF}_2$  radical densities measured using infrared diode

laser absorption spectroscopy as a function of microwave power by Miyota, et al.,<sup>219</sup>. The authors observed that CF<sub>3</sub> radical was dominant species in CHF<sub>3</sub> plasma and density of CF<sub>3</sub> decreased with increase in microwave power. On the other side, CF<sub>2</sub> was found to be dominant species in C<sub>4</sub>F<sub>8</sub> plasma. In the present study, CF<sub>3</sub> can't be observed using OES and UVA. At higher ICP power in CHF<sub>3</sub> plasma, it's possible that CF<sub>3</sub> undergoes more electron impact dissociation to form CF<sub>2</sub> and F ( $\text{CF}_3 + \text{e}^- \rightarrow \text{CF}_2 + \text{F} + \text{e}^-$ ) which should have increased the CF<sub>2</sub> density with increase in ICP power. However, at the same time, CF<sub>2</sub> is dissociating as well to form CF and F. Hence, the net density of CF<sub>2</sub> remain independent of ICP power and CF keeps increasing with increasing ICP power.

## ii. *Pressure dependence*

For CHF<sub>3</sub>/Ar/O<sub>2</sub> plasmas, emission intensity of Ar (750.4 nm) is plotted as a function of pressure in Fig. 6.16(a). Argon intensity decreases as pressure increases. The measured emission intensity ratios  $\frac{I_{\text{CF}_2}}{I_{\text{Ar}}}, \frac{I_{\text{CF}}}{I_{\text{Ar}}}, \frac{I_{\text{CO}}}{I_{\text{Ar}}}, \frac{I_{\text{C}_3}}{I_{\text{Ar}}}, \frac{I_{\text{F}}}{I_{\text{Ar}}}$ , for CF<sub>2</sub>, CF, CO, C<sub>3</sub>, F relative to Ar, as a function of pressure are presented in Fig. 6.16(a). CF<sub>2</sub>, CO and C<sub>3</sub> relative number densities increase with pressure. As pressure increases from 10mTorr to 20mTorr, CF increases by a factor of ~1.2. Beyond, 20 mTorr, CF relative emission intensity plateau. F decreases continuously with increase in pressure. The absolute number density of CF<sub>2</sub> using UV absorption is plotted as a black line and symbols corresponding to right y-axis, and the  $\frac{I_{\text{CF}_2}}{I_{\text{Ar}}}$  ratio of optical emission spectrum for CF<sub>2</sub> is plotted as a red line and symbols corresponding to left y-axis in Fig. 6.16(b). As pressure increases, both the number density and emission intensity ratio of CF<sub>2</sub> increase.

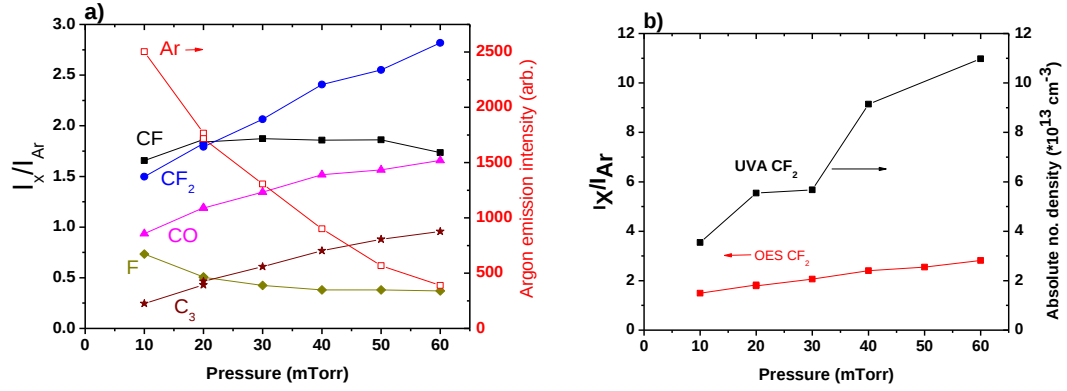


FIG. 6.16. a)  $\frac{I_{CF_2}}{I_{Ar}}, \frac{I_{CF}}{I_{Ar}}, \frac{I_{CO}}{I_{Ar}}, \frac{I_{C_3}}{I_{Ar}}, \frac{I_F}{I_{Ar}}$  for CHF<sub>3</sub>/Ar/O<sub>2</sub> plasma. ICP power=300W at 13.56 MHz, V<sub>DC</sub>= -100V at 18 MHz, flow rates (sccm) were CHF<sub>3</sub>:Ar:O<sub>2</sub>=10:2:1, pressure variation (10mTorr ~ 60mTorr). b) Pressure effect on CF<sub>2</sub> density in CHF<sub>3</sub>/Ar/O<sub>2</sub> plasma using UV absorption and OES.

For C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma, emission intensity of Ar (750.4 nm) and emission intensity ratios  $\frac{I_{CF_2}}{I_{Ar}}, \frac{I_{CF}}{I_{Ar}}, \frac{I_{CO}}{I_{Ar}}, \frac{I_{C_3}}{I_{Ar}}, \frac{I_F}{I_{Ar}}$ , for CF<sub>2</sub>, CF, CO, C<sub>3</sub>, F relative to Ar, as a function of pressure are presented in Fig. 6.17(a). CF<sub>2</sub> and CO continuously increase from 10 mTorr to 30 mTorr and then saturate at higher pressures. CF and C<sub>3</sub> has a sharp decrease as pressure increases, opposite trend to CHF<sub>3</sub>/Ar/O<sub>2</sub> plasma seen in Fig. 6.16 (a).

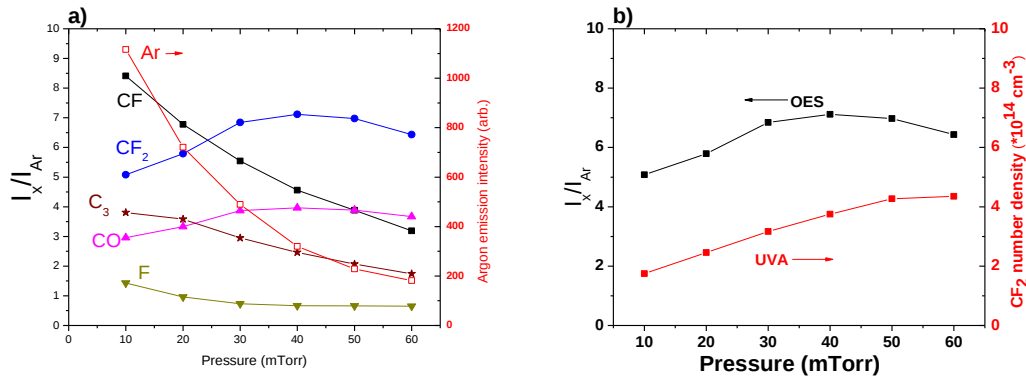


FIG. 6.17. a)  $\frac{I_{CF_2}}{I_{Ar}}, \frac{I_{CF}}{I_{Ar}}, \frac{I_{CO}}{I_{Ar}}, \frac{I_F}{I_{Ar}}$  for C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma. ICP power=300W at 13.56 MHz, V<sub>DC</sub>= -100V at 18 MHz, flow rates (sccm) were C<sub>4</sub>F<sub>8</sub>: Ar: O<sub>2</sub>=10:2:1, pressure variation (10mTorr ~ 60mTorr). b) pressure effect on CF<sub>2</sub> density in C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma using UV absorption and OES.

The absolute number density of  $\text{CF}_2$  using UV absorption (red symbol line) and relative density using OES (black symbol line) is plotted in Fig. 6.17(b). From 10mTorr to 50mTorr, the absolute number density of  $\text{CF}_2$  using UV absorption increase by a factor of  $\sim 2$ . The relative number density of  $\text{CF}_2$  using OES has similar trend as UV absorption. Overall,  $\text{CF}_2$  number density is about  $\sim 4$ -5 times higher in  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasma when compared to  $\text{CHF}_3/\text{Ar}/\text{O}_2$  plasma at similar operating conditions.

### ***iii. Gas temperature measurements***

Gas temperatures as a function of ICP power and pressure in  $\text{CHF}_3$  and  $\text{C}_4\text{F}_8$  plasmas were derived from simulating and fitting the  $\text{N}_2$  ( $\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$ ) emission band at 337.1 nm. A small amount (10%) of  $\text{N}_2$  was added to the feed gas. Emission spectra with and without added  $\text{N}_2$  were recorded using ocean optics spectrometer. The spectral resolution (full width at half maximum) was 4.5 Å. Light was collected 2 cm above the wafer.

$\text{N}_2$  emission bands in the UV region overlap strong emission from  $\text{CF}_2$  and perhaps other species, making it difficult to derive rotational temperatures from the fitting process. To “null-out” the unwanted emissions, spectra from plasmas without  $\text{N}_2$  were multiplied by a correction factor close to unity and then subtracted from spectra with added  $\text{N}_2$ . The correction factor is needed due to small changes in the intensities of the  $\text{CF}_2$  emissions caused by the presence of  $\text{N}_2$ . Fig. 6.18 shows one case where correction factors were varied from 0.93 to 1.2, with the best zeroing-out occurring for a factor of 1.14. The baseline of this spectrum (magenta symbols in Fig. 6.18) was reset to zero and used to

obtain the best fit spectrum and obtain the rotational temperature, as presented in Fig. 6.19(a).

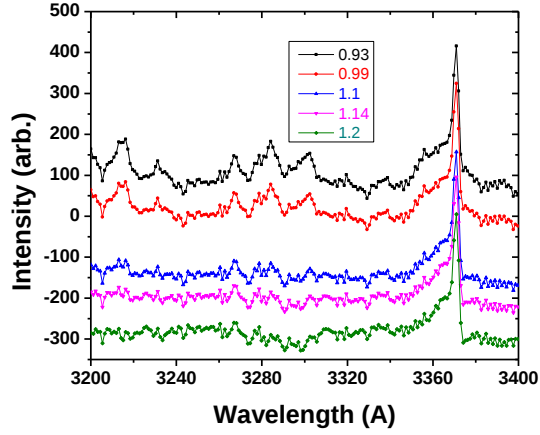


FIG. 6.18. Experimental (black) and simulated spectra (blue) for  $C_4F_8/Ar/O_2$  plasma. Flow rates were  $C_4F_8/N_2/O_2$  : 10/1/1 sccm, 20mTorr, 300W ICP power. The legend refers to the correction factors that the spectrum without  $N_2$  were multiplied by before subtracting from the spectrum with  $N_2$ .

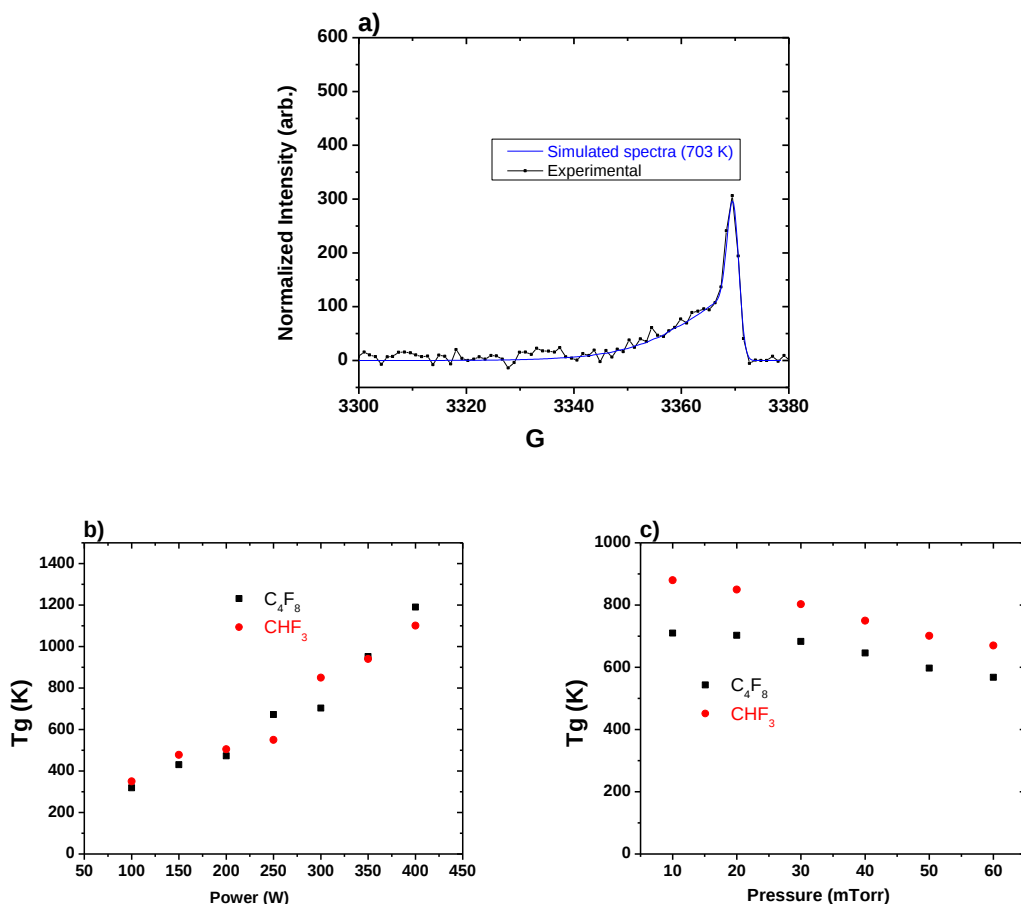


FIG. 6.19. a) Experimental (black) and simulated spectra (blue) for C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma. C<sub>4</sub>F<sub>8</sub>/N<sub>2</sub>/O<sub>2</sub>: 10/1/1 sccm, 20mTorr, 300W ICP power. b) T<sub>g</sub> vs. ICP power for CHF<sub>3</sub>/Ar/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma. 20mTorr constant pressure. c) T<sub>g</sub> vs. pressure for CHF<sub>3</sub>/Ar/O<sub>2</sub> and C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma at a power of 300W. Flow rates were CHF<sub>3</sub> or C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub>: 10/2/1 sccm.

Gas temperature (T<sub>g</sub>) as a function of ICP power is plotted in Fig. 6.18(b). As ICP power increases, gas temperature for CHF<sub>3</sub> and C<sub>4</sub>F<sub>8</sub> plasmas increases linearly. At the lowest ICP power (100W) the gas temperature equals the wall temperature of 300 K. At a constant power of 300 W, Fig. 6.18(c) shows that the gas temperature decreases by ~ 150K as pressure is increased from 10mTorr to 60mTorr.

Using the gas temperatures in Fig. 6.19, CF<sub>2</sub>/Ar and F/Ar emission ratios presented in Figs 6.14 – 6.17 were converted into relative (for CF<sub>2</sub>) and absolute (for F) number

densities. Calculation of absolute F number densities from F/Ar emission ratios was described in chapter 2. For CF<sub>2</sub>, an analogous actinometry expression to obtain relative number densities ( $n_{CF_2}$ ) is

$$n_{CF_2} = b n_{Ar} \frac{I_{CF_2}}{I_{Ar}}, \quad (6.10)$$

where  $I_{CF_2}$  and  $I_{Ar}$  are the emission intensities, of respectively, the 251.77 nm CF<sub>2</sub> peak and 750.4 nm Ar line,  $n_{Ar}$  is the number density of Ar with the plasma on, and  $b$  is a proportionality constant. The Ar number density with the plasma off is approximately

$$n_{Ar}^0 = \frac{f_{Ar}}{f_{Ar}+f_{FC}+f_{O_2}} \frac{P}{RT^0} = \chi_{Ar} \frac{P}{RT^0}, \quad (6.11)$$

where  $f_{Ar}$ ,  $f_{FC}$  and  $f_{O_2}$  are the Ar, fluorocarbon and O<sub>2</sub> flow rates, resulting in an Ar mole fraction of  $\chi_{Ar}$ ,  $P$  is the total pressure,  $T_0 = 300$  K is the wall temperature, and we have assumed that all the gases have the same effective pumping speeds. With the plasma on, the Ar number density is approximately

$$n_{Ar} = n_{Ar}^0 \frac{T^0}{T_g}, \quad (6.12)$$

where we additionally ignore the diluting effect caused by fragmentation of the feed gas into smaller products. (The higher effective pumping speeds of these smaller products such as F, H and HF will partially cancel out the error introduced by this approximation). The final actinometry expression is therefore

$$n_{CF_2} = c \frac{P}{T_g} \chi_{Ar} \frac{I_{CF_2}}{I_{Ar}}, \quad (6.13)$$

where the proportionality constant,  $c$ , is chosen such that the relative CF<sub>2</sub> number density is normalized to absolute CF<sub>2</sub> number density at 100 W and 20 mTorr.

Absolute F number densities are similarly determined from eqn. (2.2), with  $n_{Ar}$  given by eqns. (6.11) and (6.12), and are presented as a function of power and pressure in Figs. 6.20 and 6.21.

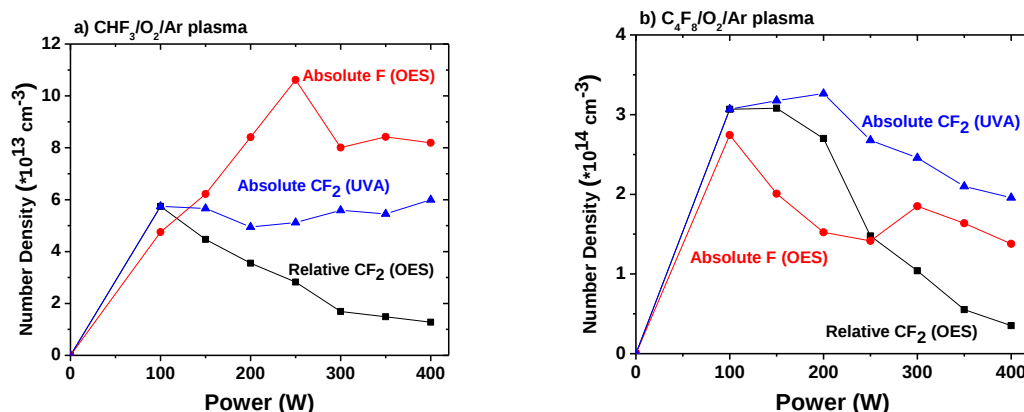


FIG. 6.20. Relative CF<sub>2</sub> number density, absolute F atom density using OES, and absolute CF<sub>2</sub> number density using UVA for a) CHF<sub>3</sub>/Ar/O<sub>2</sub> and b) C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma. Pressure=20mTorr, V<sub>DC</sub>=-100V at 18 MHz. Flow rates (sccm) were C<sub>4</sub>F<sub>8</sub> or CHF<sub>3</sub>:Ar:O<sub>2</sub>=10:2:1, ICP power (0-400W) at 13.56MHz.

Relative CF<sub>2</sub> number density determined from Ar actinometry, and absolute CF<sub>2</sub> number densities as a function of ICP power are plotted in Fig. 6.20 (a) for CHF<sub>3</sub> plasmas and Fig. 6.20 (b) for C<sub>4</sub>F<sub>8</sub> plasmas. In the case of CHF<sub>3</sub>/Ar/O<sub>2</sub> plasmas, relative CF<sub>2</sub> number density decreases as ICP power is increased, while absolute CF<sub>2</sub> number densities obtained from UVA remain nearly constant. Similarly, for C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasmas, relative CF<sub>2</sub> number density decreases sharply by a factor of  $\sim 7.5$ , while the absolute number density drops by a factor of  $\sim 1.6$  as ICP power increases from 200 to 400 W.

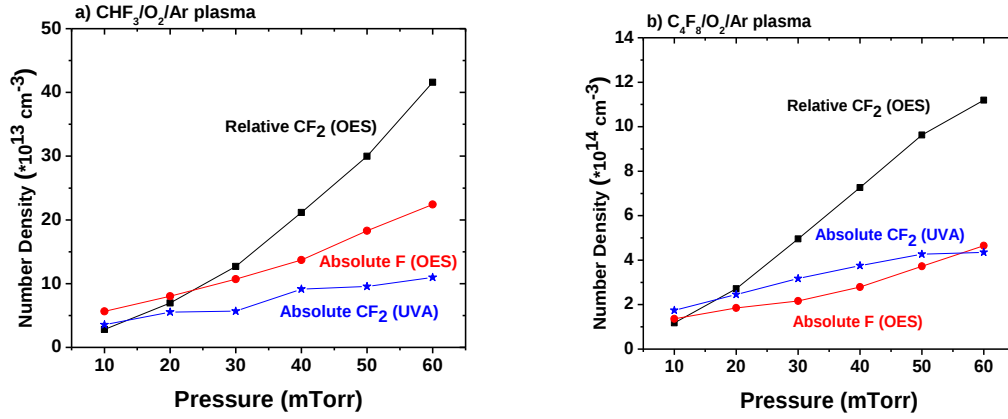


FIG. 6.21. Relative CF<sub>2</sub> number density, absolute F atom density using OES, and absolute CF<sub>2</sub> number density using UVA for a) CHF<sub>3</sub>/Ar/O<sub>2</sub> and b) C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma. ICP power = 300 W. V<sub>DC</sub>=-100V at 18 MHz. Flow rates (sccm) were C<sub>4</sub>F<sub>8</sub> or CHF<sub>3</sub>:Ar:O<sub>2</sub>=10:2:1, Pressure variation (10-60 mTorr).

Relative and absolute CF<sub>2</sub> number densities as a function of pressure are plotted in Fig. 6.21 (a) for CHF<sub>3</sub> plasma and Fig. 6.21 (b) for C<sub>4</sub>F<sub>8</sub> plasma. For CHF<sub>3</sub>/Ar/O<sub>2</sub> plasmas, as pressure is increased from 10mTorr to 60mTorr, relative CF<sub>2</sub> number densities increase by a factor of ~14 and absolute CF<sub>2</sub> number density increases ~4-fold. For C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> plasma, relative CF<sub>2</sub> number density increases by a factor of ~ 10 and absolute number density increases by a factor of ~3.

The constant,  $c$ , in eqn. 6.13 is related to the rate constants  $k_{Ar}$  and  $k_{CF_2}$  for electron impact excitation of Ar and CF<sub>2</sub> emission

$$c \propto \frac{k_{Ar}}{k_{CF_2}}. \quad (6.14)$$

The electron impact excitation cross sections of Ar<sup>220</sup>, and CF<sub>2</sub><sup>221</sup> were integrated with an assumed Maxwellian electron energy distribution to obtain  $k_{Ar}$  and  $k_{CF_2}$ . The ratio  $\frac{k_{Ar}}{k_{CF_2}}$  is plotted as a function of  $T_e$  in Fig. 6.22. To explain the discrepancies in Fig. 6.20 between

relative CF<sub>2</sub> number densities obtained from OES actinometry and absolute CF<sub>2</sub> number densities measured directly by OAS,  $\frac{k_{Ar}}{k_{CF_2}}$  would need to increase by a factor of about 5 (4.7 for CHF<sub>3</sub>/O<sub>2</sub>/Ar plasmas and 5.7 for C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar plasmas) between 100 and 400 W. From Fig. 6.22, this would correspond to  $T_e$  increasing from 2.0 to 3.4, for example. Since  $T_g$  nearly quadruples between 100 and 400 W (Fig. 6.19), corresponding to a fourfold drop in number density, such a rise in  $T_e$  with power is reasonable. Likewise, the error in relative CF<sub>2</sub> number density by OES, compared with the direct measure of CF<sub>2</sub> by OAS (Fig. 6.21) can be explained with the aid of Fig. 6.21 by  $T_e$  dropping as pressure increased from 60 to 10 mTorr (e.g., by ~3-fold if  $T_e$  decreases from 3.0 eV at 10 mTorr to 2.1 eV at 60 mTorr, a reasonable possibility).

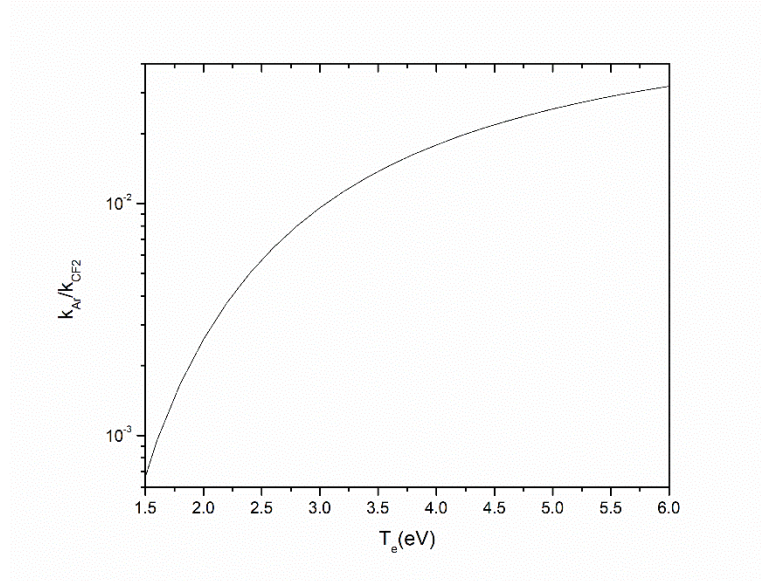


FIG. 6.22. The ratio  $\frac{k_{Ar}}{k_{CF_2}}$  as a function of  $T_e$ .

Finally, the F-content of the feed gases CHF<sub>3</sub> and C<sub>4</sub>F<sub>8</sub> is compared with summation of absolute F number density (OES) and twice the absolute number density of CF<sub>2</sub> (UVA). F-content in the feed gas and absolute F atom densities contained in F and CF<sub>2</sub> (i.e.,  $n_F +$

$2n_{CF_2}$ ) as a function of ICP power are plotted in Fig. 6.23(a) for  $CHF_3/Ar/O_2$  plasmas and Fig. 6.23(b) for  $C_4F_8/Ar/O_2$  plasmas. The fluorine content in the feed gases, also plotted in Fig. 6.23, is simply assumed to drop inversely with the gas temperatures given in Fig. 6.19(a). For  $CHF_3/Ar/O_2$  plasmas,  $n_F + 2n_{CF_2}$  increases by about 25% as power increases from 100 to 400 W, indicating that the increasing production of F and  $CF_2$  by dissociation of the feed fluorocarbon gas is balanced by the reduction in number density at constant pressure, due to gas heating and electron impact dissociation of  $CF_2$ . For  $C_4F_8$  plasmas,  $n_F + 2n_{CF_2}$  decreases by 40% between 100 and 400W, similarly ascribed to gas heating and electron impact dissociation of  $CF_2$ . For both  $CHF_3$  and  $C_4F_8$  fluorocarbon feed gases, roughly half of the fluorine content is accounted for by F and  $CF_2$  at 400W. The remaining F being present as  $CF_3$ , CF and HF (for  $CHF_3$ ).

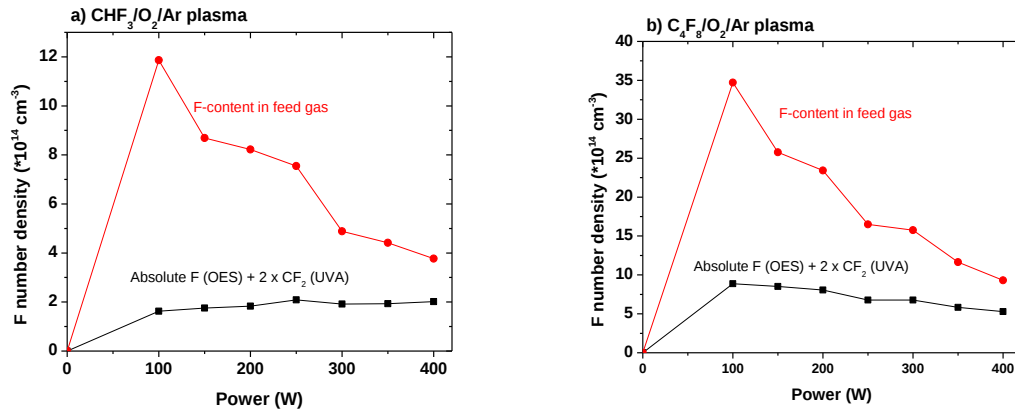


FIG. 6.23. Comparisons of F-content in feed gas and absolute F atom number densities in a)  $CHF_3/Ar/O_2$  and b)  $C_4F_8/Ar/O_2$  plasma. Pressure=20mTorr,  $V_{DC}$ =-100V at 18 MHz. Flow rates (sccm) were  $C_4F_8$  or  $CHF_3:Ar:O_2=10:2:1$ , ICP power variation (0-400W) at 13.56MHz.

F-content in the feed gas and  $n_F + 2n_{CF_2}$  are plotted as a function of pressure in Figs. 6.24(a) and Fig. 6.24(b) for  $CHF_3$  and  $C_4F_8$ -containing plasmas, respectively. For both fluorocarbon feed gases, the amount of fluorine in the sum of F and  $CF_2$  number density is

about 60% at 10 mTorr, decreasing to ~25% at 60 mTorr. This is likely due to a decrease in  $T_e$  as a function of increasing pressure, causing a drop in the rate constant for electron impact dissociation of the feed gas, and larger fragments including  $\text{CHF}_2$  and  $\text{CF}_3$  (for  $\text{CHF}_3$  feed gas) and  $\text{C}_2\text{F}_4$  (for  $\text{C}_4\text{F}_8$  feed gas).

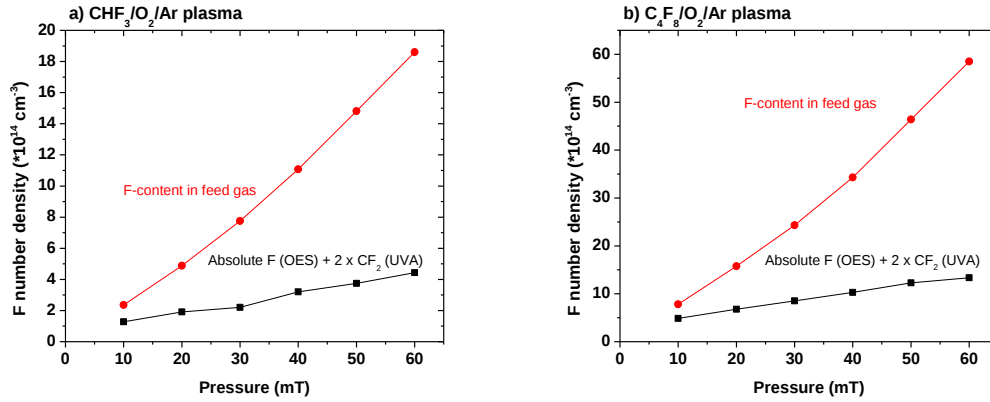


FIG. 6.24. Comparisons of F-content in feed gas and absolute F atom number densities in a)  $\text{CHF}_3/\text{Ar}/\text{O}_2$  and b)  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasma. ICP power = 300 W.  $V_{\text{DC}} = -100\text{V}$  at 18 MHz. Flow rates (sccm) were  $\text{C}_4\text{F}_8$  or  $\text{CHF}_3:\text{Ar}:\text{O}_2 = 10:2:1$ , Pressure variation (10-60 mTorr).

### 6.3 Future work

Section 6.2.1 showed time-resolved number densities of Si, SiCl and SiCl<sub>2</sub> in a pulsed plasma. A full Cl or Si mass balance cannot be achieved due to SiC<sub>3</sub> and SiCl<sub>4</sub> being unavailable for probing by UV absorption. To add these species to the analysis, VUV absorption and mass spectrometry would have to be added. The complexity of adding these analysis techniques in the current reactor configuration would be challenging but doable.

The decay of CF<sub>2</sub> in a C<sub>4</sub>F<sub>8</sub> plasma is expected to be very slow and will require many milliseconds before it decays substantially. The optical chopper at frequencies below 100 Hz starts to become unstable as the frequency oscillations become larger relative to the overall pulse frequency. To study the decay of CF and CF<sub>2</sub> in a pulsed C<sub>4</sub>F<sub>8</sub> plasma, it will be necessary to switch from the CCD/chopper setup to an intensified charge-coupled device (ICCD). An ICCD will have stable fast time-resolution for accurate absorption below 100 Hz, allowing for the decay of CF and CF<sub>2</sub> in C<sub>4</sub>F<sub>8</sub> to be detectable. Since the decay time for CF<sub>2</sub> in particular could approach the gas residence time of ~0.1 s in these experiments, it may be necessary to carry out these studies at lower flow rates.

## Chapter 7- Summary

In this dissertation, five independent chapters on fluorine and chlorine-containing gas chemistries were presented. In chapter 2, we investigated etching of SiO<sub>2</sub>-masked silicon in mixed NF<sub>3</sub>/SF<sub>6</sub> plasmas. It has been known for many years that plasmas generated in SF<sub>6</sub> etch Si much faster than those in any other fluorine-containing gas. This study showed that the chemical reaction probability of F atoms etching Si was greatly enhanced by adsorbed sulfur, either in mixtures of NF<sub>3</sub>/SF<sub>6</sub>, or by depositing S on Si and then etching with a sulfur-free plasma. Mechanisms for this catalytic enhancement were described, as well as for the smoothening effect that was found in the presence of sulfur.

In chapter 3, an experimental technique glow discharge-optical emission spectroscopy (GD-OES) was developed for *in-situ* characterization of chamber wall surfaces exposed to the plasma. A small coupon piece of aluminum covered with yttria, a common chamber wall coating in reactors used in plasma etching, was mounted on an rf-biased electrode and inserted into an opening in the reactor wall. Silicon or SiO<sub>2</sub> substrates on a separately rf-biased electrode were etched in an inductively-coupled plasma (ICP) of Cl<sub>2</sub>/Ar or C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>, respectively. Pulsed bias was applied to sputter the surface of the coupon piece in the wall at the edge of the ICP, either during etching in a halogen (Cl<sub>2</sub>)-containing plasma, or after etching in an Ar ICP. The difference in optical emission intensity between the coupon bias on and off condition was used to determine what species were present on the surface. An analytical method similar to sputter depth profiling in XPS, AES or SIMS was developed to extract atomic concentration vs. depth profiles from GD-OES sputtering in Ar plasmas after etching in Cl<sub>2</sub>/O<sub>2</sub>/Ar plasmas. Sensitivity factors were

obtained for sputtered species Si, Cl, O and Y. A sample depth profile was obtained for the film deposited on Ytria during Si etching. This technique can be extended to determine sputtering threshold of widely used yttrium containing chamber wall coating materials. This technique has the potential to observe various Y peaks at higher exposure time and large spectrometer slit width while keeping the minimum coupon bias. Measured values of sputtering threshold can help to determine the durability of these coating materials in industrial chambers.

In chapter 4, fully modulated pulsed power chlorine plasma diagnostics were performed using OES. A combination of power modulation experiments and simulations was used to measure Cl heterogeneous reaction coefficients,  $\gamma_{Cl}$ , on plasma-conditioned yttria walls during Si etching. Time-resolved OES with actinometry was carried out to record absolute Cl number densities,  $n_{Cl}$ , during the powered portion of the modulation period. A simple global model was used to predict the periodic modulation in  $n_{Cl}$  for comparison with measurements.

In chapter 5, we extended our studies to pulsed plasma with partial depth modulation. Time resolved OES, broadband emission detected with a photomultiplier tube (PMT), Langmuir probe (LP), and directional couplers were used to study transient behavior. A surprising transient effect was seen in power modulated inductively coupled  $Cl_2$  plasmas. During the high to low power transition at least two periodic steady-state conditions were seen: a mode in which ion and electron densities drop commensurate with the drop in power and a mode in which the electron and ion density drops rapidly during the power transition before recovering after a significant period of time. By considering absorbed power and power losses, unstable conditions can occur when transitioning to low power, depending

on what operating conditions and matching conditions were chosen. This type of instability could hamper the use of power modulated plasmas in the semiconductor processing industry unless careful consideration is taken to finding optimal matching conditions.

In chapter 6, we investigated  $\text{Cl}_2$ ,  $\text{CF}_4$ , and  $\text{C}_4\text{F}_8$  plasmas using OES and UV absorption. Optical emission spectroscopy using a chopper wheel was employed to study the time dependent behavior of Si, SiCl, SiCl<sub>2</sub>, CF and CF<sub>2</sub>. Additionally, UV absorption spectroscopy was used to measure number densities of Si, SiCl, CF and CF<sub>2</sub> during fully modulated pulsed power operation. The effects of pulsed power on the number densities of neutral and charged species were determined in  $\text{C}_4\text{F}_8$  plasma for various pulsing conditions. Further, we examined the effects of pressure and power on CF, CF<sub>2</sub>, CO, C<sub>3</sub>, F in  $\text{CHF}_3/\text{Ar}/\text{O}_2$  and  $\text{C}_4\text{F}_8/\text{Ar}/\text{O}_2$  plasmas.

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