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Controlling VUV photon fluxes in pulsed inductively coupled Ar/Cl₂ plasmas and potential applications in plasma etching

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Abstract

UV/VUV photon fluxes in plasma materials processing have a variety of effects ranging from producing damage to stimulating synergistic reactions. Although in plasma etching processes, the rate and quality of the feature are typically controlled by the characteristics of the ion flux, to truly optimize these ion and photon driven processes, it is desirable to control the relative fluxes of ions and photons to the wafer. In prior works, it was determined that the ratio of VUV photon to ion fluxes to the substrate in low pressure inductively coupled plasmas (ICPs) sustained in rare gases can be controlled by combinations of pressure and pulse power, while the spectrum of these VUV photons can be tuned by adding additional rare gases to the plasma. In this work, VUV photon and ion fluxes are computationally investigated for Ar/Cl₂ ICPs as used in etching of silicon. We found that while the overall ratio of VUV photon flux to ion flux are controlled by pressure and pulse power, by varying the fraction of Cl_2 in the mixture, both the ratio of VUV to ion fluxes and the spectrum of VUV photons can be tuned. It was also found that the intensity of VUV emission from $Cl(3p^44s)$ can be independently tuned by controlling wall surface conditions. With this ability to control ratios of ion to photon fluxes, photon stimulated processes, as observed in halogen etching of Si, can be tuned to optimize the shape of the etched features.

Keywords: VUV radiation transport, pulsed plasmas, inductively coupled plasmas, plasma etching, kinetic transport, modeling

(Some figures may appear in colour only in the online journal)

1. Introduction

Low pressure, chemically reactive inductively coupled plasmas (ICPs) are a base technology used in the microelectronics industry for material processing [1–10]. Such processes for etching typically involve some form of chemically enhanced sputtering, in which chemically passivated surfaces are etched by energetic fluxes from the bulk plasma. These stimulating particles are typically ions (and in some limited cases electrons) whose energy distributions are controlled by biases applied to the substrate. These processes for radicals,

ions and electrons have been extensively studied with the goal of optimizing the etch processes. Meanwhile, photon fluxes in the ultraviolet (UV) and vacuum ultraviolet (VUV) range of wavelengths are ubiquitous in low pressure plasmas. These UV/VUV fluxes have been used to advantage in many applications, ranging from sterilization of surfaces [11] to curing of polymers [12, 13]. At the other extreme, the UV/VUV fluxes are known to be damaging to sensitive materials used in semiconductor processing such as low-k dielectrics [14, 15]. UV/VUV fluxes are now recognized as being important in synergistically stimulating processes during plasma etching of silicon under conditions once thought to be dominated by ion fluxes [16].

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Previous experimental investigations have focused on measuring VUV emission from reactive ICPs, particularly those sustained in halogen-containing mixtures including Cl₂, BCl₃, and fluorocarbon gases. Using an on-wafer monitoring technique, Jinnai et al measured VUV emission (70–140 nm) of 1.5×10^{15} $\text{cm}^{-2} \text{ s}^{-1}$ ($\approx 3 \text{ mW cm}^{-2}$) from an ICP sustained in 5 mTorr of C_4F_8 at 1000 W [17]. Similar results were obtained by Woodworth et al. For a 10 mTorr ICP at 200 W, they observed VUV emission from C₄F₈, CHF₃, C₂F₆ plasmas of 8.6×10^{14} cm⁻² s⁻¹, $1.1 \times 10^{15} \,\text{cm}^{-2} \,\text{s}^{-1}$ and $3.0 \times 10^{15} \,\text{cm}^{-2} \,\text{s}^{-1}$ respectively, which was dominated by resonance lines of neutral C and F. With dilution by Ar, the total VUV flux increased by an order of magnitude, from $1.1 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ to $1.2 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1} (\approx 20)$ mW cm⁻²). The increase in VUV flux was principally due to the two argon resonance lines at 104.8 and 106.7 nm [18]. Woodworth et al also measured VUV fluxes in Cl₂/BCl₃ plasmas for metal etching. In ICPs sustained in 10 mTorr mixtures of Cl₂/BCl₃ with 1100 W (and 200 W substrate bias), the total VUV intensity from 95–250 nm exceeded 5×10^{14} cm⁻² s⁻¹ (≈ 0.7 mW cm⁻²) at the surface of the substrate. Neutral Cl emission at 138-139nm was the principal resonance line in the spectrum [19].

VUV photons in reactive plasmas initiate a variety of processes. Photon-induced damage during semiconductor processing has long been recognized, with recent attention being on damage of ultra-low dielectric constant (low-*k*) porous SiOCH films [14, 15]. Bond-breaking energy delivered by VUV photons is capable of penetrating up to 100nm beneath the surface, damaging the porous structure which may both densify the film and produce free radical sites. The densification and subsequent water uptake by the free radical sites both increase the dielectric constant of the film. Synergistic effects of ion and VUV fluxes to 193 nm photoresists have also been observed, changing the response of surface roughness to temperature and electron fluxes [20, 21].

Photon stimulated or assisted plasma etching was recently observed in experiments by Shin *et al* who found that VUV photons from Cl and Br containing ICPs can produce etching on silicon surfaces even when the energies of the incident ion fluxes are below the threshold for ion stimulated etching [16, 22]. Fukasawa *et al* also observed enhanced etch rates of SiN_x:H films with the simultaneous irradiation of VUV photons and radical fluxes in CF₄/O₂ plasma compared to that produced in the absence of the VUV flux [23].

Motivated by these observations, in prior work computational investigations were performed on the means of controlling VUV fluxes from ICPs sustained in rare gases and rare gas mixtures [24]. We found that for ICPs sustained in rare gas mixtures, the absolute fluxes of VUV photons and relative fluxes of VUV photons to ions can be controlled by combinations of pressure and pulse power formats. The spectra of photon fluxes can also be coarsely tuned by varying the ratio of rare gases in the mixtures. In this work, we report on results from a computational investigation of methods to control VUV photon fluxes and ratios of VUV to ion fluxes from ICPs sustained in Ar/Cl₂ mixtures as a model system representative of conductor plasma etching used in microelectronics fabrication, and how that control can be leveraged to tune etch profiles. ICPs were sustained at low-pressure (tens of mTorr) with both continuous wave (cw) and pulsed excitation. Radiation from

atomic resonant states of Ar and Cl are addressed as these species dominate VUV emission below 300 nm in ICPs containing Ar and Cl₂ [19]. This process is further complicated compared to rare gas mixtures by the reactivity of the Cl₂ chemistry that feeds back to the radiation transport. For example, the VUV fluxes from the resonant transition of Cl can be directly correlated with the reaction probability for Cl recombination on the side walls. The goal of this study is to further our understanding of methods to control VUV fluxes in reactive gases and the effect of such control on silicon etching profiles.

We found that the ratio of total VUV photon fluxes to ion fluxes, β , can be controlled by pressure, pulse power and gas mixture ratio in ICPs sustained in Ar/Cl₂ mixtures. For example, β increases with pressure from 0.07 (10 mTorr) to 2.3 (100 mTorr) due to the increased electronegativity of the plasma and more collisional nature of ion transport at high pressure that lengthens the ion residence time. With pulsed power, the electron energy distributions (EEDs) can be tuned such that they are more favorable to produce radiative states during the pulse, and so the β is a sensitive function of duty cycle of the pulse. The ratio of VUV to ion fluxes can also be controlled by gas mixtures. By increasing the fraction of Cl_2 in the gas mixture, β decreases from 0.43 (5% Cl_2) to 0.02 (95% Cl_2). The spectrum of the VUV fluxes (for example, emission from Ar compared to Cl) to first order is controlled by the gas mixture. However, the gas mixture also changes other plasma parameters. Over a range of powers and pressures, the intensity of VUV fluxes from Cl compared to ion fluxes is determined in large part by the surface recombination probability of Cl, and so the choice of wall materials is important to managing VUV fluxes.

Descriptions of the model and reaction mechanisms used in this investigation are in section 2. The plasma dynamics of Ar/Cl_2 ICPs are discussed in section 3. Characterization and control of VUV fluxes and ion fluxes are discussed in section 4. The effects of different ratios of VUV to ion fluxes on etch profiles of Si are demonstrated in section 5. Our concluding remarks are in section 6.

2. Description of the model

This computational investigation was performed using the Hybrid Plasma Equipment Model (HPEM) which is described in detail in [24, 25], and so only a brief description will be provided here. The HPEM is a 2D hydrodynamics model which combines both fluid and kinetic approaches. As a modular simulator, HPEM is designed to address different physical processes in different modules in an iterative manner. Communication between the modules is optimized using a time-slicing technique in which, for steady state solutions, different integration time is spent in different modules with data exchanged between modules. (For time depending calculations, such as for pulsed plasmas, integration times are the same in each module.) In this investigation, the major modules used in the HPEM are the Electromagnetics Module (EMM), the electron Monte Carlo Simulation (eMCS) within the electron energy transport module (EETM), the fluid kinetics module (FKM) and the radiation transport module (RTM).

In the FKM, continuity, momentum and energy equations are integrated to solve for heavy particle densities, fluxes and temperatures. The Sharffeter–Gummel formulation provides fluxes of electrons [26]. The electric potential is obtained by a semi-implicit solution of Poisson's equation. The EMM solves for inductively coupled electromagnetic fields by a frequency domain solution of Maxwell's equation based on the specified operating conditions (power, frequency) with the conductivity being provided by other modules. The inductively coupled electromagnetic field, electrostatic field and particle densities are collected by the eMCS in which the trajectories of electron pseudoparticles are advanced. Electron energy distributions are produced in the eMCS which in combination with particle densities, provide electron impact source functions for use in the FKM.

The geometry of the reactor used in this investigation is cylindrically symmetric and is represented by using a rectilinear 2D mesh having axes of radius (*r*-axis) and height (*z*-axis). The flux of ions to the substrate referred to below is the component of the ion flux that is perpendicular to and intersecting the substrate—the flux parallel to the *z*-axis. The ion flux is given by solution of the momentum equation for each ion species. Since the boundary condition is that all ions are neutralized when striking the substrate, the full magnitude of the ion flux is recorded.

During this process, the fluxes of photons are resolved by the RTM in which radiation transport is addressed using Monte Carlo techniques [27–29]. Photon pseudoparticles are isotropically launched from locations in the plasma weighted by the density of the radiating states, for example, $Ar(1s_4)$ and $Ar(1s_2)$ in the case of argon plasmas. The photon pseudoparticles are advanced in line-of-site trajectories until the pseudoparticles hit a surface, are resonantly absorbed by ground state Ar or are non-resonantly absorbed through, for example, photoionization of excited states. If resonantly absorbed, the quantum of energy represented by the pseudoparticle is then either reradiated assuming partial frequency redistribution [30, 31] or is quenched. By quenching, we mean that the quantum of energy resident in the excited state undergoes a collision (e.g. electron impact ionization or super-elastic relaxation, Penning ionization) prior to that quantum of energy being reradiated as a photon. The lineshape function of the emitted photons is a Voigt profile which combines Doppler, natural and pressure broadening using the local gas temperature and collision frequency.

The fluxes of photon-pseudoparticles are recorded as a function of position in the gas phase and on surfaces. The fluxes in the gas phase are used to produce photoionization sources used in the FKM. The fluxes striking surfaces are used for sources of secondary electrons by photoelectron emission, and also represent the optical output of the plasma. Pseudoparticles representing photons carry a statistical weight, w (s⁻¹). This weight results from *N* photon pseudoparticles being launched from random locations from a computational cell having volume *V* (cm³) and rate of optical emission *R* (cm⁻³ s⁻¹): w = RV/N. All photon pseudoparticles striking a surface cell on the substrate having area *A* (cm²) are summed to provide a total statistical weight of W (s⁻¹). The photon flux to that location is then *W/A* (cm⁻² s⁻¹). A detailed description of RTM can be found in [24].

Although quenching of the radiative quanta between absorption and re-emission is included in the model, it is not a particularly important effect for the conditions of this study. The longest natural radiative lifetime of the states considered is 2.7 μ s for the resonance state $Cl(3p^44s)$. This lifetime implies a collision frequency in excess of 4×10^5 s⁻¹ to produce significant quenching. At the maximum gas pressure of 100 mTorr, a quenching rate coefficient by ground state species of 1.2×10^{-10} cm³ s⁻¹ would be required for significant quenching, a value larger than occurs in this mechanism. With maximum electron and ion densities of 5×10^{11} cm⁻³, the required rate coefficient for significant quenching by charged particles is about 8×10^{-7} cm³ s⁻¹. This exceeds quenching coefficients due to ions by, for example, charge transfer. The sum of the rate coefficients for electron collision quenching of $Cl(3p^44s)$ (dominantly by excitation to higher states) is about 4×10^{-7} cm³ s^{-1} for electron temperatures of 5–6eV. So for the most extreme conditions (high electron density, high electron temperature) there may be some quenching of the $Cl(3p^44s)$ between absorption and re-emission of radiative quanta, but this is not a large effect.

When the plasma properties reach a steady or quasi-steady state, ion trajectories and fluxes from the bulk plasma to surfaces will be computed and recorded by the plasma chemistry Monte Carlo module (PCMCM). In the PCMCM, source functions for those species, as well as electric fields are extracted from the results of the FKM. Pseudoparticles, representing ions, and neutrals are launched at locations weighted by these source functions throughout the plasma volume. The trajectories of the pseudoparticles are then integrated in time using time dependent electric fields interpolated from the results of FKM. The magnitude of fluxes, energy and angle of such pseudoparticles striking surfaces are then recorded.

Evolution of surface features resulting from radical, ion and photon fluxes from the plasma is then predicted by the Monte Carlo feature profile model (MCFPM) using these energy and angular resolved distributions. In the MCFPM, the surface materials are resolved using a 2D rectilinear mesh with an individual material identity assigned to each cell. Pseudoparticles are then launched towards the surface randomly selected from the energy and angular distributions of ions, neutrals and photons. The trajectories of the pseudoparticles are tracked until they hit a surface cell. Surface chemical reactions are then used to determine whether to remove, add or modify the chemical properties of the surface cell, corresponding to etching, deposition or chemical reaction. A detailed description of the MCFPM can be found in [32, 33].

In this paper, we discuss results for ICPs sustained in Ar/Cl₂ gas mixtures. The atomic model for Ar consists of 8 levels, Ar, Ar(1s₅), Ar(1s₄), Ar(1s₃), Ar(1s₂), Ar(4p), Ar(4d) and Ar⁺. Ar(4p) is a lumped excited state that includes Ar(4p, 3d, 5s, 5p). Ar(4d) is a lumped excited state that includes Ar(4d, 6s, Rydberg states). The molecular states Ar₂⁺ and Ar₂⁺ were also included, however their densities are at least 100–1000 times lower than their atomic counterparts. The molecular/atomic model for Cl₂ consists of 9 species, Cl₂, Cl₂(v), Cl(3p⁵), Cl(3p⁴4s), Cl(3p⁴4p), Cl(3p⁴3d), Cl₂⁺, Cl⁺ and Cl⁻. The reaction mechanism for Ar/Cl₂ used in this investigation is listed in table 1. The table includes only reactions for the chlorine species and between the chlorine and argon

Table 1. Reaction mechanism for Ar/Cl_2 plasmas.					
Species					
Ar	$Ar(1s_5)$	$Ar(1s_4)$	Ar(1 <i>s</i> ₃)	$\operatorname{Ar}(1s_2)$	
$\operatorname{Ar}(4p)^{\mathbf{a}}$	$\operatorname{Ar}(4d)^{\mathbf{b}}$	Ar^+	Ar_2^*	Ar_2^+	
Cl_2	$Cl_2(v)$	Cl	$Cl(3p^44s)$	$Cl(3p^44p)$	$Cl(3p^43d)$
Cl_2^+	Cl^+	Cl^-	е		
$h\nu_{105 \text{ nm}}$	$h\nu_{107~\rm nm}$	$h\nu_{121\mathrm{nm}}$	$h\nu_{139 \text{ nm}}$		

(Reactions involving only Ar species are the same as in [24])

Process	Rate coefficient or cross section ^c	Reference	$-\Delta H ({\rm eV})^{\rm d}$
Photoionization			
$h\nu_{139\mathrm{nm}} + \mathrm{Ar}(1s_5) \rightarrow \mathrm{Ar}^+ + e$	$9.97 imes 10^{-20}{ m cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Ar}(1s_4) \rightarrow \mathrm{Ar}^+ + e$	$9.97 imes 10^{-20}{ m cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Ar}(1s_3) \rightarrow \mathrm{Ar}^+ + e$	$9.97 imes 10^{-20}{ m cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Ar}(1s_2) \rightarrow \mathrm{Ar}^+ + e$	$9.97 imes 10^{-20}{ m cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Ar}(4p) \to \mathrm{Ar}^+ + e$	$1.0 imes 10^{-19}{ m cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Ar}(4d) \to \mathrm{Ar}^+ + e$	$1.0 imes 10^{-19} { m cm}^2$	Est. [48] ^e	
$h\nu_{105 \text{ nm}} + \text{Cl}(3p^44s) \rightarrow \text{Cl}^+ + e$	$9.6 imes 10^{-20}{ m cm}^2$	Est. [48] ^e	
$h\nu_{105 \text{ nm}} + \text{Cl}(3p^44p) \rightarrow \text{Cl}^+ + e$	$8.4 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{105 \text{ nm}} + \text{Cl}(3p^43d) \rightarrow \text{Cl}^+ + e$	$8.7 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{107 \text{ nm}} + \text{Cl}(3p^44s) \rightarrow \text{Cl}^+ + e$	$9.6 imes 10^{-20}{ m cm}^2$	Est. [48] ^e	
$h\nu_{107 \text{ nm}} + \text{Cl}(3p^44p) \rightarrow \text{Cl}^+ + e$	$8.4 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{107 \text{ nm}} + \text{Cl}(3p^43d) \rightarrow \text{Cl}^+ + e$	$8.7 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{121 \text{ nm}} + \text{Cl}(3p^44s) \rightarrow \text{Cl}^+ + e$	$9.0 imes 10^{-20} { m cm}^2$	Est. [48] ^e	
$h\nu_{121 \text{ nm}} + \text{Cl}(3p^44p) \rightarrow \text{Cl}^+ + e$	$9.0 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{121 \text{ nm}} + \text{Cl}(3p^43d) \rightarrow \text{Cl}^+ + e$	$9.0 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Cl}(3p^44s) \rightarrow \mathrm{Cl}^+ + e$	$9.9 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Cl}(3p^44p) \rightarrow \mathrm{Cl}^+ + e$	$9.9 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{139\mathrm{nm}} + \mathrm{Cl}(3p^43d) \rightarrow \mathrm{Cl}^+ + e$	$9.9 imes10^{-20}\mathrm{cm}^2$	Est. [48] ^e	
$h\nu_{105 \text{ nm}} + \text{Cl}_2 \rightarrow \text{Cl}_2^+ + e$	$1.0 imes 10^{-19} { m cm}^2$	Est.	
$h\nu_{105 \text{ nm}} + \text{Cl}_2(\nu) \rightarrow \text{Cl}_2^+ + e$	$1.0 imes10^{-19}\mathrm{cm}^2$	Est.	
$h\nu_{105 \text{ nm}} + \text{Cl} \rightarrow \text{Cl}^+ + e$	$1.0 \times 10^{-19} \mathrm{cm}^2$	Est.	
$h\nu_{107\text{nm}} + \text{Cl}_2 \rightarrow \text{Cl}^+ + e$	$1.0 \times 10^{-19} \mathrm{cm}^2$	Est.	
$h\nu_{107} + Cl_2(v) \rightarrow Cl_2^+ + e$	$1.0 \times 10^{-19} \mathrm{cm}^2$	Est.	
$h\nu_{107} + Cl \rightarrow Cl^+ + \rho$	$1.0 \times 10^{-19} \text{ cm}^2$	Est.	
Radiative transitions			
$Cl(3p^44s) \leftrightarrow Cl$	$3.7 imes 10^5 { m s}^{-1}$	[49] ^f	
Electron impact processes			
$e + \operatorname{Cl}_2 \rightarrow \operatorname{Cl}_2 + e$	g	[50]	h
$e + \mathrm{Cl}_2 \rightarrow \mathrm{Cl} + \mathrm{Cl}^-$	g	[50]	1.2
$e + \operatorname{Cl}_2 \rightarrow \operatorname{Cl}_2(v) + e$	g	[50]	
$e + Cl_2 \rightarrow Cl + Cl + e$	g	[50]	0.8
$e + Cl_2 \rightarrow Cl + Cl + e$	g	[50]	5.8
$e + \operatorname{Cl}_2 \rightarrow \operatorname{Cl}_2^+ + e + e$	g	[50]	
$e + Cl_2(v) \rightarrow Cl_2(v) + e$	g	[50] ⁱ	h
$e + Cl_2(v) \rightarrow Cl + Cl^-$	g	[50] ⁱ	1.2
$e + Cl_2(v) \rightarrow Cl_2 + e$	g	[50] ^j	
$e + Cl_2(v) \rightarrow Cl + Cl + e$	g	[50] ⁱ	0.8
$e + \operatorname{Cl}_2(v) \rightarrow \operatorname{Cl} + \operatorname{Cl} + e$	g	[50] ⁱ	5.7
$e + \operatorname{Cl}_2(v) \rightarrow \operatorname{Cl}_2^+ + e + e$	g	[50] ⁱ	
$e + Cl_{2}^{+} \rightarrow Cl_{2}^{+} + e$	g	[51]	h
$e + Cl \rightarrow Cl + e$	g	[52]	h
$e + Cl \leftrightarrow Cl(3p^44s) + e$	g	[52]	
		[]	

(Continued)

Plasma Sources Sci. Technol. 26 (2017) 024005

Table 1. (Continued)				
Process	Rate coefficient or cross section ^c	Reference	$-\Delta H (\mathrm{eV})^{\mathrm{d}}$	
$\overline{e + \operatorname{Cl} \leftrightarrow \operatorname{Cl}(3p^44p) + e}$	gj	[52]		
$e + \operatorname{Cl} \leftrightarrow \operatorname{Cl}(3p^43d) + e$	g.j	[52]		
$e + \mathrm{Cl} ightarrow \mathrm{Cl}^+ + e + e$	g	[53]		
$e + \mathrm{Cl}^+ ightarrow \mathrm{Cl}^+ + e$	g	[51]	h	
$e + \operatorname{Cl}(3p^44s) \to \operatorname{Cl}(3p^44s) + e$	g	[52]	h	
$e + \operatorname{Cl}(3p^44s) \leftrightarrow \operatorname{Cl}(3p^44p) + e$	g,e	[54] ^j		
$e + \operatorname{Cl}(3p^44s) \leftrightarrow \operatorname{Cl}(3p^43d) + e$	g.	[54] ^j		
$e + \operatorname{Cl}(3p^{+}4s) \rightarrow \operatorname{Cl}^{+} + e + e$	5 2	[53]	h	
$e + \operatorname{Cl}(3p^{+}4p) \rightarrow \operatorname{Cl}(3p^{+}4p) + e$	g,e	[32] [54]İ	i	
$e + \operatorname{Cl}(3p^4qp) \leftrightarrow \operatorname{Cl}(3p^5q) + e$	g	[54]*		
$e + \operatorname{Cl}(3p 4p) \rightarrow \operatorname{Cl}^{*} + e + e$ $e + \operatorname{Cl}(3n^4 3d) \rightarrow \operatorname{Cl}(3n^4 3d) + e$	g	[52]	h	
$e + Cl(3p^{4}3d) \rightarrow Cl^{+} + e + e$	g	[52]		
$e + Cl(3p + 3u) \rightarrow Cl + e + e$	g	Est.		
$e + \mathrm{Cl}_2^+ \rightarrow \mathrm{Cl} + \mathrm{Cl}$	$1.0 imes 10^{-7}T_{ m e}^{-1/2}$	Est. [56, 57]	9.0	
Heavy particles processes				
$\mathrm{Cl}^- + \mathrm{Cl}^+ ightarrow \mathrm{Cl} + \mathrm{Cl}$	$1.0 imes 10^{-7} T_{ m n}^{1/2}$	Est. [58]		
$\mathrm{Cl}^- + \mathrm{Cl}_2^+ \to \mathrm{Cl} + \mathrm{Cl} + \mathrm{Cl}$	$1.0 imes 10^{-7} T_{ m n}^{1/2}$	Est. [58]	7.9	
$Cl + Cl_2(\nu) \leftrightarrow Cl + Cl_2$	$1.0 \times 10^{-10} T_{\rm n}^{1/2}$	Est. ^j	0.07	
$Cl_2+Cl_2(\nu)\leftrightarrow Cl_2+Cl_2$	$1.0 imes 10^{-10} T_{ m n}^{1/2}$	Est. ^j	0.07	
$\mathrm{Cl}^+ + \mathrm{Cl}_2 \mathop{\rightarrow} \mathrm{Cl} + \mathrm{Cl}_2^+$	$5.4 imes 10^{-10} T_{ m n}^{1/2}$	Est. [59]	k	
$\mathrm{Cl}^+ + \mathrm{Cl}_2(\nu) \rightarrow \mathrm{Cl} + \mathrm{Cl}_2^+$	$5.4 \times 10^{-10} T_{\rm n}^{1/2}$	Est. [59]	k	
$Cl^+ + Cl \rightarrow Cl + Cl^+$	$1.0 imes 10^{-9} T_{n}^{1/2}$	Est.	k	
$\mathrm{Cl}_2^+ + \mathrm{Cl}_2 \rightarrow \mathrm{Cl}_2 + \mathrm{Cl}_2^+$	$0.8 imes 10^{-9} T_{ m p}^{1/2}$	Est.	k	
$\operatorname{Cl}_{2}^{+} + \operatorname{Cl}_{2}(v) \to \operatorname{Cl}_{2} + \operatorname{Cl}_{2}^{+}$	$0.8 imes 10^{-9} T_{ m p}^{1/2}$	Est.	j	
$Cl^- + Ar^+ \rightarrow Cl + Ar$	$1.0 imes 10^{-7} T_{ m n}^{1/2}$	Est.	12.4	
$\operatorname{Ar}^* + \operatorname{Cl}_2 \rightarrow \operatorname{Cl}_2^+ + \operatorname{Ar} + e$	$2.2 \times 10^{-10} T_{\rm n}^{1/2}$	[60]		
$\operatorname{Ar}^* + \operatorname{Cl}_2(v) \to \operatorname{Cl}_2^+ + \operatorname{Ar} + e$	$2.2 imes 10^{-10} T_{ m n}^{1/2}$	[60]		
$Ar^* + Cl_2(v) \rightarrow Cl + Cl(3p^44s) + Ar$	$1.1 imes 10^{-10} T_{ m p}^{1/2}$	[60]	$-0.5 \sim 2.7$	
$Ar^* + Cl \rightarrow Cl(3p^44s) + Ar$	$0.7 \times 10^{-11} T_{-}^{1/2}$	Est.	2.7-5.8	
$Ar^+ + Cl_2 \rightarrow Cl_2^+ + Ar$	$0.84 \times 10^{-10} T_{\rm n}^{1/2}$	[59]	4.5	
$Ar^+ + Cl_2 \rightarrow Cl^+ + Cl + Ar$	$0.64 \times 10^{-10} T_{\rm h}^{1/2}$	[59]	-0.2	
$Ar^+ + Cl_2(v) \rightarrow Cl_2^+ + Ar$	$0.84 \times 10^{-10} T_{\rm h}^{1/2}$	[59]	4.6	
$Ar^+ + Cl_2(v) \rightarrow Cl^+ + Cl + Ar$	$0.64 \times 10^{-10} T_{\rm h}^{1/2}$	[59]	-0.1	
$\mathrm{Ar^+} + \mathrm{Cl} \rightarrow \mathrm{Cl^+} + \mathrm{Ar}$	$2.0 \times 10^{-10} T_{\rm e}^{1/2}$	[59]	3.0	
$Cl + Cl + Ar \rightarrow Cl_2 + Ar$	$1.28 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$	Est. [61, 62]	3.2	
$Cl + Cl + Cl \rightarrow Cl_2 + Cl$	$3.84 imes 10^{-32} { m cm}^6 { m s}^{-1}$	Est. [61, 62]	3.2	
$Cl + Cl + Cl_2 \rightarrow Cl_2 + Cl_2$	$2.00 imes 10^{-32} { m cm}^6 { m s}^{-1}$	Est. [61, 62]	3.2	
$Cl + Cl + Cl_2(v) \rightarrow Cl_2 + Cl_2$	$2.00 imes 10^{-32} { m cm}^6 { m s}^{-1}$	Est. [61, 62]	3.3	
$\operatorname{Cl}(3p^44s) + \operatorname{Cl}(3p^44s) \rightarrow \operatorname{Cl}^+ + \operatorname{Cl} + e$	$10 imes 10^{-9} T_{ m n}^{1/2}$	Est.		
$Cl(3p^44s) + Cl(3p^44p) \rightarrow Cl^+ + Cl + e$	$10 imes 10^{-9} T_{r}^{1/2}$	Est.		
$\operatorname{Cl}(3p^44s) + \operatorname{Cl}(3p^43d) \to \operatorname{Cl}^+ + \operatorname{Cl} + e$	$10 \times 10^{-9} T_{\rm p}^{1/2}$	Est.		
$\operatorname{Cl}(3p^44p) + \operatorname{Cl}(3p^44p) \to \operatorname{Cl}^+ + \operatorname{Cl} + e$	$10 \times 10^{-9} T^{1/2}$	Est.		
$\operatorname{Cl}(3p^44p) + \operatorname{Cl}(3p^43d) \rightarrow \operatorname{Cl}^+ + \operatorname{Cl} + e$	$10 \times 10^{-9} T_{1/2}^{1/2}$	Est.		
$\operatorname{Cl}(3p^43d) + \operatorname{Cl}(3p^43d) \rightarrow \operatorname{Cl}^+ + \operatorname{Cl} + e$	$10 \times 10^{-9} T^{1/2}$	Est.		
$Cl(3p^44s) + Cl(3p^44s) \rightarrow Cl_2^+ + e$	$1.0 \times 10^{-10} T^{1/2}$	Est.		
$Cl(3p^44s) + Cl(3p^44n) \rightarrow Cl^+_+ + e$	$1.0 \times 10^{-10} T_{\rm n}^{1/2}$	Est.		
$(c_r, c_r) + c_r (c_r, c_r) + c_r (c_r) + c_r$	1.0 / 10 In			

(Continued)

Table 1. (Continued)			
Process	Rate coefficient or cross section ^c	Reference	$-\Delta H (\mathrm{eV})^{\mathrm{d}}$
$\overline{\operatorname{Cl}(3p^44s) + \operatorname{Cl}(3p^43d) \to \operatorname{Cl}_2^+ + e}$	$1.0 imes 10^{-10}T_{ m n}^{1/2}$	Est.	
$\operatorname{Cl}(3p^44p) + \operatorname{Cl}(3p^44p) \to \operatorname{Cl}_2^+ + e$	$1.0 imes 10^{-10} T_{ m n}^{1/2}$	Est.	
$\operatorname{Cl}(3p^44p) + \operatorname{Cl}(3p^43d) \to \operatorname{Cl}_2^+ + e$	$1.0 \times 10^{-10} T_{\rm n}^{1/2}$	Est.	
$\operatorname{Cl}(3p^43d) + \operatorname{Cl}(3p^43d) \to \operatorname{Cl}_2^+ + e$	$1.0 imes 10^{-10} T_{ m n}^{1/2}$	Est.	

^a Ar(4p) is a lumped state representing Ar(4p, 3d, 5s, 5p).

^b Ar(4d) is a lumped state representing Ar(4d,6s,Rydberg).

^c Values shown in this column are second order rate coefficients having units of cm³ s⁻¹ unless noted. First order rate coefficients have units of s⁻¹. Cross

sections have units of cm². T_c is electron temperature (eV). T_g is gas temperature (K), T_n is normalized gas temperature ($T_g/300$ K).

 $^{d} - \Delta H$ is the contribution to gas heating (eV).

^e Estimated from corresponding Ar photoionization reactions. Cross sections for higher levels were scaled based on energy of the ejected electron.

^f Rate shown is for emission. Absorption is addressed using a radiation trapping factor. (See text.)

^g Rate coefficient obtained from electron energy distribution and cross section from the indicated reference.

^h The rate of heating by elastic collisions is $k_m(3/2)k_B(2m_e/M)(T_e - T_g)$ eV cm³ s⁻¹, for elastic rate coefficient k_m , electron mass m_e , neutral mass M and Boltzmann's constant k_B .

¹Same cross section is the same as for Cl₂ while shifting threshold energy by 0.0689 eV for inelastic processes.

^j Cross section or rate is for forward reaction. Reverse cross section or rate obtained by detailed balance.

^k The rate of heating exchange of energy between the neutral and ionized reaction partners.

species. The reaction mechanism for argon only is the same as in [24]. The two resonance transitions of Ar, $Ar(1s_4) \rightarrow Ar$ $(104.8 \text{ nm}), \text{Ar}(1s_2) \rightarrow \text{Ar}(106.7 \text{ nm})$; the resonance transition of Cl, $Cl(3s^44s) \rightarrow Cl(3p^5)$ at 139 nm; and excimer emission from Ar_2^* at 121 nm are tracked in the RTM. The secondary emission coefficient for electrons on the substrate by ions was estimated to be 0.15 and is 0.05 on other surfaces based on measurements by Bohm and Perrin [34]. For excited states, the secondary emission probability was 0.03 on the substrate and 0.01 on other surfaces. For VUV photons, the secondary emission probability was 0.01 on all surfaces. The Eley-Rideal mechanism is used for Cl surface recombination which depends on the surface site density of adsorbed Cl atoms. This value is determined by a sequence of reactions including chlorination, and photon and ion induced Cl desorption. The resulting average recombination probability for incidence Cl atoms is approximately 0.15.

3. Plasma dynamics in Ar/Cl₂ ICP

The simplified ICP reactor geometry used in this investigation is schematically shown in figure 1. The reactor is intended to be a generic ICP to focus on the study of ion and VUV fluxes scaling without necessarily addressing the details of a specific industrial tool. The cylindrically symmetric reactor is 22.5 cm in diameter with a plasma region of 12 cm in height. ICP power is coupled into plasma by a 3-turn planar antenna from the top through a dielectric window. We assumed purely inductive coupling without a capacitive component from the coil voltage. Gas is injected from an annular inlet beneath the dielectric window and pumped out through an annular exhaust port at the bottom. A substrate is at the bottom of the plasma region, over which ion and VUV fluxes are averaged. The conditions of the base case are Ar/Cl₂ = 80/20 at 20 mTorr with 200 sccm gas flow with the plasma sustained by 150 W ICP power at 10 MHz.

In the steady state for the base case, a diffusive plasma is formed with a peak electron density of 1.4×10^{11} cm⁻³ at



Figure 1. Schematic of the inductively coupled plasma reactor used in the model.

the center of the reactor, as shown in figures 2 and 3. The maximum electron temperature is 2.8 eV beneath the coil and gradually decreases to 2.0 eV near the substrate. The majority of positive ions are Cl_2^+ and Cl^+ , with maximum densities of 1.1×10^{11} cm⁻³ and 0.8×10^{11} respectively. The density of Ar⁺ is over an order of magnitude lower, due to its higher threshold energy for ionization (16 eV) compared to Cl_2 and Cl (11.5 and 13 eV) and loss through charge exchange processes to Cl_2 and Cl. Due to their lower mobilities, the spatial distributions of the positive ions are skewed towards the electromagnetic skin depth centered beneath the coil where most of the power is deposited. An exception is Cl_2^+ , whose spatial distribution is relatively uniform as a function of height at the edge of skin depth. This structure results from Cl_2^+



Figure 2. Time averaged plasma properties for base case conditions $(Ar/Cl_2 = 80/20, 20 \text{ mTorr}, 200 \text{ sccm}, 10 \text{ MHz}, 150 \text{ W cw})$. (a) Electron temperature, (b) gas temperature, (c) Ar^+ density, (d) Cl^+ density, (e) Cl_2^+ density, and (f) electron density. The densities are on log-scales of 2 decades.

having the lowest ionization potential among the ions, a condition that makes it the terminal species for charge exchange reactions. Ar⁺ and Cl⁺ quickly charge exchange to form Cl₂⁺, after which Cl₂⁺ undergoes dominantly diffusive transport. The density of Cl⁻, reaches up to 9×10^{10} cm⁻³, comparable to the electron density.

The densities of metastable and resonant states of both Ar and Cl follow the same spatial distributions as for the ions. In spite of superelastic collisions and heavy particle quenching



Figure 3. Time averaged plasma properties for base case conditions $(Ar/Cl_2 = 80/20, 20 \text{ mTorr}, 200 \text{ sccm}, 10 \text{ MHz}, 150 \text{ W cw})$. (a) Random VUV fluxes for 106.7 nm, 104.8 nm and 139 nm. (b) Densities of Cl(4s), resonant Ar(1s_4) and metastable Ar(1s_5). The densities and fluxes are on log-scales of 2 decades.

reactions, the effective lifetime of the metastable states are still long, resulting in the peak densities of the metastable states being an order of magnitude higher than the corresponding radiative states (which share the same profile). For example, the density of the metastable state $Ar(1s_5)$ is 3×10^{10} cm⁻³ while that of the resonant state $Ar(1s_4)$ is 5×10^9 cm⁻³. The Cl metastable state $Cl(3p^44p)$ and resonant state $Cl(3p^44s)$ have densities of 1.7×10^{11} cm⁻³ and 5.5×10^9 cm⁻³ respectively.

Transport of VUV photons at 104.8 (radiating state Ar(1s₂)), 106.7 (Ar(1s₄)) and 139 nm (Cl($3p^44s$)) are addressed in the simulation. As shown in figure 3, the random flux of 106.7 nm photons has a maximum value of 1×10^{17} cm⁻² s^{-1} (≈ 0.2 W cm⁻²) which is 4 times and 40 times larger than for 104.8 and 139 nm photons. Those random fluxes inside the plasma are magnified by the re-circulation of photons as a result of radiation trapping and are orders of magnitude higher than the fluxes observed from outside the plasma or reaching the substrate. The collisional coupling between the metastable state $Ar(1s_5)$ and radiative state $Ar(1s_4)$ is stronger than that between $Ar(1s_3)$ and $Ar(1s_2)$, a condition that maintains the $Ar(1s_4)$ density an order of magnitude higher than $Ar(1s_2)$. Since both of the resonance lines of Ar are absorbed by the ground state of the feedstock gas Ar that has a high density throughout the reactor, the radiation trapping factors are large, 216 for the 104.8 nm transition, and 368 for the 106.7 nm transition. However, the resonant line of Cl is absorbed by a dissociation product which intrinsically has a lower density and is less uniformly distributed. The radiation trapping factor for 139nm is smaller, 10, and so its circulating intensity is smaller.

Fluxes of ions and VUV photons were collected and averaged over the substrate. The total ion flux reaching the substrate is 4.5×10^{15} cm⁻² s⁻¹ for the base case. The majority of the ions reaching the substrate are Cl_2^+ , $\approx 77\%$ of the total flux, with Cl^+ constituting 21% and Ar^+ being about 2% of the flux. Charge exchange reactions favor transfer of Cl⁺ and Ar⁺ to Cl_2^+ . Production of the Ar⁺ and Cl⁺ takes place primarily in the skin depth of the electromagnetic wave from the coil, after which both species charge exchange along the diffusion length from the skin depth to the substrate. On the other hand, the largest portion of the VUV flux onto the substrate results from Ar emission. The total VUV photon flux reaching the substrate is $6.2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ (1.14 mW cm⁻²) of which 106.7 nm (Ar($1s_4$)) and 104.8 nm (Ar($1s_2$)) photons constitute 90% of the spectra, with fluxes of 3.7×10^{14} cm⁻² s⁻¹ and 1.9×10^{14} cm⁻² s⁻¹ respectively.

4. Controlling ion and photon fluxes in Ar/Cl₂ ICPs

4.1. Photon and ion fluxes versus pressure

The scaling of ion and VUV fluxes to the substrate was investigated as a function of pressure from 10 to 100 mTorr. To maintain a constant residence time for the injected gases, the flow rate was scaled with pressure. All other conditions are the same as for the base case. Reactor averaged plasma properties as a function of pressure are shown in figure 4, and VUV photon and ion fluxes to the substrate are shown in figure 5. (The symbols in these and following figures are the actual results from the simulations. The lines are polynomial or exponential fits through the symbols.) Representative lineshape functions and radiation trapping factors as a function of pressure are shown in figure 6. With a constant power of 150 W, the electron and total positive ion densities monotonically decrease with increasing pressure. The electron temperature



Figure 4. Reactor averaged properties for ICPs sustained in different pressures of $Ar/Cl_2 = 80/20$ (10 MHz, 150 W cw). (a) Electron and ion densities, (b) resonant state densities, and (c) plasma potential, electron temperature and Cl_2 dissociation fraction.

 $T_{\rm e}$ decreases with increasing pressure up to 60 mTorr until reaching a near plateau at 2.2 eV, perhaps slightly increasing. The negative ion density monotonically increases with increasing pressure, albeit becoming nearly constant above 60 mTorr. With increasing pressure the rate of loss of charged particles by diffusion decreases, which enables a decrease in $T_{\rm e}$ to lower the rate of ionization to match losses. This trend continues until the plasma transitions to an ion–ion plasma at about 60 mTorr. At this time, charged particle losses are



Figure 5. Substrate averaged fluxes for ICPs sustained in different pressures of $Ar/Cl_2 = 80/20$ (10 MHz, 150 W cw). (a) Photon fluxes, (b) ion fluxes, and (c) total photon/ion flux ratio. Total photon fluxes are the sum of fluxes for 106.7 nm, 104.8 nm and 139 nm.

dominated by ion–ion neutralization. The rate of charged particle loss then remains nearly constant, and so T_e is nearly constant. The plasma potential decreases from 20 V at 10 mTorr to 13.5 V at 100 mTorr. This decrease is monotonic in spite of T_e not continuing to decrease since the electronegativity of the plasma continues to increase.



Figure 6. Optical properties for ICPs sustained in different pressures of $Ar/Cl_2 = 80/20$ (10 MHz, 150 W cw). (a) Line shape function of 139 nm emission. (b) Line shape function of 106.7 nm emission. (c) Trapping factors for 106.7 nm, 104.8 nm Ar emission and 139 nm Cl emission.

At 10 mTorr, positive ions dominantly consist of Cl⁺ (7.4 × 10¹⁰ cm⁻³), nearly double the density of Cl⁺₂ (3.7 × 10¹⁰ cm⁻³). As the pressure increases to 100 mTorr, the density of Cl⁺ decreases to 3.9×10^9 cm⁻³ while that of Cl⁺₂ increases to 5.7×10^{10} cm⁻³. The change in the identity

of the chlorine ions has several reasons. First, with constant power and increasing pressure, the fraction of Cl₂ dissociation decreases from 51% to 22%. So on a relative basis fewer Cl⁺ are produced by electron impact ionization. Second, since Cl⁺ has a higher ionization potential compared with Cl⁺₂, the lower T_e at higher pressure is more favorable towards electron impact ionization of Cl₂. Finally, a higher ion collision frequency at higher pressure results in more charge transfer reactions, producing the lower energy state Cl⁺₂.

The reactor averaged density of radiative states shows two diverging trends. The density of VUV radiating states of Ar decrease with increasing pressure— $Ar(1s_4)$ decreases from 1×10^9 cm⁻³ to 4.8×10^8 cm⁻³ and Ar(1s₂) decreases from 2×10^8 cm⁻³ to 7.4×10^7 cm⁻³ from 10 mTorr to 100 mTorr. This decrease is in part due to the decrease in $T_{\rm e}$ but is also attributable to the increasing rate of quenching of $Ar(1s_2)$ (from $6.6 \times 10^{12} \text{ cm}^{-3} \text{ s}^{-1}$ at 10 mTorr to $6.5 \times 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$ at 100 mTorr) and Ar(1s₄) $(1.3 \times 10^{12} \text{ cm}^{-3} \text{ s}^{-1} - 1.0 \times 10^{13}$ $cm^{-3} s^{-1}$) by chlorine species. Meanwhile, the density of $Cl(3p^44s)$ increases with pressure: from 1.2×10^9 cm⁻³ at 10 mTorr to 9.2×10^9 cm⁻³ at 100 mTorr. The increase in $Cl(3p^44s)$ density is in part due to the increase in trapping factor for 139nm radiation, from 4 at 10 mTorr to 110 at 100 mTorr. This increase in radiation trapping extends the lifetime of $Cl(3p^44s)$ to 11.6 μs . With increasing pressure and decreasing mean free path (MFP) for electron collisions, the specific power deposition (W cm^{-3}) beneath the coils increases in a small volume. Although the reactor averaged densities of $Ar(1s_2)$ and $Ar(1s_4)$ decrease with increasing pressure, the density of the radiating states increases in this small volume adjacent to the dielectric under the coils. For example in this small volume, the density of $Ar(1s_2)$ increases from $4.5 \times 10^8 \text{ cm}^{-3}$ at 10 mTorr to $2.5 \times 10^9 \text{ cm}^{-3}$ at 100 mTorr; and the density of Ar(1s₄) increases from 2.1×10^9 cm⁻³ to 1.5×10^{10} cm⁻³. This disproportionate increase in density of radiating state close to the top surface impacts the trapping factors, discussed below.

For these conditions, both the total VUV flux and total ion flux to the substrate decrease with increasing pressure. The VUV flux decreases by a factor of four, from 9.5×10^{14} cm⁻² s⁻¹ to 2.2×10^{14} cm⁻² s⁻¹. In contrast, the ion flux to the substrate decreases by a factor of 100, from 1.3×10^{16} cm⁻² s⁻¹ to 0.9×10^{14} cm⁻² s⁻¹. In addition to the decrease in ion densities with increasing pressure, the dominant loss for ions transitions from diffusion to ion–ion neutralization, which then reduces the ion fluxes leaving the plasma.

The decrease in the ion flux also has a contribution from the spatial distribution of electron impact sources. At low pressure, the MFP for electrons is longer, while the skin depth is anomalous which results in fluxes of high energy electrons emanating out of the skin depth. This results in the electron impact ionization sources being more uniformly distributed throughout the reactor. At high pressure, the shorter MFP of electrons and the thinner skin depth being largely collisional produces a relatively confined plasma beneath the coils, where ions tend to diffuse more towards the top surface of the reactor. As a result, the substrate at the bottom of the reactor then collects a comparably smaller flux of ions. As the ion flux decreases with pressure the composition also changes. At 10 mTorr, the majority of the ion flux is Cl^+ , $8.7 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ compared with Cl_2^+ at $4.2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$. At 100 mTorr, the Cl^+ flux drops to $5 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ while the Cl_2^+ is essentially the entire flux at $8.4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. The dominance in the Cl_2^+ flux to the substrate is much larger than its contribution to the total reactor averaged ion density. This dominance in ion flux is due to the charge exchange reactions that occur as the Cl^+ and Ar^+ ions diffuse from the source region to the substrate.

The VUV photon flux that reaches the substrate not only decreases in magnitude but also undergoes a spectral shift. Due to the decrease in the density of argon radiative states and the shift in their maxima towards the top of the reactor, the VUV fluxes to the substrate from Ar (104.8 nm and 106.7 nm) decrease by a factor of 10 while increasing pressure from 10 to 100 mTorr. Meanwhile the VUV flux from $Cl(3p^44s)$ (139 nm) increases by a factor of two, and becomes the dominant VUV photon flux. The ratio of total VUV flux versus ion flux, β , then monotonically increases with pressure, from 0.07 at 10 mTorr to 2.33 at 100 mTorr. Photon fluxes are comparable with ion fluxes at 60 mTorr and exceed ion fluxes by a factor of two at 100 mTorr. The smaller decrease in photon flux compared to ions is in large part due to the VUV flux that does reach the substrate being emitted in the wings of the lineshape function where the MFP is longer than the size of the reactor even at 100 mTorr.

The VUV spectra for 106.7 nm and 139 nm, and trapping factors for all lines as a function of pressure are shown in figure 6. The lineshape functions are for VUV photons collected and averaged on all the surfaces in contact with the plasma. With a smaller MFP and so a higher probability of reabsorption, photons with frequencies near the center of the lineshape function are trapped longer in the plasma, during which time the quanta energy of those photons are more likely to be quenched by collisional reactions. Photons emitted in the wings of the Voigt profile have a proportionately longer MFP and have a higher probability of escaping from the plasma. An inverted profile at the center of the lineshape function therefore indicates heavily trapped photon emission. The lineshape function for Ar emission at 106.7 nm transitions from being moderately trapped at 10 mTorr (trapping factor 161) to heavily trapped at 100 mTorr (trapping factor 428). Cl emission at 139 nm is not significantly trapped in this pressure range due to the low Cl ground state density. The trapping factor increases from 5 to 110 when increasing pressure from 10 to 100 mTorr.

The trapping factors for Ar emission saturate with pressure, which is at first counter-intuitive as one expects trapping factors to monotonically increase with pressure. This monotonic increase would be the case if the distribution of excited states was uniform throughout the volume of the plasma. The dominant cause for the saturation in trapping factors is the confinement of the region of high power deposition closer to the top dielectric with increasing pressure. This confinement results in a larger fraction of the radiative states being located closer to a surface. From the perspective of radiation transport, having excited states closer to the surface has the same effect on radiation trapping as the plasma being in a chamber of smaller radius or height which produces a lower radiation trapping factor.

4.2. Sensitivity of photon and ion fluxes to CI recombination on surfaces

In other studies of Cl₂ containing plasmas, investigators have discussed factors affecting the rate of dissociation of Cl₂ producing Cl radicals, the recombination of Cl on surfaces, and their influence on the electronegativity of the plasma (density of Cl⁻ ions) [35–38]. For example, at low pressure, the major source of negative ions is dissociative attachment to Cl₂ as the three-body rates of direct attachment to Cl₂ and Cl are small. The recombination of Cl on surfaces not only replenishes Cl₂ but also provides a means to replenish the source of Cl⁻. The recombination of Cl atoms on surfaces is often characterized by a surface recombination coefficient γ , which is the probability of a Cl atom abstracting a Cl atom from the chlorinated surface and returning to the plasma as Cl₂. This recombination probability is a function of the material properties, surface temperature and Cl surface coverage. For example, γ can vary from 0.02 to 0.85 for materials ranging from ceramics to stainless steel [24, 39]. In other experiments, Luc et al [40] and Joydeep et al [41] measured γ in real-time in an ICP sustained in Cl₂. They reported values for γ of 0.004–0.03 for anodized Al, and 0.01-0.1 for stainless steel, lower values believed to be the result of passivation of the surface. Saurabh et al [42] and Cunge et al [43, 44] observed that the Cl atom density as a function of power varies with different wall conditions, indicating the influence of surface recombination probabilities for Cl.

During an etching process, it is common for the surface conditions of the walls to change which, in turn, may affect γ [39, 43, 44]. This change in γ not only affects the balance between Cl and Cl₂ but also potentially changes the spectra of VUV fluxes that reach the substrate. To investigate this possibility, we varied the surface recombination coefficient for Cl, γ , from 0.005 to 0.80. This was implemented as having the fraction γ of the flux of Cl atoms, ϕ , striking the wall be lost from the plasma. The Cl atoms return to the plasma as Cl₂ with a flux at the wall of $(\gamma/2)\phi$. We acknowledge that this is a simplification of the actual surface kinetics that results in Cl recombination that may involve some combination of the Eley-Rideal and Langmuir-Hinshelwood mechanisms, which in turn depend on the surface coverage of adsorbed Cl atoms [45]. This approach also does not account for feed-back from the VUV fluxes that may, for example, produce photodesorption of Cl from the surface. However, with the goal of isolating the consequences of only surface recombination, we have chosen to use the simpler approach.

Reactor averaged densities, fractional dissociation of Cl_2 and substrate averaged VUV and ion fluxes as a function of γ are shown in figures 7 and 8. The gas mixture is Ar/ $Cl_2 = 80/20$ at 20 mTorr and 100 mTorr, with a power deposition of 150 W. The flow rates of 200 sccm for 20 mTorr and 1000 sccm for 100 mTorr were implemented to keep a constant average residence time. At 20 mTorr, as γ increases



Figure 7. Reactor averaged properties for ICPs having different recombination probabilities for Cl atoms on surfaces in Ar/ Cl₂ = 80/20 (20 mTorr, 200 sccm, 10 MHz, 150 W cw). (a) Cl⁺ and Cl₂⁺ densities, (b) Cl($3p^{4}4s$) densities, and (c) Cl₂ dissociation fraction.

from 0.005 to 0.80, the density of Cl⁺ decreases by 78% from 5.6×10^{10} cm⁻³ to 1.2×10^{10} cm⁻³, while the density of Cl₂⁺ increases from 5.2×10^{10} cm⁻³ to 6.5×10^{10} cm⁻³. The density of Cl₂⁺ exceeds Cl⁺ as for $\gamma > 0.01$. Though not shown, the densities of the radiative states of Ar (Ar(1s₂) and Ar(1s₄)), stay relative constant over this range of γ , at 1.2×10^9 cm⁻³ and 0.15×10^9 cm⁻³ respectively. In contrast, the density of



Figure 8. Substrate averaged fluxes for ICPs having different recombination probabilities for Cl atoms on surfaces in Ar/ Cl₂ = 80/20 at 20 and 100 mTorr. (a) Total photon flux and fraction of Cl($3p^44s$) emission (139 nm), (b) Cl⁺, Cl⁺₂ and total ion fluxes, (c) total photon/ion flux ratio. Total photon fluxes are the sum of the fluxes for 106.7 nm, 104.8 nm and 139 nm.

the resonant state of Cl (Cl($3p^{4}4s$)) significantly decreases, from 5.7 × 10⁹ cm⁻³ at $\gamma = 0.005$ to 0.31 × 10⁹ cm⁻³ at $\gamma = 0.8$. This decrease reflects the decrease in the dissociation fraction of Cl₂ from 0.61 to 0.16 (see figure 7(c)). As the pressure increases to 100 mTorr, the densities of both Cl⁺ and Cl⁺₂ decrease over almost the entire range of γ . The density of $Cl(3p^44s)$ however, is larger at 100 mTorr due to the higher overall density of Cl species and a lower T_e , which is more favorable to electron-impact excitation reactions than ionization.

As γ increases from 0.005 to 0.80 at 20 mTorr, the fluxes of Cl⁺ and of photons at 139 nm (originating from Cl($3p^44s$)) generally decrease. The increasing loss of Cl due to conversion of Cl₂ at the walls is directly reflected in these fluxes. The total fluxes of both ions and photons decrease until γ increases to 0.3–0.4, at which point these fluxes saturate since the fraction of Cl₂ remaining in the reactor is determined by the residence time due to gas flow. The end result is that the fraction of the VUV flux at 139nm significantly decreases as γ increases. For example, with $\gamma = 0.005$, the fraction of the VUV flux at 139 nm is 25% while for $\gamma = 0.8$, the fraction is 2%. The trends for 100 mTorr are similar though the fraction of VUV flux at 139nm is generally higher, decreasing from 76% with $\gamma = 0.005$ to 28% with $\gamma = 0.8$. With the 139 nm flux being a larger fraction of the total at 100 mTorr, the ratio of photon flux to ion flux, β , is also more sensitive to γ at the higher pressure.

These results suggest that the conditions of the walls, which in turn determine recombination coefficients, have a first order effect on the spectra and magnitude of the VUV flux incident onto surfaces. It is true that these dependencies of VUV fluxes on γ find their origins in the dependence of gas phase species on γ , and it is difficult to separate VUV fluxes and gas phase species. However, it is also true that the consequences of ion or radical fluxes, and VUV fluxes on materials properties can have very different outcomes. For example, the processing depth of neutral and ion fluxes on typical semiconductor materials is at best a few nm, whereas VUV fluxes can penetrate tens to hundreds of nm.

4.3. Photon and ion fluxes versus Cl₂ ratio

Another method to tune the spectra of VUV fluxes incident onto the substrate is gas mixture. In this regard, mixtures of Ar/ $Cl_2 = 95/5$ to 5/95, at 20 mTorr and 150 W were investigated. Reactor averaged plasma properties and species densities, dissociation fraction of Cl₂ and substrate averaged VUV and ion fluxes as a function of Cl₂ fraction are shown in figures 9 and 10. Spatial distributions of electrons and of the radiating states $Ar(1s_4)$ and $Cl(3p^44s)$ are shown in figure 11. The plasma density (total positive ion density) decreases from $1.4 \times 10^{11} \, \mathrm{cm^{-3} \, s^{-1}}$ to 0.72×10^{11} cm⁻³ s⁻¹ as the Cl₂ fraction increases from 5% to 95%. This lower plasma density is caused by several reasons. First, the rate of power dissipation by electrons colliding with Cl₂ (having vibrational excitation, dissociation and dissociative attachment processes) is greater than that for Ar. A larger Cl₂ fraction for a fixed power deposition would require a lower electron density. A decrease in the electron energy relaxation length and increase in rates of electron energy dissipation produces a lower electron temperature— T_e decreases from 2.5 eV at 5% Cl₂ to 2.1 eV at 95% Cl₂. The lower T_e then favors reactions with lower energy thresholds, thereby directing power flow away from ionization processes in the bulk plasma. The decrease in $T_{\rm e}$ and the transition to an ion–ion dominated plasma produce a decrease in the plasma potential.



Figure 9. Reactor averaged properties for ICPs having different Cl_2 fractions in Ar/Cl_2 (20 mTorr, 200 sccm, 10 MHz, 150 W cw). (a) Ion densities, (b) resonant state densities and (c) plasma potential, electron temperature and Cl_2 dissociation fraction.

For our conditions this shift in power dissipation to lower energies with the increase in Cl₂ mole fraction increases the rate of dissociative reactions, thereby increasing the density of Cl by a factor of 3 (2.9×10^{13} cm⁻³ to 7.7 $\times 10^{13}$ cm⁻³) and the density of Cl⁻ by a factor of 7 (7.8×10^9 cm⁻³ to 4.9×10^{10} cm⁻³). The increase in Cl⁻ produces a more electronegative plasma having a lower electron density and lower electron temperature. Collectively these trends produce a plasma in which



102

Figure 10. Substrate averaged fluxes for ICPs having different Cl_2 fractions in Ar/Cl_2 (20 mTorr, 200 sccm, 10 MHz, 150 W cw). (a) Photon fluxes, (b) ion fluxes and (c) total photon/ion flux ratio and fraction of 139 nm in the spectra. Total photon fluxes are the sum of fluxes for 106.7 nm, 104.8 nm and 139 nm.

diffusion plays a smaller role in ionization balance and where ion–ion recombination is a major ion loss channel. This less diffusive regime is shown in figure 11. For 5% Cl₂, the diffusive plasma has the peak of electron and $Cl(3p^44s)$ densities near the center of the reactor, while at 95% Cl₂, the plasma is largely confined near the maximum in power deposition within the skin depth of the electromagnetic field.

P Tian and M J Kushner



Figure 11. Time averaged plasma properties for ICPs having different Cl₂ fractions in Ar/Cl₂ (Ar/Cl₂ = 95/5 and 5/95, 20 mTorr, 200 sccm, 10 MHz, 150 W cw). (a) Electron density, (b) resonant Ar(1s₄) density and (c) Cl($3p^44s$) density The densities and fluxes are on log-scales of 2 decades.

By about a mole fraction of 30% Cl₂, the majority of discharge power is dissipated in electron collisions with Cl and Cl₂. As power dissipation shifts from Ar to Cl₂ and with the drop in T_e , the densities of Ar(1s₄) and Ar(1s₂) decrease to below Cl(3p⁴4s) by 20% Cl₂. The density of Cl(3p⁴4s) has a broad maximum between 15% and 20% Cl₂ which is caused by competing mechanisms. At low Cl₂ fractions, the rate of excitation of Cl is limited by the low Cl density, and so the increasing density of Cl produces more $Cl(3p^44s)$. Meanwhile, the decrease in T_e with increasing Cl_2 fraction, lowers the rate of excitation of $Cl(3p^44s)$, which accounts for its decrease with increasing Cl_2 fraction.

Photon fluxes and ion fluxes to the substrate are shown in figure 10 as a function of Cl₂ fraction in the mixture. Adding Cl₂ (5% to 95%) decreases ion fluxes to the substrate by a factor of 10, from 1.2×10^{16} cm⁻² s⁻¹ to 1.3×10^{15} cm⁻² s⁻¹. This trend is attributed to a decrease in plasma density, a less diffusive plasma having weaker ambipolar diffusion, ion losses being dominated by ion–ion neutralization (instead of diffusion) and the peak in the ion density being confined more in the electromagnetic skin depth under the coil. Ar⁺ and Cl⁺ fluxes, dominant at low Cl₂ fraction, are replaced by Cl₂⁺ fluxes by 30% Cl₂. Among the three ions, Cl₂⁺ fluxes are relatively stable. The variation of Cl₂⁺ fluxes is only a factor of 3 for the range of gas mixtures, compared to 2 or 3 orders of magnitude change in Cl⁺ and Ar⁺ fluxes.

Total photon fluxes and VUV fluxes from the resonant lines of Ar and Cl are shown in figure 10 and demonstrate the possibility of coarse spectral control using Cl₂ mole fraction. The total VUV fluxes decrease by a factor of 200 from 5.1×10^{15} cm⁻² s⁻¹ to 2.3×10^{13} cm⁻² s⁻¹ when increasing Cl₂ fraction from 5% to 95%. This decrease is in large part due to the decrease of the density of radiative states in the bulk plasma. While VUV emission from Ar has a monotonic decrease, VUV emission from Cl at 139 nm largely follows the density of $Cl(3p^44s)$ and decreases by half from 5% to 95% Cl₂, with a maximum of 5.4×10^{13} cm⁻² s⁻¹. The proportion of VUV emission from Cl in the total VUV spectra steadily increases due to its comparably smaller variation compared to emission from Ar over the range of Cl₂ fraction. With 80% Cl_2 , the VUV emission from $Cl(3p^44s)$ is equal to that from Ar($1s_2, 1s_4$) while dominating the spectrum at higher Cl₂ mole fraction. The ratio of VUV-to-ion fluxes β decreases from 0.4 to 0.02 with increasing Cl₂ fraction.

Spectral lineshape functions for Ar (106.7 nm) and Cl (139nm) emission and radiation trapping factors are shown in figure 12 for different Cl_2 fractions. The trapping factor of Cl (139nm) emission is small and increases from 4 to 11 as Cl₂ increases from 5% to 95%. This moderate increase in trapping factor reflects the increase in Cl density which increases the ground state absorber density and so the trapping factor. It also reflects the contraction of the emitting $Cl(3p^44s)$ density towards the top surface, which decreases the trapping factor. Trapping factors for emission from Ar (106.7 nm) greatly decrease, from 534 to 10, as the Ar fraction decreases from 95% to 5%. The lineshape function of Cl (139nm) has a non-inverted Voigt profile due to its weak trapping. The Ar (106 nm) lineshape function is significantly self-absorbed at low Cl₂ fraction (high Ar fraction) and transitions to being optically thin with no line reversal at 95% Cl₂ fraction.

4.4. Pulsing: photon and ion fluxes versus duty cycle (DC)

As discussed in our prior investigation of rare gas plasmas, pulsing the ICP plasma provides another mechanism to control the VUV-to-ion flux ratio [24]. With continuous wave (cw)



Figure 12. Optical properties for ICPs having different Cl_2 fractions in Ar/Cl_2 ($Ar/Cl_2 = 95/5$ to 5/95, 20 mTorr, 200 sccm, 10 MHz, 150 W cw). Lineshape function for (a) 106.7 nm emission and (b) 139 nm emission. (c) Trapping factors for 106.7 nm, 104.8 nm Ar emission, and 139 nm Cl emission.

excitation, there is limited ability to control species densities for a given set of conditions (e.g. varying pressure, power, mixture, flow rate). The reactor-averaged T_e is constrained by the need to balance sources of resonant states and ionization, and their losses at all times. With pulsed power, the balance between sources and losses need only be balanced averaged over the pulsed period. This considerably larger range for varying T_e through modulating the electron energy distributions enables us to gain additional control over VUV and ion fluxes [6, 46, 47].

With the goal of controlling the fluxes of VUV photons and ions to the substrate in Ar/Cl₂ mixtures, we investigated pulsed plasma excitation of the ICP. The pulsed power waveform is characterized by the pulse repetition frequency, PRF, the number of power pulses per second; the duty cycle, DC, the fraction of the pulsed period the ICP power is applied; and the cycle average power deposition, CAP. The base case for pulsing is Ar/Cl₂ = 80/20 at 20 mTorr, with a PRF of 50kHz (20 μ s period), and CAP of 150 W. The DC will be a control variable.

By varying DC while keeping a constant CAP of 150 W, the power density during the pulse-on period, and particularly during the leading edge, is controlled. Smaller duty cycle requires not only more power during the shorter power-on period but also has a smaller electron density at the end of the longer afterglow-both of which contribute to a spiking of the electron temperature during the leading edge of the power-on pulse [6]. This spiking in T_e , often called an overshoot, then translates to a different distribution of excited states and ionization. VUV fluxes, ion fluxes, the ratio of VUV-to-ion fluxes, β , and T_e are shown as a function of time for duty cycles of 10% to 60% in figures 13 and 14. The overshoot of $T_{\rm e}$ reaches up to 5.4 eV at 10% DC and decreases to 3.5 eV at 60% DC, compared to a cw value of about 2.8 eV. In the afterglow, $T_{\rm e}$ maintains about 1 eV regardless of DC, largely sustained by super-elastic relaxation of excited states.

The modulation of the 104.8 nm fluxes originating with $Ar(1s_2)$ is up to a factor of 50 at 10% DC, whereas the modulation in the 106.7 nm line originating with the $Ar(1s_4)$ at 10% DC is a factor of 9. This smaller degree of modulation of 106.7 nm indicates a longer life time of $Ar(1s_4)$ compared with $Ar(1s_2)$. Other than the intrinsic longer lifetime of $Ar(1s_4)$ (8.4 ns) compared to $Ar(1s_2)$ (2.0 ns), there are two major factors in this disparity. First, the 106.7 nm line has a radiation trapping factor of 360 compared to the smaller trapping factor of 217 for the 104.8 nm transition. Second, $Ar(1s_4)$ is more closely coupled to the lowest metastable state of $Ar(1s_5)$ which has the largest density during the afterglow among Ar excited states, $1.0-1.5 \times 10^{10}$ cm⁻³. Being replenished by collisions with $Ar(1s_5)$, $Ar(1s_4)$ maintains a relative large density during the afterglow. The 104.8 nm emission originating with $Ar(1s_2)$ more closely follows the time evolution of $T_{\rm e}$.

The 139 nm line originating with $Cl(3p^44s)$ has a maximum modulation of a factor of 9 at 10% DC. As a result, the spectra of VUV fluxes is highly modulated by the pulse power. For example, the ratio of Ar to Cl VUV emission is shown in figure 15 as a function of time for different duty cycles. During a single pulse, Ar emission (sum of 104.8 nm and 106.7 nm) reaches up to 29 times the magnitude of Cl emission (139 nm) with 10% DC. The ratio of Ar/Cl photon fluxes approaches 9 by the end of the afterglow. These trends indicate that the over shoot of T_e at the beginning of the pulse is more favorable to producing Ar emission compared to Cl emission. As the DC increases and the overshoot in T_e decreases, the dominance of VUV emission from Ar decreases.



Figure 13. Photon fluxes collected on and averaged over the bottom substrate as a function of time for two ICP pulses for different duty cycles. The dashed lines indicate the end of the power-on period. (a) 106.7 nm (originating from $Ar(1s_4)$), (b) 104.8 nm (originating from $Ar(1s_2)$) and (c) 139 nm (originating from $Cl(3p^44s)$). Plasma conditions are $Ar/Cl_2 = 80/20$, 20 mTorr, 200 sccm, 10 MHz, 150 W CAP, PRF = 50 kHz.

Cycle averaged and peak fluxes of VUV emission from Ar and Cl are shown in figure 16. The cycle average ratio of Ar emission is 4-5 times that of Cl, decreasing with increasing duty cycle, but is not tremendously sensitive to duty cycle.



6

3

0

(a)

0.8

0.6

0.4

ĺ٥

Total Ion Flux $(10^{15} \text{ cm}^2 \text{s}^{-1})$



Figure 14. Plasma properties as a function of time for two ICP pulses with different duty cycles. Fluxes are collected on and averaged over the substrate. Dashed lines indicate the end of the power-on period. (a) Ion flux, (b) ratio of total VUV flux to ion flux, and (c) electron temperature. Plasma conditions are $Ar/Cl_2 = 80/20$, 20 mTorr, 200 sccm, 10 MHz, 150 W CAP, PRF = 50 kHz.

The maximum of Ar emission is 35 times that of Cl at 10% duty cycle, decreasing to a factor of 12 at the higher duty cycle. This decrease in ratio is dominantly due to the decrease in the overshoot in $T_{\rm e}$.



Figure 15. Spectra of VUV fluxes for pulsed ICPs. (a) Ratio of Ar/ Cl VUV fluxes over two pulse periods. (b) Cycle averaged Ar/Cl photon fluxes ratio as a function of duty cycle, and (c) peak Ar/Cl photon fluxes ratio as a function of duty cycle. The Ar emission is the sum of fluxes at 106.7 and 104.8 nm.

The modulation in the ion fluxes to the substrate during the pulsed cycle is about 35%–40% and is not as sensitive to DC as either T_e or photon fluxes. This lack of sensitivity is in large part a result of the diffusion times for ion transport to the substrate being commensurate with the pulsed period. The ion fluxes to the substrate then reflect something of an average over the pulsed period. Since, however, the VUV fluxes are modulated during the pulse period, the ratio of overall VUVto-ion fluxes, β , is also highly modulated over a pulse period, as shown in figure 14. The maximum value of β is 0.8 for 10% DC at the beginning of the power pulse, and 0.2 for 60% DC during most of the pulse-on time. β decreases to 0.08 at the end of the afterglow. During the entire pulse, ion fluxes exceed photon fluxes. The peak (maximum during one pulse) and cycle averaged VUV and ion fluxes, and ratio of VUVto-ion flux, β , are shown in figure 16. VUV flux is the sum of the fluxes of the 104.8, 106.7 and 139.0 nm lines, and ion flux is the sum of the fluxes of Ar^+ , Cl^+ and Cl_2^+ . The VUV fluxes increase with decreasing DC, and ion fluxes decrease at lower DC. The ratio of VUV-to-ion fluxes, β , increases with decreasing DC. This indicates the overshoot in T_e is more favorable to populating excited states of Ar and Cl than for producing more ions for these conditions.

5. Optimizing feature profiles during plasma etching

As discussed in the introduction, VUV photon fluxes are now recognized as being important in plasma material processing [11–16, 20–23]. The consequences of VUV photons on materials processing is highly dependent on the system. However we anticipate that the impact of VUV stimulated processes is perhaps greatest in semiconductor processing where the need for critical dimension control now approaches a monolayer. To achieve this critical dimension, control of activating fluxes onto wafers should extend beyond ion fluxes to include VUV fluxes. For example, the recent discovery of photon assisted etching of Si in halogen containing plasmas [16, 22] emphasizes the need to separately control VUV fluxes, or at least control the ratio of VUV to ion fluxes.

In section 4, we discussed different methods whereby the intensity of VUV emission or the ratio of VUV photon to ion fluxes could be controlled. These techniques may also change the absolute reactant fluxes of etch precursors, both ions and Cl radicals. Other than when ions are near or below threshold for etching, it is not likely that the VUV stimulated etching will compete with the ion induced etching in terms of total etch rate. The importance influence of VUV stimulated etching is likely due to the fact that VUV fluxes to the surface are nearly isotropic whereas ion fluxes are anisotropic. Etching may be stimulated at different rates on vertical and horizontal surfaces by photons and ions, and this relates to profile control.

To demonstrate the possible impact of VUV stimulated processes, profile evolution during etching of Si by ICPs sustained in Ar/Cl_2 mixtures was simulated using the MCFPM. As mentioned in section 2, VUV photon fluxes are included in the MCFPM in the same manner as ion and neutral fluxes. Since the energy of each photon is fixed, the distribution of individual photon fluxes produced by the HPEM consists of only angular distributions. Otherwise, the algorithms for selecting photon-pseudoparticles and reactions stimulated by the photons on the surface are identical to those for ions.



Figure 16. Properties of fluxes striking and averaged over the substrate for pulsed excitation for different duty cycles and for cw excitation. (a) Total VUV photon flux, (b) ion flux and (c) ratio of VUV flux to ion flux. Plasma conditions are $Ar/Cl_2 = 80/20$, 20 mTorr, 200 sccm, 10 MHz, 150 W CAP, PRF = 50 kHz.

The reaction mechanism used for Ar/Cl_2 plasma etching of Si is essentially the same as that described in [32, 33] and is listed in table 2. The mechanism consists first of successive passivation of Si sites by Cl atoms

$$\operatorname{SiCl}_{n}(s) + \operatorname{Cl}(g) \to \operatorname{SiCl}_{n+1}(s), \ n = 0, 1, 2$$
(1)

where (*s*) and (*g*) refer to solid and gas phase species. A low rate of spontaneous etching also occurs,

$$\operatorname{SiCl}_3(s) + \operatorname{Cl}(g) \to \operatorname{SiCl}_4(g).$$
 (2)

The vast majority of etch processes proceeds by chemically enhanced ion sputtering and to a lesser degree by direct ion sputtering,

$$\operatorname{SiCl}_{n}(s) + M^{+}(g) \to \operatorname{SiCl}_{n}(g) + M(g), \quad n = 1, 2, 3,$$
$$M = \operatorname{Ar}, \operatorname{Cl}, \operatorname{Cl}_{2}.$$
(3)

$$\operatorname{Si}(s) + M^+(g) \to \operatorname{Si}(g) + M(g), \quad M = \operatorname{Ar}, \operatorname{Cl}, \operatorname{Cl}_2.$$
 (4)

Hot atoms (usually produced by gazing ions neutralizing on side walls) produce analogous reactions as for ion stimulated processes. When including VUV photon fluxes, we also included the phenomenological reactions

$$\operatorname{SiCl}_n(s) + h\nu \to \operatorname{SiCl}_n(g), \quad n = 1, 2, 3.$$
 (5)

The probability of reaction for photon stimulated etching, p_n , for SiCl_n was calibrated based on the experimental results of Shin *et al* [16] who equated the VUV stimulated etch rate to be equivalent to that of 40 eV ions. With that observation and allowing for higher probabilities for higher states of passivation, the probabilities for photon stimulated etching we used in the model are $p_n = 0.1$, 0.2 and 0.2 for n = 1, 2 and 3. The same probability was used for all VUV wavelengths (104.8 nm, 106.7 nm, 139 nm).

A second approximation made in this study was that VUV photons can be treated using ray-optics, and for this reason we simulated etching of only fins and not trenches, and reasonably large features. We acknowledge that for the small dimensions of trenches in modern microprocessors and for the wavelengths of interests, diffractive effects are likely important and that ray tracing is at best an approximation.

The conditions for this part of the investigation are an Ar/ $Cl_2 = 80/20$ mixture, 150 W ICP power with a 200 V bias at 10 MHz applied to the substrate for pressures from 10 to 100 mTorr. The photon-to-ion flux ratio, photon and ion angular distributions collected on and averaged over the substrate are shown in figure 17. Compared to ICPs with unbiased substrates, the total ion fluxes increase with the bias, producing a smaller β between 0.1–0.3 (compared with a max β of 2.3 in unbiased condition), with a peak value near 60 mTorr. Angular distributions of VUV fluxes in the bulk plasma are essentially isotropic, and so the angular distribution of photons incident onto the surface resembles a Lambertian distribution, peaked at near normal incidence and falling towards grazing incidence as $\cos(\theta)$. Note that as the pressure increases, there is a small angular asymmetry in the photon fluxes. This asymmetry results from the contraction of the power deposition and maxima in excited states to a small volume in the electromagnetic skin depth of the coil. This contraction is analogous to that shown in figure 11 for large fractions of Cl₂. As a result, the photon sources begin to look like an off-axis point source that produces a photon flux to the substrate having an angular slant. In comparison to the photon fluxes, the ion fluxes are essentially anisotropic with angular distributions contained well within 10 degrees

Table 2. Reaction mechanism for Si etching.

M(s) surface site	
M gas phase species	
M^+ ion	
$M^{\#}$ hot neutral from neutralized ion	
ϕ photon species	

Reactions ^{a,b,c}	Probability (P_0)	Threshold energy (eV)	Ref., footnote
$M^+ + M(s) \rightarrow M^\# + M(s)$	с		d
$M^{\#} + M(s) \rightarrow M^{\#} + M(s)$	с		d
$M(s) + \mathrm{Si} \rightarrow M(s) + \mathrm{Si}(s)$	с		d
$M(s) + \phi \rightarrow M(s)$	с		d
Chlorination reactions			
$Si(s) + Cl \rightarrow SiCl(s)$	0.99		
$\operatorname{SiCl}(s) + \operatorname{Cl} \rightarrow \operatorname{SiCl}_2(s)$	0.4		
$\operatorname{SiCl}_2(s) + \operatorname{Cl} \to \operatorname{SiCl}_3(s)$	0.3		
$SiO_2(s) + Cl \rightarrow SiO_2Cl(s)$	0.1		
$SiO_2Cl(s) + Cl \rightarrow SiO_2Cl_2(s)$	0.1		
$Si(s) + SiCl \rightarrow Si(s) + SiCl(s)$	0.15		
$SiCl(s) + SiCl \rightarrow SiCl(s) + SiCl(s)$	0.15		
$SiCl_2(s) + SiCl \rightarrow SiCl_2(s) + SiCl(s)$	0.15		
$SiCl_3(s) + SiCl \rightarrow SiCl_3(s) + SiCl(s)$	0.15		
$SiO_2(s) + SiCl \rightarrow SiO_2(s) + SiCl(s)$	0.1		
$SiO_2Cl(s) + SiCl \rightarrow SiO_2Cl(s) + SiCl(s)$	0.1		
$SiO_2Cl_2(s) + SiCl \rightarrow SiO_2Cl_2(s) + SiCl(s)$	0.1		
$Si(s) + SiCl_2 \rightarrow Si_2Cl_2(s)$	0.9		
$SiCl(s) + SiCl_2 \rightarrow Si_2Cl_3(s)$	0.9		
$SiCl_2(s) + SiCl_2 \rightarrow Si_2Cl_4(s)$	0.9		
$SiCl_3(s) + SiCl_2 \rightarrow SiCl_3(s) + SiCl_2(s)$	0.15		
$SiO_2(s) + SiCl_2 \rightarrow SiO_2(s) + SiCl_2(s)$	0.05		
$SiO_2Cl(s) + SiCl_2 \rightarrow SiO_2Cl(s) + SiCl_2(s)$	0.05		
$SiO_2Cl_2(s) + SiCl_2 \rightarrow SiO_2Cl_2(s) + SiCl_2(s)$	0.05		
$Si(s) + SiCl_3 \rightarrow Si(s) + SiCl_3(s)$	0.15		
$SiCl(s) + SiCl_3 \rightarrow SiCl(s) + SiCl_3(s)$	0.15		
$SiCl_2(s) + SiCl_3 \rightarrow SiCl_2(s) + SiCl_3(s)$	0.15		
$SiCl_3(s) + SiCl_3 \rightarrow SiCl_3(s) + SiCl_3(s)$	0.15		
$SiO_2(s) + SiCl_3 \rightarrow SiO_2(s) + SiCl_3(s)$	0.1		
$SiO_2Cl(s) + SiCl_3 \rightarrow SiO_2Cl(s) + SiCl_3(s)$	0.1		
$SiO_2Cl_2(s) + SiCl_3 \rightarrow SiO_2Cl_2(s) + SiCl_3(s)$	0.1		
$Si-O(s) + Cl \rightarrow Si-OCl(s)$	0.3		
$Si-O(s) + SiCl \rightarrow Si-O(s) + SiCl(s)$	0.25		
$Si-O(s) + SiCl_2 \rightarrow Si-O(s) + SiCl_2(s)$	0.15		
$Si-O(s) + SiCl_3 \rightarrow Si-O(s) + SiCl_3(s)$	0.05		
$Si-OCl(s) + SiCl \rightarrow Si-OCl(s) + SiCl(s)$	0.25		
$Si-OCl(s) + SiCl_2 \rightarrow Si-OCl(s) + SiCl_2(s)$	0.15		
$Si-OCl(s) + SiCl_3 \rightarrow Si-OCl(s) + SiCl_3(s)$	0.05		
$Si_2Cl_2(s) + SiCl \rightarrow Si_2Cl_2(s) + SiCl(s)$	0.15		
$Si_2Cl_3(s) + SiCl \rightarrow Si_2Cl_3(s) + SiCl(s)$	0.15		
$Si_2Cl_4(s) + SiCl \rightarrow Si_2Cl_4(s) + SiCl(s)$	0.15		
$Si_2Cl_2(s) + SiCl_2 \rightarrow Si_2Cl_2(s) + SiCl_2(s)$	0.15		
$Si_2Cl_3(s) + SiCl_2 \rightarrow Si_2Cl_3(s) + SiCl_2(s)$	0.15		
$Si_2Cl_4(s) + SiCl_2 \rightarrow Si_2Cl_4(s) + SiCl_2(s)$	0.15		
$Si_2Cl_2(s) + SiCl_3 \rightarrow Si_2Cl_2(s) + SiCl_3(s)$	0.15		
$Si_2Cl_3(s) + SiCl_3 \rightarrow Si_2Cl_3(s) + SiCl_3(s)$	0.15		
$Si_2Cl_4(s) + SiCl_3 \rightarrow Si_2Cl_4(s) + SiCl_3(s)$	0.15		

(Continued)

Plasma Sources Sci. Technol. 26 (2017) 024005

	Table 2. (Continued)			
Reactions ^{a,b,c}	Probability (P_0)	Threshold energy (eV)	Ref., footnote	
$\overline{\mathrm{Si}(s) + \mathrm{Si}\mathrm{Cl}_{2}^{+}} \rightarrow \mathrm{Si}_{2}\mathrm{Cl}_{2}(s)$	0.5		e	
$SiCl(s) + SiCl_2^+ \rightarrow Si_2Cl_2(s)$	0.5		e	
$\operatorname{SiCl}(s) + \operatorname{SiCl}^+ \rightarrow \operatorname{SicCl}(s)$	0.5		e	
$\operatorname{SiO}_2(s) + \operatorname{SiO}_2(s) + \operatorname{SiO}_2(s)$	0.01		e	
$SiO_2(3) + SiCl_2 \rightarrow SiO_2(3) + SiCl_2(3)$	0.01		e	
$SIO_2CI(s) + SICI_2 \rightarrow SIO_2CI(s) + SICI_2(s)$	0.01		e	
$\operatorname{SiO}_2\operatorname{Cl}_2(s) + \operatorname{SiCl}_2 \rightarrow \operatorname{SiO}_2\operatorname{Cl}_2(s) + \operatorname{SiCl}_2(s)$	0.03		e	
$S_1 - O(s) + S_1 C_1^2 \rightarrow S_1 - O(s) + S_1 C_2(s)$	0.03		e	
$Si-OCl(s) + SiCl_2^- \rightarrow Si-OCl(s) + SiCl_2(s)$	0.05		e	
$\operatorname{Si}_2\operatorname{Cl}_2(s) + \operatorname{Si}_2\operatorname{Cl}_2(s) + \operatorname{Si}_2\operatorname{Cl}_2(s)$	0.15		e	
$\operatorname{Si}_2\operatorname{Cl}_3(s) + \operatorname{Si}_2\operatorname{Cl}_2(s) + \operatorname{Si}_2\operatorname{Cl}_3(s) + \operatorname{Si}_2\operatorname{Cl}_2(s)$	0.15		e	
$\operatorname{Si}_2\operatorname{Cl}_4(s) + \operatorname{Si}_2\operatorname{Cl}_2^+ \to \operatorname{Si}_2\operatorname{Cl}_4(s) + \operatorname{Si}_2\operatorname{Cl}_2(s)$	0.15		e	
Etching reactions				
$SiCl_2(s) + Cl \rightarrow SiCl(s) + Cl_2$	0.02			
$SiCl_3(s) + Cl \rightarrow SiCl_4$	0.0001		[63]	
$SiCl_3(s) + Cl \rightarrow SiCl_2(s) + Cl_2$	0.08			
$\mathrm{Si}(s) + \mathrm{Cl}^+ \rightarrow \mathrm{SiCl}$	0.001	16	[16] ^e	
$\operatorname{Si}(s) + \operatorname{Cl}_2^+ \to \operatorname{SiCl}_2$	0.001	16	[16] ^e	
$SiCl(s) + Cl^+ \rightarrow SiCl_2$	0.2	16	[16] ^e	
$SiCl_2(s) + Cl^+ \rightarrow SiCl_2 + Cl\#$	0.5	16	[16] ^{e,f}	
$SiCl_3(s) + Cl^+ \rightarrow SiCl_3 + Cl\#$	0.5	16	[16] ^{e,f}	
$\operatorname{SiCl}(s) + \operatorname{Cl}_2^+ \rightarrow \operatorname{SiCl}_2 + \operatorname{Cl}_2 \#$	0.2	16	[16] ^{e,f}	
$\operatorname{SiCl}_2(s) + \operatorname{Cl}_2^+ \rightarrow \operatorname{SiCl}_3 + \operatorname{Cl}_\#$	0.25	16	[16] ^{e,f}	
$\operatorname{SiCl}_3(s) + \operatorname{Cl}_2^+ \rightarrow \operatorname{SiCl}_3 + \operatorname{Cl}_2 \#$	0.25	16	[16] ^{e,f}	
$\operatorname{SiCl}_3(s) + \operatorname{Cl}_2^+ \rightarrow \operatorname{SiCl}_4 + \operatorname{Cl}_\#$	0.25	16	[16] ^{e,f}	
$SiCl(s) + Ar^+ \rightarrow SiCl + Ar#$	0.2	16	[16] ^{e,f}	
$SiCl_2(s) + Ar^+ \rightarrow SiCl_2 + Ar \#$	0.5	16	[16] ^{e,f}	
$SiCl_3(s) + Ar^+ \rightarrow SiCl_3 + Ar^+$	0.5	16	[16] ^{e,f}	
$SiO_2Cl_2(s) + Ar^+ \rightarrow Si-O(s) + SiCl_2 + Ar$	0.025	20	e,f	
$SiO_2Cl_2(s) + Cl^+ \rightarrow Si-O(s) + SiCl_2 + Cl$	0.025	20	e,f	
$SiO_2Cl_2(s) + Cl_2^+ \rightarrow Si-O(s) + SiCl_2 + Cl_2$	0.025	20	e,f	
$Si-OCl(s) + Ar^+ \rightarrow Si(s) + ClO + Ar$	0.025	20	e,f	
$Si-OCl(s) + Cl^+ \rightarrow Si(s) + ClO + Cl$	0.025	20	e,f	
$Si-OCl(s) + Cl_2^+ \rightarrow Si(s) + ClO + Cl_2$	0.025	20	e,f	
$Si_2Cl_2(s) + Cl \rightarrow SiCl(s) + SiCl_2$	0.008			
$Si_2Cl_3(s) + Cl \rightarrow SiCl(s) + SiCl_2 + Cl$	0.008			
$Si_2Cl_4(s) + Cl \rightarrow SiCl_2(s) + SiCl_2 + Cl$	0.008			
$Si_2Cl_2(s) + Cl^+ \rightarrow SiCl(s) + SiCl_2$	0.9		e	
$Si_2Cl_3(s) + Cl^+ \rightarrow SiCl(s) + SiCl_2 + Cl$	0.99		e	
$Si_2Cl_4(s) + Cl^+ \rightarrow SiCl_2(s) + SiCl_2 + Cl$	0.99		e	
$Si_2Cl_2(s) + Ar^+ \rightarrow Si(s) + SiCl_2 + Ar$	0.9		e	
$Si_2Cl_3(s) + Ar^+ \rightarrow SiCl(s) + SiCl_2 + Ar$	0.99		e	
$Si_2Cl_4(s) + Ar^+ \rightarrow SiCl_2(s) + SiCl_2 + Ar$	0.99		e	
$\mathrm{Si}_{2}\mathrm{Cl}_{2}(s) + \mathrm{Cl}_{2}^{+} \rightarrow \mathrm{Si}(s) + \mathrm{Si}\mathrm{Cl}_{2} + \mathrm{Cl}_{2} \#$	0.6		e	
$Si_2Cl_3(s) + Cl_2^+ \rightarrow SiCl(s) + SiCl_2 + Cl_2 #$	0.6		e	
$Si_2Cl_4(s) + Cl_2^+ \rightarrow SiCl_2(s) + SiCl_2 + Cl_2 #$	0.6		e	
Photon-assisted etching reactions				
$\operatorname{SiCl}(s) + \phi(105\mathrm{nm}) \rightarrow \operatorname{SiCl}$	0.1		g	
$SiCl(s) + \phi(106 \mathrm{nm}) \rightarrow SiCl$	0.1		g	
$SiCl(s) + \phi(139 \mathrm{nm}) \rightarrow SiCl$	0.1		g	
$\operatorname{SiCl}_2(s) + \phi(105\mathrm{nm}) \to \operatorname{SiCl}_2$	0.2		g	
$\operatorname{SiCl}_2(s) + \phi(106\mathrm{nm}) \rightarrow \operatorname{SiCl}_2$	0.2		g	

(Continued)

	Table 2. (Continued)			
Reactions ^{a,b,c}	Probability (P_0)	Threshold energy (eV)	Ref., footnote	
$\overline{\operatorname{SiCl}_2(s) + \phi(139\mathrm{nm})} \to \operatorname{SiCl}_2$	0.2		g	
$\operatorname{SiCl}_3(s) + \phi(105\mathrm{nm}) \rightarrow \operatorname{SiCl}_3$	0.2		g	
$SiCl_3(s) + \phi(106 \mathrm{nm}) \rightarrow SiCl_3$	0.2		g	
$\operatorname{SiCl}_3(s) + \phi(139\mathrm{nm}) \to \operatorname{SiCl}_3$	0.2		g	

^a Unless specified, all ions neutralize on surfaces, returning as their neutral counterparts

^b Gas phase species have units of flux ($cm^{-2} s^{-1}$). Surface species have units of fractional coverage.

^c This is the default reaction when other material altering reactions do not occur.

^d Reactions are applicable to all surfaces unless otherwise noted.

^e All reactions of ions are applicable to corresponding hot neutrals.

^f When threshold energy (\vec{E}_{th}) is not zero, reaction probability (P_e) is a function of ion incident energy (E_{in}) with a reference energy (E_{ref}) of 100 eV: $P_e = P_0 \times (E_{in} - E_{th})^{0.5} / (E_{ref} - E_{th})^{0.5} \times Angular yield.$

^g See text.



Figure 17. Properties of ion and VUV fluxes in biased ICPs at pressure range 10–100 mTorr. (a) ratio of VUV/ion fluxes and (b) angular distribution of total VUV and ion fluxes plasma conditions are $Ar/Cl_2 = 80/20$, 10–100 mTorr, 10 MHz, 150 W CAP, PRF = 50 kHz, RF bias 10 MHz.

of the vertical. These differences in angular distributions (photons being isotropic and ions being anisotropic) in large part explain the results of our simulations.

The geometry used for profile simulation is shown in figure 18. The photoresist has a width of 120 nm and height

of 180 nm over Si. A non-eroding hard-mask is used to isolate the effects of photon-stimulated etching on the profile. The Si has a height of 390 nm over SiO₂. Etching (and over-etching) continued until the feature was cleared. Etch profiles of the Si fin are shown in figure 18(b) for pressures of 10, 60 and 100 mTorr. Undercutting of the mask can be observed in these profiles, particularly at higher pressures. Even though there is a small chemical component to etching and ions which graze the sidewall, about half of the undercutting results from the nearly isotropic VUV fluxes that strike the sidewalls of the feature and stimulate the etch. Since the Cl passivation of the sidewalls is nearly independent of location, the rate of photon stimulated etching is largely determined by the convolution of the view-angle of the surface site to the plasma and the angular distribution of the VUV fluxes.

The photon-stimulated undercutting can be quantified by integrating all volume etched beneath the mask, and plotted against pressure in figure 19. Undercutting increases with pressure from 10 mTorr, reaching a peak at 60 mTorr and slightly decreasing thereafter. This behavior coincides well with the dependence of β on pressure, which also peaks near 60 mTorr. Since the energies of the incident ions are well above the threshold for Si etching, clearing of the feature is mainly determined by the fluence of ions, and so the total fluence of ions is approximately the same at different pressures at the time of clearing the feature. The relative amount of isotropic VUV fluxes which strike the side wall is therefore directly proportional to β , which then determines the amount of undercut.

For $\beta \leq 0.3$, the undercut produced by the isotropic VUV fluxes is noticeable, but may not be that different from what may occur by grazing ions or an unusually broad ion angular distribution. However, as shown above, depending on process conditions β may be as large as 2–4. To demonstrate the potential impact of large VUV fluxes on feature evolution, the magnitudes of photon fluxes were artificially adjusted to produce $\beta = 0-4$ while maintaining all other conditions the same for the 20 mTorr case. The resulting profiles are shown in figure 18(c) and the amount of undercut is shown in figure 19. As β increases, the profiles are significantly undercut beneath the mask by the isotropic VUV fluxes. The undercut increases nearly linearly with β . These results



Figure 18. Predictions for feature profiles for Si etching. (a) Mask and feature before etching (b) profiles for different pressures (c) profiles resulting from specifying magnitudes of VUV fluxes using the angular distributions at 20 mTorr.

indicate that the photon-assisted etching process, which facilitates the undercut, is limited by the fluence of photon fluxes for conditions where the Si remains highly chlorinated.



Figure 19. Undercut for pressure 10–60 mTorr and VUV/ion flux ratios from 0.2 to 4. The curve labeled ratio is for varying the VUV/ ion flux ratio whose scale is at the top. The curved labeled pressure is for varying the gas pressure, whose scale is on the bottom.

6. Concluding remarks

In this work, we have discussed results from a numerical investigation of radiation transport in ICPs sustained in Ar/ Cl₂ mixtures with the goal of controlling the magnitude of VUV photon fluxes incident onto a substrate, and assessing possible repercussions on etching of Si features. VUV emission originating from $Ar(1s_4)$ (106.7 nm), $Ar(1s_2)$ (104.8 nm) and $Cl(3p^44s)$ (139nm) were compared to ion fluxes to the substrate. Potential control of VUV-to-ion fluxes ratio was demonstrated by changing pressure, Cl₂ fraction in the mixture, and reactor wall conditions (through surface recombination reaction of Cl) with continuous wave power. Coarse spectra control of the spectrum of VUV fluxes can also be achieved through Cl₂ fraction and reactor wall conditions. Pulsed power also provides a means to spectrally control the VUV fluxes due to the overshoot in T_e that is a function of duty cycle.

The potential impact of controlling VUV fluxes, and their ratio to ion fluxes, on semiconductor processing was demonstrated by model predictions of etching Si fins. VUV fluxes from ICPs sustained in Ar/Cl₂ are angularly more isotropic than ion fluxes. VUV stimulated etching processes are therefore, on a relative basis, therefore more important on side walls compared to ion fluxes, and so account for undercutting of the mask in fin-like structures. VUV stimulated processes during semiconductor processing now occur to some degree, in all low pressure plasma systems since all low pressure plasmas produce VUV fluxes to surfaces. Controlling the VUV fluxes provides the opportunity to refine these processes.

The final choice of processing conditions for plasmas producing significant VUV fluxes, as discussed here, depends on the intended application. For microelectronics fabrication where undercut is usually not desirable, choosing conditions which minimize VUV fluxes, that is lower β , would likely be the best strategy. For the conditions of this study, lower β is achieved with lower pressures, less surface recombination, higher Cl₂ fractions and cw operation (as opposed to pulsed operation). On the other hand, processes that require soft activation energy (e.g. polymer curing while minimizing ion bombardment) might benefit from having larger VUV fluxes compared to ion fluxes- that is, larger β (higher pressures, more surface recombination, lower Cl₂ fractions and pulsed operation).

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