Insights into the mechanism of in-plasma photo-assisted etching using optical emission spectroscopy

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Various mechanisms have been proposed to explain photo-assisted etching (PAE) of Si, including photogenerated carrier-mediated etching, photon-stimulated desorption, and photon-induced damage (breaking of Si–Si bonds) caused mainly by vacuum ultraviolet photons irradiating the substrate. In this study, the authors use optical emission spectroscopy to gain an insight into possible in-plasma PAE mechanisms. Emissions from Cl, Si, SiCl, and Ar were recorded as a function of power while etching p-Si in Cl_2/Ar Faraday-shielded inductively coupled plasmas at a pressure of 60 mTorr with no substrate bias. Under these conditions, ion-assisted etching was negligible and PAE was dominant. The Si:Ar optical emission intensity ratio, I_{Si}/I_{Ar} (proportional to the etching rate of Si), increased substantially with power. Accounting for the contribution to this signal from the dissociation of $SiCl_x$ (x = 1–4) etch products, the residual increase in the emission indicated that the PAE rate also increased with power. Time resolved emissions were also recorded in a pulsed plasma where power was modulated between 500 and 300 W. I_{Si}/I_{Ar} was found to modulate with the instantaneous power. This rules out the photon-induced damage mechanism since, if this mechanism was dominant, the I_{Si}/I_{Ar} signal would not be modulated. *© 2016 American Vacuum Society.*
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I. INTRODUCTION

Plasma etching continues to play a crucial role in the fabrication of nanoelectronic devices. Plasma etching (or reactive ion etching) is typically an ion-assisted process in which energetic ion bombardment results in breaking substrate lattice bonds, promoting surface reactions and desorption of etch products. Recently, it was discovered for p-type silicon that, in addition to ion-assisted etching, vacuum ultraviolet (VUV) photons (<180 nm) generated in the plasma also contribute substantially toward etching, especially at ion energies lower than the ion-assisted etching threshold.[1,2] This in-plasma photo-assisted etching (PAE) could be detrimental to the development of self-limiting processes required for atomic layer etching.[3] Hence, it is imperative to understand the role of VUV photons in etching silicon, especially at very low ion energies.

A number of studies have been carried out to elucidate the role of visible and ultraviolet (UV) photons in the etching of silicon in a halogen environment *without a plasma*. Most of these studies attributed photo-assisted etching to the creation of electron–hole pairs and reactions of these carriers at the surface.[4,5] Other researchers have proposed that VUV photons possess sufficient energy (>7 eV) to enhance photodesorption, thereby facilitating etching.[6] Photon induced damage was reported for thin films of SiO_2,[7] and SiCOH (Refs. 8 and 9) due to scission of Si–O and Si–C bonds, respectively. UV irradiation was found to enhance etching of silicon using a chlorine atom beam and was attributed to generation of crystal defects that promoted silicon etching by Cl atoms in the damaged layer.[10,11]

The two processes discussed above should behave differently in that carrier-mediated etching should cease rapidly after the plasma is extinguished and photo-generated carriers decay rapidly, while etching caused by defects should continue after the plasma is extinguished until the damaged layer etches away. This can be verified by modulating the plasma power between two different values at a rate that is much faster than that required to remove a monolayer. Defects (broken Si–Si bonds) created by VUV photons when the plasma is operated at a higher power would remain even after the plasma power is turned down, as it takes longer for the plasma to etch one monolayer compared to the power modulation period. The defect sites would therefore not be modulated, nor would the Cl number density if the modulation frequency is chosen to be faster than the Cl loss rate, and etching would continue at a high rate even after plasma power is turned down.

On the other hand, if photo-generated carriers dominate, then etching would be proportional to the instantaneous carrier density. If the carrier recombination occurs at a rate that is higher than the power modulation frequency, then the carrier density should be modulated in proportion to light intensity. Minority carrier recombination near the surface will dominate and be fast on these highly defective surface layers. Minority carrier lifetimes of $\sim 10\,\mu s$ have been reported[12] on native oxide covered Si surfaces; hence, carrier lifetimes in plasma-exposed Si will be $\ll 10\,\mu s$. Light intensity is proportional to the product of plasma electron density (n_e) and the electron impact excitation rate coefficient for

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producing emission, which is a function of electron temperature (T_e). T_e should be nearly independent of power and n_e will be proportional to power. Therefore, a carrier-mediated PAE etching rate should be proportional to power over much of the modulation period. A concerted, photo-stimulated desorption process will behave in a similar manner.

In this work, we use optical emission spectroscopy (OES), in an effort to gain insight into the mechanism of in-plasma photo-assisted etching of Si. The light intensity of key emitting radicals was monitored in both continuous wave (cw) and pulsed plasmas.

II. EXPERIMENT

The apparatus consisted of a Faraday-shielded inductively coupled plasma (ICP) powered by a 3 turn copper coil, as described previously.[1] Radio frequency (RF) power (13.56 MHz) was delivered to the plasma by a RF amplifier (ENI A500) that was driven by a function generator (HP 3325A). For some experiments, the plasma was modulated between 500 and 300 W power at 1 kHz with 50% duty cycle. A Cl_2/Ar gas mixture was fed through the electrically grounded top flange. The fraction of chlorine in the gas mixture was varied between 10% and 71% by changing Ar flow rate for a fixed Cl_2 flow of 25 sccm. A needle valve was employed to introduce a trace amount of $SiCl_4$ for some experiments. The pressure downstream from the ICP source was measured using a capacitance manometer (MKS 629). Pressure above the sample (corrected for the pressure drop between the ICP source and the point at which the measurement was made) was maintained at 60 mTorr using a throttle valve. At this pressure, with no bias applied to the substrate, it is expected that very few ions will have energies above the ion-assisted etching threshold of silicon (~16 eV).[2]

The sample to be etched [p-Si (100), resistivity = 5–50 Ω/cm] was cleaved into small pieces (approximately 1.5 cm^2), cleaned with acetone and methanol to remove carbon contaminants, followed by dipping in 48% hydrofluoric acid solution to strip the native oxide, and blown dry with nitrogen. The cleaned sample was fixed to a 1 in. diameter stainless steel sample holder using carbon tape to ensure good electrical contact. The sample holder was mounted on a water cooled rod that served to maintain the sample at a fixed temperature, and transferred into the plasma, where it was held against a grounded stage.

OES was used to monitor the light intensity of key emitting species Si (288.1 nm), Ar (750.4 nm), Cl (724 nm), SiCl (280.3 nm), and Cl_2 (band centered at 305 nm). A periscope, comprised of two right angle prisms (1 × 1 cm along the perpendicular faces), was employed to collect light integrated over a region ~1 cm above the Si surface. The light was imaged with lenses (magnification slightly smaller than 1:1) onto a 1 cm long, vertically oriented entrance slit of a monochromator. The scanning monochromator had a 1200 grooves/mm diffraction grating which, combined with entrance and exit slit widths of 100 μm, produced a resolution of 2 Å full width at half maximum (FWHM). The dispersed light was detected by a GaAs photomultiplier tube (RCA C31034). For time resolved emission measurements, current from the photomultiplier tube was measured as the voltage drop across a R = 3 kΩ resistor using an oscilloscope, and further damped by the capacitance, C of the input. The detector response time determined from the RC time constant was ~0.3 μs, very small compared to the time of flight (~10 μs) of etching products across the 1 cm region over which light was collected. For low intensity emissions (e.g., Si), the slits of the monochromator were set to 500 μm, yielding a resolution of 10 Å FWHM.

III. RESULTS

A. Silicon etching in Cl_2/Ar plasmas with cw power

As mentioned above, the contribution of ion-assisted etching was negligible in the Faraday-shielded ICP at a pressure of 60 mTorr, and no substrate bias. In addition, Cl atoms do not etch p-type Si spontaneously at room temperature.[13] Hence, photo-assisted etching was the prevailing mode of etching.[1,2] An emission spectrum recorded while etching at a power of 350 W is shown in Fig. 1. SiCl and Si peaks are observed due to etching of the Si substrate, as found previously.[1,2] (It should be pointed out that if the bare Si substrate is replaced with a SiO_2-coated Si sample, and the plasma is ignited with no intervening "conditioning" of the chamber walls, Si and SiCl emissions are not detected, indicating that very little of these emissions detected with a Si substrate on the stage are due to etching of Si-containing layers that could be present on the chamber walls.) The broad emission band corresponding to $SiCl_2$ (band centered ~323.5 nm) is not observed, and emission corresponding to $SiCl_3$ (band centered at ~385.5 nm) is not clearly distinguished from other broad emitters in this region (Cl_2 and Cl_2^+). Cl_2 emission bands near 255 and 305 nm can also be seen clearly. Several lines expected for Ar are observed between ~700 and 900 nm, where the vast majority of emission is from Cl.

Optical emissions from Si, SiCl, Cl, and Ar were recorded as a function of power and gas composition. Not surprisingly, the Ar emission intensity increases with power and %Ar in the feed gas (Fig. 2). The super-linear increase in

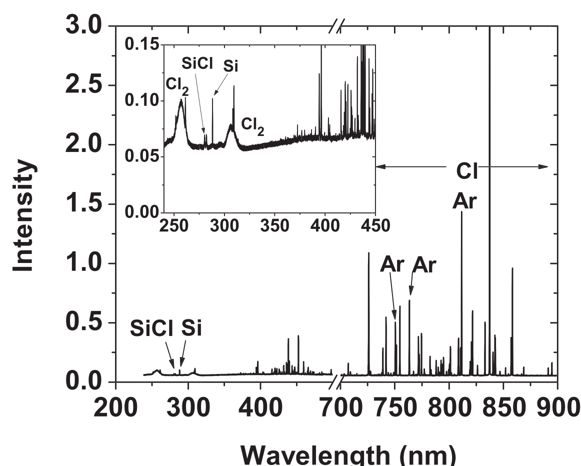

FIG. 1. Optical emission spectrum (200–900 nm) recorded while etching Si in a 50%Cl_2/50%Ar ICP with 300 W of power.

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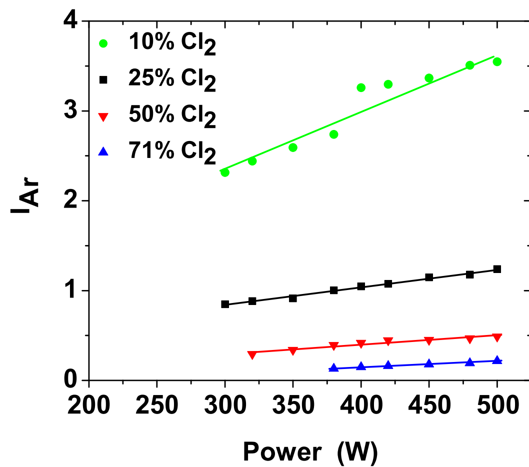

FIG. 2. (Color online) Ar (750.4 nm) intensity as a function of power for different gas compositions.

intensity with increasing %Ar is attributed mainly to the increasing electron-to-Cl^- number density ratio between 29% and 90% Ar. The Ar 750.4 nm emission is produced when the 4p′[1/2] level at 13.48 eV decays to the 4s′[1/2]° level at 11.83 eV. This in turn decays to the ground state by emitting the most intense of the VUV Ar emissions at 104.8 nm. It therefore follows that the relative intensity of the Ar VUV emission is expected to depend on power in a manner similar to that for the 750.4 nm emission shown in Fig. 2.

Cl/Ar emission intensity ratios (I_{Cl}/I_{Ar}) are presented in Fig. 3. Since the Cl_2 feed gas is probably substantially dissociated, and the electron temperature is rather low at 60 mTorr, the higher-energy process of dissociative excitation of Cl_2 to produce Cl emission[14] is expected to be negligible. Hence, I_{Cl}/I_{Ar} is expected to be proportional to Cl number density. At a given power, I_{Cl}/I_{Ar} scales nearly with the Cl_2 to Ar feed gas ratio. At higher $\%Cl_2$, I_{Cl}/I_{Ar} increases sublinearly with power, as might be expected. For chlorine addition $<50\%$, however, I_{Cl}/I_{Ar} is independent of power, suggesting that Cl_2 is mostly dissociated into Cl, as reported in Refs. 14 and 15.

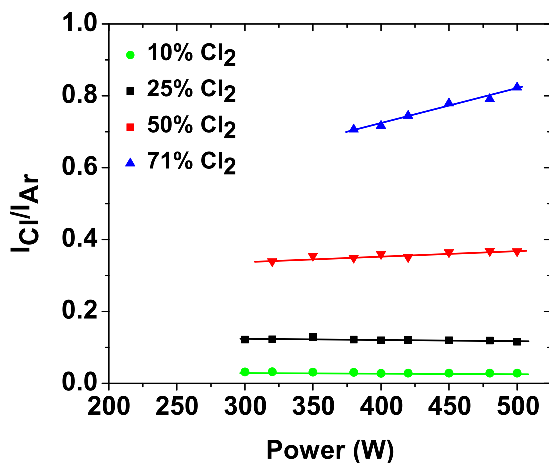

FIG. 3. (Color online) I_{Cl}/I_{Ar} as a function of power for different gas compositions.

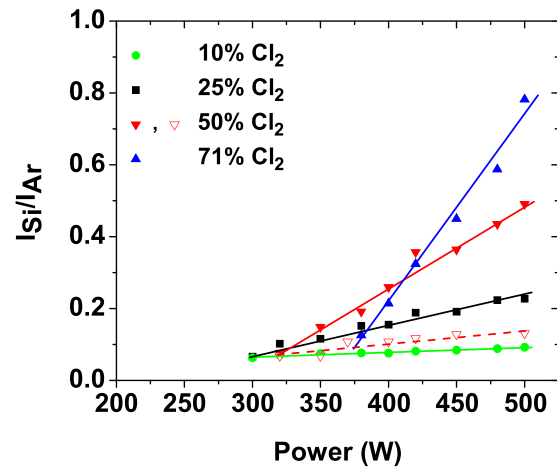

FIG. 4. (Color online) I_{Si}/I_{Ar} as a function of power for different gas compositions. Open inverted triangles denote I_{Si}/I_{Ar} when a trace amount of $SiCl_4$ gas was added to the gas mixture with no Si substrate present.

Emission intensity ratios for Si/Ar (I_{Si}/I_{Ar}) and SiCl/Ar (I_{SiCl}/I_{Ar}) are presented in Figs. 4 and 5, respectively. Si and SiCl emission intensities are expected to arise, at least in part, from electron impact excitation of these species, and to therefore scale, at least qualitatively, with their relative number densities in the plasma. These emissions can also come from electron-impact dissociative excitation of more highly chlorinated species such as $SiCl_2$. Previously, it was shown that Si emission intensity was directly proportional to etching rate, which was varied by changing substrate bias power at constant ICP power, pressure, and feed gas composition.[1,2] In the present study, I_{Si}/I_{Ar} increases with power, especially at higher Cl_2 percentages. Since the VUV photon flux to the substrate increases with power between 300 and 500 W (assumed proportional to the 750.4 nm Ar line intensity), the increase in I_{Si}/I_{Ar} likely reflects an increasing photo-assisted Si etching rate.

To determine how much of the rise in I_{Si}/I_{Ar} with increasing power is due to the increasing dissociation of $SiCl_x$ (x = 1–4) etching products (eventually producing Si), a trace

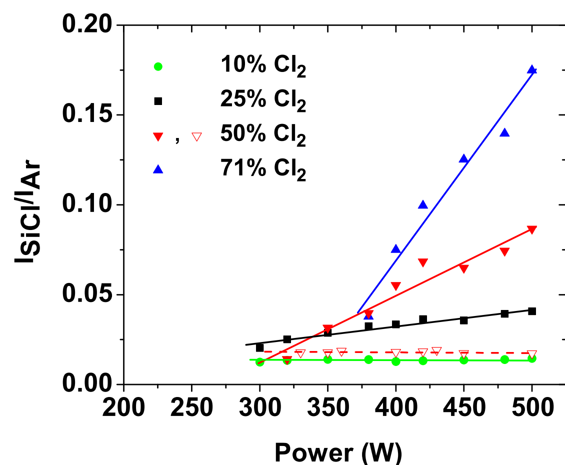

FIG. 5. (Color online) I_{SiCl}/I_{Ar} as a function of power for different gas compositions. Open inverted triangles denote I_{SiCl}/I_{Ar} when a trace amount of $SiCl_4$ gas was added to the gas mixture with no Si substrate present.

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amount of $SiCl_4$ gas was introduced in a 50%Cl_2/50%Ar gas mixture, with no Si substrate present, to simulate the dissociation of $SiCl_x$ etching products. At 320 W, a flow of 0.3 sccm $SiCl_4$ was found to produce a I_{Si}/I_{Ar} value equal to that observed during Si etching in a 320 W 50%Cl_2/50%Ar plasma. As power was then increased from 320 to 500 W, I_{Si}/I_{Ar} increased ~2-fold (red open inverted triangles in Fig. 4). During Si etching (with no added $SiCl_4$), however, I_{Si}/I_{Ar} increased ~6.5-fold between 320 and 500 W (red solid inverted triangles in Fig. 4). If half of this increase is due to fragmentation of etching products, then a remaining factor of ~3.2 is attributed to an increase in etching rate. This is somewhat in excess of the ~1.9-fold increase in the product of VUV (using the 750.4 nm Ar line as a surrogate) and Cl fluxes determined from Figs. 2 and 3, respectively (the product is simply given by the Cl emission intensity). Given the large mismatch in energies of the levels involved in Ar and Si emission [13.5 (Ref. 16) and 5 eV, (Ref. 17), respectively], the remaining unexplained factor of ~1.8 increase of I_{Si}/I_{Ar} with power is perhaps not surprising.

The dependence of I_{Si}/I_{Ar} on power is much stronger with increasing Cl_2 percentage. This trend can be qualitatively explained as a transition from chlorine-starved conditions at 10% Cl_2 addition, where etching is limited by the flux of Cl and Cl_2, and is nearly independent of VUV flux, to chlorine-saturated conditions at 71% Cl_2 addition, where etching is limited by photon flux and depends less on chlorine flux. Additional complications in relating I_{Si}/I_{Ar} to etching rate at higher Cl_2 percentages, due to changes in the electron energy distribution and the mismatch in threshold energies to excite the Ar and Si emitting levels (see above), precludes quantitative interpretations. The trends in I_{SiCl}/I_{Ar} as a function of power and gas composition are very similar to those in I_{Si}/I_{Ar} versus power and gas composition (Fig. 5). This implies that I_{SiCl}/I_{Ar} is also proportional to the Si etching rate.

B. Silicon etching in Cl_2/Ar plasmas with pulsed power

The results presented above would be consistent with either the lattice damage or carrier mediated processes discussed earlier. To distinguish between these two mechanisms, Si was etched as power to the ICP coil was switched between 500 and 300 W at a frequency of 1 kHz and 50% duty cycle. The etching rate at 400 W was reported to be 330 nm/min at 60 mTorr in a previous publication.[2] During the 500 μs period at 500 W, approximately 0.00275 nm of Si is removed, which is about 1% of a monolayer. The density of any defects created by the VUV photons would not be altered during this period. In addition, the chlorine coverage on the surface is not expected to change significantly because the Cl flux (proportional to the Cl number density) is nearly the same at 500 and 300 W (see optical emission actinometry measurements below). Therefore, photo-assisted etching due to a photon-induced damage mechanism would not be modulated. Conversely, for a carrier-mediated etching mechanism, the etching rate would be modulated in proportion to the VUV flux, and therefore plasma power, since the carrier lifetime is ≪500 μs (Ref. 12), i.e., much less than the period of plasma modulation. Other mechanisms such as photo-stimulated desorption of products would also exhibit a modulated signal.

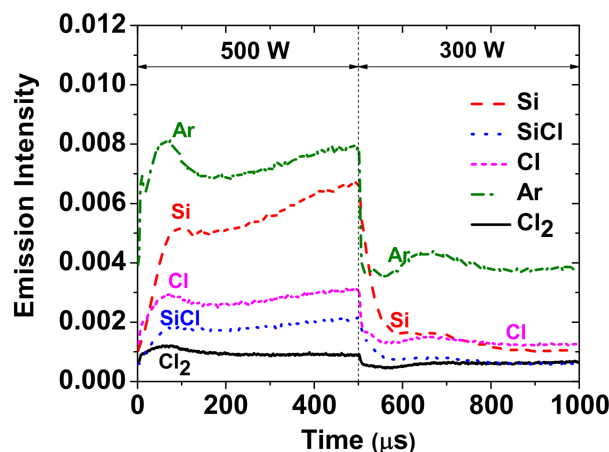

Fig. 6. (Color online) Time resolved optical emission of Ar, Cl, Si, SiCl, and Cl_2 recorded while etching Si in a 50%Cl_2/50%Ar pulsed plasma. Plasma power was modulated between 500 and 300 W at a frequency of 1 kHz and 50% duty cycle. Emission intensity of Si and SiCl are multiplied by a factor of 2 for clarity.

Time resolved emission intensities of Ar, Si, SiCl, Cl, and Cl_2 were recorded during Si etching (Fig. 6). As the plasma power is modulated from 500 to 300 W, emissions are also found to modulate. At 500 W, Ar emission intensity rises quickly and reaches a quasisteady state level which is about twice that at 300 W. This modulation in intensity is comparable to the factor of 1.66 (500/300) modulation in the plasma power and is attributed to the change in electron density with plasma power. Similar behavior is observed for the Cl emission. Si and SiCl emissions rise and fall at slower rates, relative to Ar and Cl emissions. This is ascribed to the slower modulation in the population of low energy electrons capable of exciting Si and SiCl emissions.

Time-resolved emission intensities for Cl, Si, and SiCl, normalized to Ar emission, are presented in Fig. 7. I_{Cl}/I_{Ar} exhibits small spikes when power first drops to 300 W, but

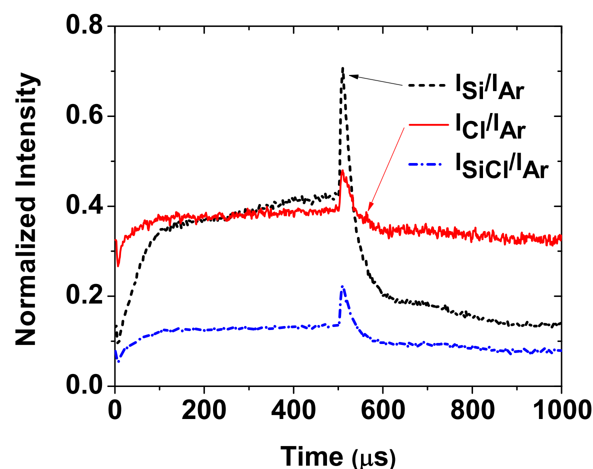

Fig. 7. (Color online) Time resolved normalized emission intensities recorded during Si etching in a 50%Cl_2/50%Ar plasma where power was modulated between 500 and 300 W, at a frequency of 1 kHz and 50% duty cycle.

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then settles to values that are nearly equal to (~85% of) that at 500 W. Conversely, when power drops from 500 to 300 W, I_{Si}/I_{Ar} spikes but finally settles to a quasisteady value that is about 25% of that at 500 W. I_{SiCl}/I_{Ar} exhibits similar but less pronounced trends, settling to a value at the end of the 300 W period that is about 60% that at 500 W. The more pronounced spikes in I_{Cl}/I_{Ar} and I_{SiCl}/I_{Ar} accompanying power switching are due to the lower-energy emitting levels of Si and SiCl being less sensitive to rapid transients in T_e, compared with Ar. The modulation in I_{Si}/I_{Ar} and I_{SiCl}/I_{Ar} suggests that the Si etching rate is also modulated.

The time response of the normalized emission intensities may be understood by considering the localized and global Si production and loss mechanisms. For an etching rate of 330 nm/min (measured under similar conditions[2]), the flux of Si-containing products is $F_{SiCl_x} = 2.78 \times 10^{16}\,cm^{-2}\,s^{-1}$. For the 1.5 cm^2 sample, this corresponds to a flow rate of 0.092 sccm. For the Cl_2 and Ar feed gas flow rates of 25 and 25 sccm (50%Cl_2/50%Ar), the total flow rate through the reactor is between 50 (if no Cl_2 dissociation) and 75 sccm (for complete dissociation in Cl atoms). Taking the average of the two, the mole fraction of Si etching products released into the reactor is $0.092/67 = 1.37 \times 10^{-3}$. An upper limit to the partial pressure in the reactor (if no Si products deposit on the walls) is then 0.08 mTorr at the total pressure of 60 mTorr. If the gas temperature is 600 K (typical for these conditions), then this corresponds to a number density, C_{av}, of about $1.4 \times 10^{12}\,cm^{-3}$ for the background etching product gas in the chamber.

The number density above the sample will be enriched in primary products of Si etching. The mean free path at 60 mTorr is ~0.1 cm, thus at a distance of $l = 1$ cm from the surface, desorbing products will be escaping by ordinary diffusion. At 600 K and 60 mTorr, the binary diffusion coefficient D_{bin} for $SiCl_3$, $SiCl_2$, SiCl, and Si in Ar was estimated to be 3570, 4080, 5230, and 4480 cm^2/s, respectively, from Chapman–Enskog theory,[19] using Lennard-Jones parameters.[20]

The reactor geometry was approximated in 1D as a Si surface a distance H from a plane at which diffusing species evolving from the surface (i.e., etching products, $SiCl_x$) are removed from the gas through pumping or are depositing on the walls. Then, the concentration of species at a distance l from the surface, C_l, relative to the average concentration, C_{av}, in the reactor (defined above) is given by

$$C_l/C_{av} = 1 + \frac{F_{SiCl_x}}{C_{av} D_{bin}}\left(\frac{H}{2} - l\right), \tag{1}$$

where a linear concentration profile was assumed. Equating H with the discharge tube radius of 4.3 cm, and assuming a uniform temperature of 600 K yields a value of $C_l/C_{av} = 6.1$ at a distance of $l = 1$ cm from the substrate surface. Therefore, the large majority of the signal is coming from the primary products diffusing through the near-surface region imaged by the spectrometer optics. The time it takes for products to reach the 1 cm distance from the Si surface is $\sim l^2/D \approx 225\,\mu s$, or about the time it takes for I_{Si}/I_{Ar} and I_{SiCl}/I_{Ar} in Fig. 7 to reach quasisteady state, after power changes from 500 to 300 W. The conclusion that emission from Si and SiCl is enriched near the surface is also supported by the fact that only 0.092 sccm of the equivalent product flow rate from etching in a 50%Cl_2/50%Ar plasma at 320 W produces the same I_{SiCl}/I_{Ar} and I_{Si}/I_{Ar} values as that obtained from the addition of 0.3 sccm of $SiCl_4$ background gas, as discussed above. The ratio of $0.3/0.092 = 3.3$ is comparable to the factor of 6.1 found above.

It appears that C_{av} is also modulated, as verified by experiments and simple estimates based on the Si loss processes. Emission signals shown in Fig. 8 were recorded through a window on the boundary electrode that is about 10 cm away from the sample stage. I_{Si}/I_{Ar} was recorded while etching silicon in the power-modulated plasma. The signal modulated by a factor of 1.67 (≈power ratio = 500/300) which is similar to the modulation of the signal recorded with a trace amount of $SiCl_4$, where the Si emission is solely due to the dissociation of $SiCl_4$ (also shown in Fig. 8). This modulation in Si emission intensity is less compared to the modulation in C_l observed in the vicinity ($l = 1$ cm) of the substrate (Fig. 7).

Away from the Si surface, the loss of Si etch products in the plasma is due to pumping, as well as reactions on the walls, and in the gas-phase. At 60 mTorr and 50 sccm, the gas residence time within the combined ~10 l volume of the plasma chamber and tubing above the pump is ~1 s. If we just take the ~1 l discharge tube volume, then the gas residence time is 0.1 s. Both are much longer than the 1 ms modulation period. For a cylindrical chamber of radius R and height h, the loss to the walls by diffusion and reaction is given by[21]

$$\frac{1}{k_d} = \frac{\Lambda^2}{D_{bin}} + \frac{V}{A}\frac{2(2-\gamma)}{\gamma v_{th}}, \tag{2}$$

where V/A ($= Rh/2[R + h]$) is the volume to surface area ratio of the chamber, Λ is an effective length ($1/\Lambda^2 = [\pi/h]^2 + [2.405/R]^2$),[18] and γ is the probability that the species

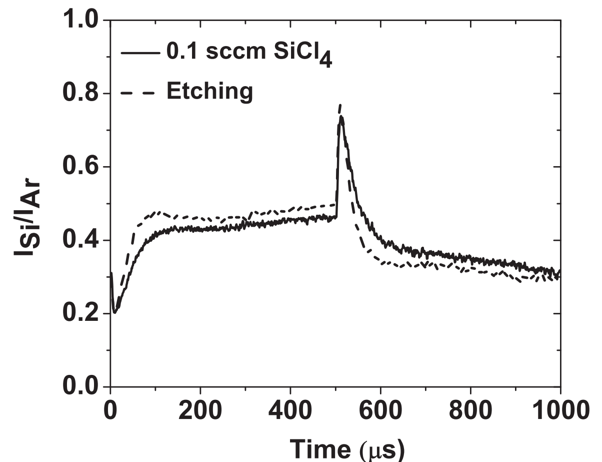

Fig. 8. Time resolved I_{Si}/I_{Ar} in a 50%Cl_2/50%Ar plasma where power is modulated between 500 and 300 W, recorded through a window on the top flange. The modulation of the signal in the background gas (thicker line) is due to the dissociation of the etch products alone (no Si sample present) by adding 0.1 sccm of $SiCl_4$.

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(etch product) sticks to the wall. Si and SiCl have wall sticking probabilities greater than those for the higher chloride etching products.[22,23] Assuming that they are lost at the walls (and probably converted to higher chlorides that subsequently desorb) with a high 50% probability (i.e., $\gamma = 0.5$), and further assuming the volume is defined by just the discharge tube and not the downstream chamber (R = 4.3 cm, h = 17.8 cm, and V = 1 L), then $1/k_d$ is estimated to be $\sim$1 ms, or about equal to the modulation period.

A far more important loss process, at least for Si, is the gas phase reaction with Cl_2

$$Si + Cl_2 \rightarrow SiCl + Cl. \quad (3)$$

With a reported rate coefficient of 3.3×10^{-10} cm^3 s^{-1},[24] this is the dominant loss process. Even if Cl_2 were 90% dissociated, this reaction would occur in $\sim$100 μs, i.e., much faster than the modulation period and the time for loss at the walls. A similar process for SiCl, forming $SiCl_2$, could also be the rate-limiting reaction.

The lifetime for the loss of Cl atoms to the walls by diffusion and recombination was estimated from Eq. (2) to be 6.4 ms for a recombination coefficient of $\gamma = 0.04$ (Ref. 25) on plasma-conditioned stainless steel. A lower average recombination probability is expected in the present case because of the more inert alumina tube surface, favoring a still longer lifetime for Cl, and thus much longer than the 1 ms modulation period. Therefore, the Cl atom density (proportional to the I_{Cl}/I_{Ar} intensity ratio) recorded in the pulsed plasma is hardly modulated (Fig. 7).

Assuming that the Si and SiCl emission signals are mostly coming from species that have not reached the walls and become part of the background gas, we can finally determine how the instantaneous etching rate scales with instantaneous power. As given above (Fig. 7), I_{Si}/I_{Ar} is 3.8 times higher at 500 W than at 300 W. To remove the portion of this increase that is due to increased fragmentation of $SiCl_x$ products at higher power, we note that I_{Si}/I_{Ar} produced by adding a trace of $SiCl_4$ to the Cl_2/Ar feed gas with no Si substrate present is 2.2 times higher at 500 W, compared with 300 W (derived from a linear least squares fit to the open red inverted triangles in Fig. 4). Thus the corrected increase in I_{Si}/I_{Ar}, which is expected to reflect the relative change in instantaneous etching rate, is 3.8/2.2 = 1.7, which is comparable to the ratio of powers (1.67), as well as the ratio of Ar emission at 750.4 nm (2.0 from Fig. 6) that is assumed to be proportional to the VUV flux. Similarly for I_{SiCl}/I_{Ar}, the corrected rise is 1.7 between 300 and 500 W (using the data in Figs. 5 and 7). Therefore, it appears that the instantaneous etching rate is proportional to the instantaneous VUV flux.

Lastly, it has to be mentioned that the ratio of I_{Si}/I_{Ar} (Fig. 4) in a cw plasma at 500 W to that at 300 W (0.491/0.076 $\approx$ 6.5), is higher than the ratio of the quasisteady state values of I_{Si}/I_{Ar} (Fig. 7) in a pulsed plasma operating between 500 and 300 W ($\approx$3.4). This implies that, under the conditions used, the modulation period of the pulsed plasma is not long enough to reach the plateau that would be obtained in a cw plasma, under otherwise the same operating conditions. This disparity could be due to a long time scale process (for example, changing wall conditions).

IV. SUMMARY

OES was used to study in-plasma photo-assisted etching (PAE) of p-Si in Cl_2-Ar plasmas at 60 mTorr, without substrate bias. The light intensity from key species (Si, Ar, Cl, and SiCl) was monitored in both cw and pulsed plasmas. The emission intensity ratio, I_{Si}/I_{Ar}, was found to increase super-linearly with plasma power during silicon etching in cw plasmas. To account for the contribution to this signal from the dissociation of silicon etch products, a trace amount of $SiCl_4$ gas was introduced into the plasma (without a Si substrate present) to simulate the emission of etching products. With added $SiCl_4$, it was found that the ratio I_{Si}/I_{Ar} increased roughly by a factor of two, which was smaller compared to the six fold increase observed while etching silicon (no added $SiCl_4$). This super-linear increase in the signal may be attributed to the addition of silicon etch products into the plasma due to PAE that increases with power. The increase in PAE with power is due to the corresponding increase in the VUV photon flux to the substrate.

Time resolved emission was also recorded during Si etching in a pulsed plasma where the power was modulated between 500 and 300 W. The time evolution of the signal (I_{Si}/I_{Ar}) over the pulse period was explained based on the rate of production and loss of the silicon etch products. It was found that the region in the immediate vicinity of the sample, where the emission signals were recorded, was enriched with the etching products in comparison to the reactor bulk. The contribution to the signal due to back diffusion of the etching products was minimal, and modulation of the signal was mainly due to the modulation of the PAE rate with power. The observation of a substantially modulated I_{Si}/I_{Ar} signal rules out a damage-induced mechanism of in-plasma PAE since, if this mechanism was dominant, I_{Si}/I_{Ar} would not be modulated.

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