Alternating fluxes of positive and negative ions from an ion–ion plasma

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Relatively electron-free positive- and negative-ion plasmas (ion–ion plasmas) have been achieved in the afterglow of pulsed-power Cl_2 discharges. The application of a low-frequency (20 kHz) bias voltage phase locked to the source power modulation and synchronous with the ion–ion plasma, resulted in alternating fluxes of positive (Cl_2^+) and negative (Cl^-) ions on a substrate. These results qualitatively agree with a one-dimensional fluid model. This technique to produce alternate irradiations could be used to reduce differential charging-induced damage in high-aspect-ratio etching processes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1338500]

The high-aspect-ratio features and thin etch-stop films characteristic of modern devices have led to requirements for highly anisotropic, uniform, and selective plasma etches. While new high-density plasma etch tools have better etch capabilities than previous generations, they can also cause significant problems such as lateral etching (notching), trenching, bowing, and dielectric breakdown. Computer simulations have shown differential charging of high-aspect-ratio features due to electron shading and subsequent ion deflections to be a cause.[1–3]

Bringing electrons to the bottom of high-aspect-ratio features could improve plasma-etch performance and, consequently, has been tried. For example, Hashimoto *et al.* observed reduced-oxide damage resulting from a polysilicon etch when the wafer was biased so as to attract electrons during the afterglow.[4] That study was performed using pulsed-argon discharges. Of course, electrons cannot contribute directly to the etching process, but negative ions carry the same charge and might contribute. As a consequence, finding a technique to extract negative ions with an anisotropic velocity distribution like that of positive ions could reduce device damage while maintaining a larger etch rate. In addition, halogen chemistry discharges, used extensively to etch polysilicon gate structures, crystalline Si trenches, via holes, and other features of modern devices, are rich in negative ions.[5–7]

While etching using negative ions appears desirable, the plasma potential in all but the most electronegative plasmas is sufficiently positive to prevent it. For example, we had simulated sheath field inversion (inversion allows negatively charged particles to be accelerated out of the glow center) and found that extraordinarily large electronegativities ($N_-/Ne \geqslant 1000$) were required to extract negative ions with any significant flux density.[8] It turns out that pulsing the plasma excitation in the presence of an attaching gas can enable such electronegativities and even form a nearly electron-free ''positive-ion–negative-ion'' plasma.[9,10] It is firmly believed that these ion–ion plasmas can be biased to extract either positive or negative ions, unfortunately, experimental proof is not yet published. Ahn, Nakamura, and Sugai, tried something related to this by applying a single positive-voltage pulse during the afterglow of a chlorine plasma.[5] The afterglow was very short lived, however, so the pulse was applied before an ion–ion plasma could be obtained. Despite this, they observed an enhanced etch rate and attributed it to negative ion assisted etching. In another related experiment, Shibayama, Shindo, and Horike observed F^- effusing from the downstream of a continuous wave SF_6 plasma using a mass spectrometer with no bias on the input aperture.[6] They observed a correlation between this F^- signal and the etch rate of silicon obtained in another reactor using a substantially different plasma source technology and a 400 kHz wafer bias. They also attributed the result to negative-ion-assisted etching.

In this work, we have shown that alternating fluxes of positive and negative ions can be brought to a substrate from ion–ion plasmas. This was achieved by applying a low-frequency bias voltage to the input aperture of a mass spectrometer during the afterglow of a Cl_2 discharge and observing the positive- and negative-ion signals.

The vacuum chamber consisted of a 10.2 cm (diameter) $\times$56 cm (length) Pyrex pipe with stainless-steel electrodes on each end (see Fig. 1). The electrode in front of the mass spectrometer has a 100 μm aperture and is isolated from ground while the electrode at the back end of the chamber is grounded. A Faraday shielded, 11.4-cm-long, three-turn helical antenna excites a plasma midway between the electrodes. The 13.56 MHz excitation is pulsed at 1 kHz and 50% duty ratio to provide a power of 300 W during the active glow. It produces ''on'' and ''afterglow'' times of 500 μs. A 13.56 MHz capacitive-coupled ''ignition antenna'' 4.5 cm from the back electrode is operated for a burst of 10 μsec to help ignite the ''ICP on'' (inductively coupled plasma) time. The ignition time-averaged power is less than 10 W. The antennae are connected through matching networks to ENI A500 and ENI A300 power amplifiers, respectively. A

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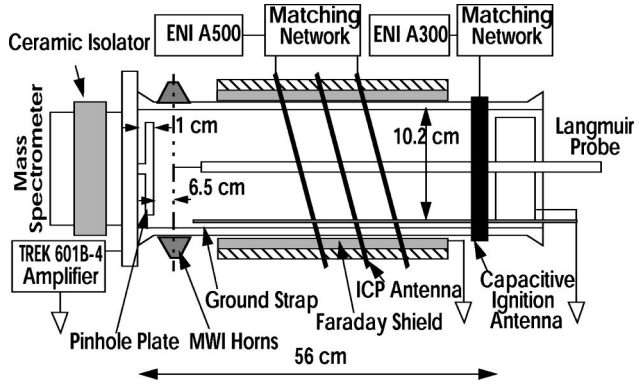

FIG. 1. System schematic.

TREK 601B-4 amplifier fills the 500 μs afterglow period with a sinusoidal voltage burst of 10 cycles at 20 kHz and 225 V_p applied to the mass spectrometer aperture electrode. This voltage is lower than the approximately 400 V required to ignite dc discharges in this reactor. It is what produced the alternate fluxes of positive and negative ions to the aperture electrode. It should be noted that similar results were obtained with much smaller amplitude bias voltages (5 V_p), but this set was chosen for this letter for comparison to the simulation results. The plasmas were formed in Cl_2 at 1 mTorr and 5 sccm and probed by a variety of diagnostics in addition to mass spectroscopy. Two diagnostics of importance to this letter include a time-resolved Langmuir probe and a 8.6 GHz microwave interferometer placed adjacent to the aperture electrode. The interferometer can detect down to a density of 10^8 cm^{-3}. It should be noted that a nickel-coated aluminum strap attached to the back electrode runs along the length of the tube to provide ground reference for the Langmuir-probe measurements. It stops 8.5 cm from the mass spectrometer. The interferometer horns are positioned between the biased electrode and the ground strap to detect any electrons possibly generated by the low-frequency bias.

Experimental evidence that alternating fluxes of positive and negative ions can be brought to the mass spectrometer's aperture electrode is shown in Figs. 2(a) and 2(b). There, the signals of positive ions (Cl_2^+, Cl^+) and negative ions (Cl^-) measured using the mass spectrometer have been plotted as a function of time. Alternating signals of Cl_2^+ and Cl^- are observed during the afterglow corresponding to the appropriate phases of the aperture electrode bias.

After plasma turn off and a short delay, the first spurt of Cl^- negative ions is measured by the mass spectrometer. Even under no bias conditions (not shown) this first spurt of negative ions is observed and decays with the same decay constant as the Cl^+ flux. This is in excellent agreement with work by Smith, Dean, and Adams in O_2.[11] In addition to the initial spike of Cl^-, we observe nine spurts (A–I) corresponding to the nine positive half cycles of bias. Interlaced spurts of Cl_2^+, one for each of the ten negative half cycles (1–10) are also observed. The successive peaks of both polarity ions gently decay in time as the ions are lost to extraction by the applied 20 kHz bias, ion–ion mutual neutralization, recombination and diffusion. A spurt of Cl_2^+ ions due to the capacitive ignition is also present. Note the two nonidealities in Fig. 2(a). First, the different transmission efficiencies for positive and negative ions of the mass spectrometer

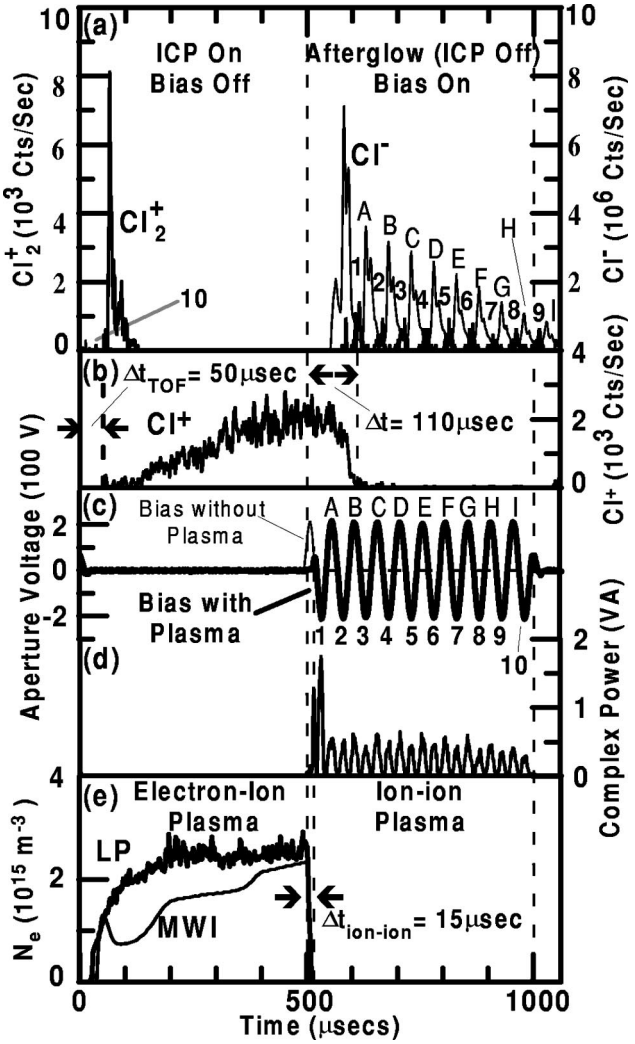

FIG. 2. Mass spectrometer signals for (a) Cl_2^+ and Cl^-, (b) Cl^+, (c) bias voltage on the pinhole plate, (d) amplitude of complex power supplied to the ion–ion plasma due to bias, and (e) Electron-density temporal variation by Langmuir probe (LP) and microwave interferometry (MWI) 6.5 cm from the plate.

lead to a factor of 1000 difference in the Cl_2^+ and Cl^- counts even though equal positive- and negative-ion fluxes are expected. We note that the ion currents to the aperture electrode are equal and opposite. As the mass spectrometer is pumped to 10^{-8} Torr, we do not think this disparity is due to a ''lifetime'' of positive ions during flight. It may be caused by differences in the ion lensing by the pinhole aperture or in the channeltron sensitivity to the two ions. Second, the time of flight (TOF) of the ions through the long quadrupole mass filter shifts the data by an amount $\Delta t_{TOF} \approx 50$ μs for both Cl^+ and Cl^-. The Cl_2^+ spurts to be shifted slightly more due to the larger mass.

While the alternating fluxes are of primary importance, several other characteristics of the data shown in Fig. 2 are also significant. For example, we note that the Cl_2^+ signal is large during the capacitive ignition and gives way to an increasing Cl^+ signal during the ICP-on stage. We think this is due to dissociative ionization. The Cl^+ flux would then reach a relative plateau once dissociation reaches near quasiequilibrium. A small Cl_2^+ signal (not shown) does exist after the ignition during the ICP-on stage. We also note the quick shift

from Cl^+ to Cl_2^+ after rf turn-off. This is most likely due to the following energetically favorable charge-exchange reaction.

$$Cl^+ + Cl_2 \rightarrow Cl + Cl_2^+, \quad \Delta E = -1.52 \text{ eV}.$$

This could cause the Cl^+ density to decrease much faster than the Cl_2^+ density in the afterglow. Helmsen *et al.* have shown that this reaction can alter the Cl^+/Cl_2^+ ratio in continuous chlorine plasmas.[12] Kushner estimated a reaction rate constant of $5.4\times10^{-10}\,cm^3\,s^{-1}$ using data from Ikezoe *et al.*[13,14] This rate constant indicates a decay time of approximately 57 μs for Cl^+ ions in 1 mTorr of Cl_2. Adding this to the 50 μs time of flight produces a delay of $\approx$110 μs from turn-off for the Cl^+ signal to vanish. This agrees well with our observed Cl^+ decay time [see Fig. 2(b)].

Because of concern over whether the applied bias might generate electrons, we have plotted the voltage on the mass spectrometer aperture plate in Fig. 2(c). The presence of electrons in combination with the TREK amplifier's finite output current capacity ($\leqslant$20 mA) results in the applied voltage being suppressed for the first 15 μs after rf turn-off. Once the electrons vanish, the voltage ''snaps back'' to its open circuit (i.e., no plasma) value as the ion saturation currents are smaller than 20 mA. The electron-density near the aperture electrode measured using the Langmuir probe and microwave interferometer is plotted in Fig. 2(e). Both techniques indicate negligible electron density production due to the bias. Moreover, the product of the pinhole voltage and plasma current (difference between the currents measured with and without plasma) is less than 2 V A, ruling out any significant plasma generation by the bias [see Fig. 2(d)]. The power is deposited into accelerating the ions instead. Finally, we note that the generation of any electrons by the bias would have likely prevented the negative-ion signal as well.

We have begun comparisons of these measurements with a one-dimensional (1D) fluid simulation. The applied bias frequency for the experiment ($f_b = 20$ kHz) is much larger than the ion collision frequency ν_i (estimated at 2 kHz for 1 mTorr) and much smaller than the ion plasma frequency f_i (estimated at 30 MHz for a measured ion–ion plasma density of $10^{10}\,cm^{-3}$). This does not allow the ions to be in quasiequilibrium with the instantaneous fields as temporal inertia dominates. These are the frequency relationships of the 1D fluid simulation (see Fig. 3), whose details can be found elsewhere.[15,16] Under these conditions, the model predicts alternating fluxes of Cl^- and Cl^+ from an ion–ion plasma even for bias frequencies of 10 MHz. (The mass spectrometer is unable to time resolve signals at such large frequencies; consequently, we examined a lower frequency while holding the frequency relationships.) Like the experiment, the model predicts a slow decay in the peak intensities of ion spurts with time due to ion–ion neutralization. In addition, the simulation predicts weak shielding by the ion–ion plasma for $\nu_i \leqslant f_b \leqslant f_i$, and a consequent enhancement in the ion flux over the no-bias thermal diffusion value. The discrepancy between simulation and experiment in the positive-ion identity (Cl^+ vs Cl_2^+) occurs because the simulation does not yet include the charge-exchange reaction.

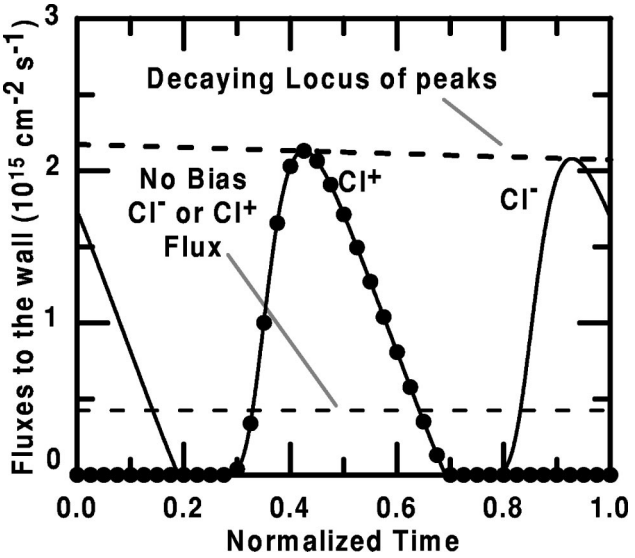

FIG. 3. Model prediction for fluxes of Cl^+ and Cl^- from an ion–ion plasma under no bias and a 10 MHz, 260 V_{pp} sinusoidal bias.

In summary, we have observed by mass spectroscopy, alternate fluxes of positive and negative ions to a substrate caused by applying a low-frequency bias across an ion–ion plasma. This qualitatively agrees with our 1D fluid simulations. Such alternate irradiations hold the potential to deliver equal and, hence, electrically neutral bombardment fluxes of positive and negative ions to the bottom of high-aspect-ratio features, thereby reducing or eliminating differential charging and the attendant etch nonidealities.

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