The excitation of a low-temperature, capacitively coupled plasma with non-sinusoidal, tailored voltage waveforms (TVWs) has been demonstrated as an effective tool to separately control the ion energy and ion flux to a substrate, both theoretically [1, 2] and experimentally [3–6]. By applying TVWs that consist of a fundamental frequency and its consecutive harmonics, an asymmetric plasma response will be produced and a DC self-bias voltage (η) can be generated even in geometrically symmetric reactors, an effect called the electrical asymmetry effect [7]. By then adjusting the phase shift φ (ranging from 0 to 2π) between these frequencies, asymmetric voltage waveforms having different voltage maxima and minima can be obtained. By controlling this amplitude asymmetry, the ion bombardment energy (IBE) on the electrode can be continuously controlled while keeping the ion flux constant, and several research groups have shown its various advantages to better control and understand the plasma enhanced chemical vapour deposition (PECVD) of silicon thin films [8–10].
More recently, a particular group of temporally asymmetric TVWs, resembling a sawtooth waveform, have also attracted considerable research interest. Such waveforms present no amplitude asymmetry in the applied voltage, but are distinguished by having differing rise and fall rates during each fundamental RF period, leading to different sheath motions in front of the powered and grounded electrodes. The effect of this slope asymmetry has been thoroughly studied [11, 12] and depending on the gas properties, different electron heating modes can lead to drastically different discharge dynamics. For an electropositive discharge operating in the $\alpha$-heating mode, the electron heating can be directly linked to the velocity of sheath expansion [13]. In this case, when employing sawtooth-type waveforms, intense local power absorption would occur near the electrode where the sheath expands rapidly, but weak power absorption would be observed near the other electrode where the sheath expansion is slow. For electronegative discharges, electron heating can operate in the drift-ambipolar mode due to the presence of a strong electric field in the plasma bulk. Significant electron acceleration from the plasma bulk towards one electrode occurs during the fast sheath contraction [14], and therefore a reversed discharge asymmetry can be observed for sawtooth waveforms compared to electropositive discharges. Although the slope asymmetry effect caused by sawtooth TVWs has been shown to be useful to understand fundamental aspects of single-gas discharges, the practical applications of such discharges have not been clear. In this letter, we report such an application, compared to electropositive discharges. As shown in figure 1, sawtooth waveforms can be generated with $\varphi$ equaling to either 0.5$\pi$ or 1.5$\pi$; the former gives a sawtooth-up waveform comprising a slow rise and a fast fall, while the latter gives a sawtooth-down waveform with a reversed rate of rise and fall. It is worth noting that in a geometrically symmetric reactor, switching the waveform from sawtooth-up to its counterpart simply results in reversing the role of each electrode.

Process conditions were chosen similar to those in the work of Dornstetter et al [16] which thoroughly investigated the deposition of silicon thin films from an SiF$_4$/H$_2$/Ar gas mixture using a standard 13.56 MHz radio frequency (RF) excitation source. In this study samples have been deposited on the grounded electrode with an SiF$_4$/Ar flux ratio of 3.6/88 sccm and an H$_2$ flow rate varied between 0 and 6 sccm using sawtooth TVWs. A working pressure of 3 Torr was used in all the experiments. The $V_{PP}$ and $d_i$ were kept constant at 285 V and 30 mm. The temperatures of the powered and grounded electrode were set to 80 °C and 150 °C, respectively. Ex situ spectroscopic ellipsometry (UVISEL-Horiba Jobin Yvon) measurements in the range from 1.5–4.5 eV were performed to estimate the thicknesses of the deposited films. To determine the consumption of feed gases during processing, a Residual Gas Analyzer (RGA, Microvision 2-MKS ins.) was deployed in the downstream of the discharge.

As shown in figure 2(a), for both types of sawtooth waveforms, the deposition rate $r_d$ increases with H$_2$ flow rate up to a value of 3 sccm, and then slightly decreases for greater H$_2$ flows. One can note that the sawtooth-down waveform leads to a higher $r_d$ than its counterpart at low H$_2$ flow rates, while the reverse situation is observed for H$_2$ flow rates above 3 sccm. Most interestingly, there is almost no deposition process occurring for H$_2$ flow rates below 1.5 sccm in the case of sawtooth-up waveform. Since the deposition of this material results from a competition between deposition and etching processes, a second series of two-step depositions was performed to allow us to see if etching is occurring. For these experiments, before the plasma processing by the SiF$_4$/H$_2$/Ar gas mixture, an underlying hydrogenated amorphous silicon (a-Si:H) film of 100 nm thickness was deposited using a standard 13.56 MHz RF source, an SiH$_4$/H$_2$ mixture with a flow ratio of 10/20 sccm and a pressure of 400 mTorr.

![Figure 1. Sawtooth-up (blue solid) and sawtooth-down (red dash) waveforms with $\varphi$ equal to 4.](image)
This sublayer allows us to observe that indeed, an etching of the underlying a-Si:H layer is occurring at low H2 flow rates, indicated by the shaded region in figure 2(b). For the sake of simplicity, we classify all these results by a net deposition rate $r_{\text{d,net}}$. Similar to the results of the one-step depositions of figure 2(a), $r_{\text{d,net}}$ increases with the H2 flow rate initially, followed by a slight decrease at higher H2 injection rates. One can see that when there is no H2 injection, etching processes are obtained for both types of waveform. However, once a small amount of H2 is added to the mixture, completely different surface processes for the sawtooth-up and sawtooth-down waveforms are observed. In the case of only 1 sccm H2, the sawtooth-up waveform leads to a strong etching effect, while almost no thickness variation of the underlying a-Si:H layer is observed for the sawtooth-down waveform. When the H2 flow is increased to 1.5 sccm, an etching process ($r_{\text{d,net}} = -1.2 \ \text{Å s}^{-1}$) is still observed for the sawtooth-up waveform, whereas a deposition process ($r_{\text{d,net}} = 0.82 \ \text{Å s}^{-1}$) is observed for its counterpart. By further increasing the H2 flow rate up to 2 sccm, the etching effect is essentially suppressed for the sawtooth-up waveform, while for the sawtooth-down waveform, a further increase in $r_{\text{d,net}}$ up to 1.2 Å s$^{-1}$ is seen.

In brief, by applying the two types of sawtooth TVWs, conspicuously different surface processes are observed during the SiF4/H2/Ar plasma processing, despite the fact that all other processing conditions are kept constant. It should be noted that a difference in the maximum energy of ions impinging on the growing surface is expected (up to ~40 eV) when switching the driving voltage waveform. However, previous studies on the PECVD of silicon thin films [17–19], have shown that while such variations in ion energy can modify film quality, they have very little effect on the deposition/etching rate, as was observed in this study.

Recalling that in a geometrically symmetric reactor, switching between these two waveforms is equivalent to reversing the roles of the two electrodes, figure 2 therefore indicates that differing deposition or etching processes could be achieved on each electrode of a CCP system, as determined by the relative H2 flow rate. In short, one can realize either a deposition or etching process on one electrode (or substrate) without influencing the other, or even a deposition process on one electrode but an etching process on the other.
Figure 5. Qualitative comparison of the hydrogen (solid green circles) and active fluorinated (open orange circles) species concentration distribution with increasing H$_2$ injection using sawtooth-up voltage waveform. The strength of local electron power absorption is represented by the color shades of the two sheaths (see text for details).

One additional note should be made concerning the selective process observed above. As the reactor in this study is geometrically asymmetric, the maximum ion energy observed on the substrate for both types of waveform is lower than would be observed a symmetric reactor. However, as ion energy alone is not a determining factor for deposition rate [17–19], this would at most result in a shifted process window for selective processing when transferring this process from a small, asymmetric reactor to a large, symmetric one.

To further understand the changes in the plasma that enable selective processing, we have measured the effluent gas composition by RGA and the DC self-bias voltage during processing. The use of RGA allows us to quantify the consumption of SiF$_4$ and H$_2$ molecules in the plasma, and the results as a function of H$_2$ flow rate are presented in figure 3. When no H$_2$ is injected, SiF$_4$ is barely consumed at all, relative to its actual consumption of H$_2$. For H$_2$ flow values above about 3 sccm, the consumption of SiF$_4$ and H$_2$ molecules in the plasma, and the results as a function of H$_2$ flow rate are presented in figure 3. When no H$_2$ is injected, SiF$_4$ is barely consumed at all, relative to its actual flow (3.6 sccm). For low values of H$_2$ flow, H$_2$ is essentially fully consumed, and SiF$_4$ is consumed at about half the rate of H$_2$. For H$_2$ flow values above about 3 sccm, the consumption of H$_2$ remains constant, as does that of SiF$_4$. A second complementary measurement is that of the $\eta$ value for both types of waveform remain quite different, and in fact, reverse in relative magnitude at around 1 sccm.

These results allow us to make some assertions about what is occurring in the plasma with increasing H$_2$ flow. From figure 3, we see that at low H$_2$ flow rates, the consumption of SiF$_4$ increases with H$_2$ flow. This is consistent with the phenomenological model described in [16] to understand the otherwise complex SiF$_4$/H$_2$/Ar discharge. In that model, the role of H$_2$ is to remove the fluorine produced by the SiF$_4$ dissociation through the formation of HF molecules. Without the scavenging of fluorine through this process, fluorine atoms etch any silicon surface. Therefore, the presence of H$_2$ is the limiting factor in the consumption of SiF$_4$.

The additional complexity in this experiment is the spatial variation in the fluorine removal process due to local variations in the electron power absorption. These variations (caused by the slope asymmetry of the sawtooth waveform) can be partially observed through the measurements of $\eta$. In figure 4, for no H$_2$ flow, the $\eta$ value for the sawtooth-down waveform is more negative than that for the sawtooth-up. This indicates that for these conditions, the discharge acts as an electropositive one (like argon) [12]; an electron power absorption maximum occurs near the electrode experiencing a fast sheath expansion, as described by the hard-wall model proposed by Godyak [20]. This leads to a much higher charge density within that sheath. Considering the expression given by Heil et al [7] and the situation of sawtooth TVWs [12], the $\eta$ can be estimated by:

$$\eta = -\frac{V_{PP}}{2} \times \frac{1 - \varepsilon}{1 + \varepsilon}$$

where $\varepsilon$ is a symmetry parameter that can be determined by the surface area ratio between the powered and grounded electrodes, as well as the respective mean charge densities in the sheath regions near said electrodes. Therefore, a more negative $\eta$ is generated by applying the sawtooth-down waveform, consistent with the results in [12].

With increasing H$_2$ flow rate, a significant increase of $\eta$ is found for the sawtooth-down waveform, while less so for the sawtooth-up waveform. This trend is actually the superposition of two effects, both due to the plasma taking on a more electronegative character. Firstly, the absolute value of $\eta$ is decreasing for both waveforms, as previously observed for the same plasma chemistry excited with a single frequency (13.56 MHz) waveform [16]. Secondly, the relative values of $\eta$ for the sawtooth-up and sawtooth-down waveforms switch places, and the sawtooth-up waveform takes on the more negative value (as observed for CF$_4$ [21, 22]). This is due to the change in where the most intense electron power absorption occurs as the plasma acts more electronegative. Opposite to the case of electropositive Ar, the most intense power absorption for an electronegative gas is near the electrode where a fast sheath contraction occurs. This is due to the electron attachment process leading to a depletion of local electron density and conductivity. Hence, a strong reversed electric field is generated.
near the edge of the rapidly collapsing sheath, which accelerates the electrons from the plasma bulk towards the grounded electrode. These energetic electrons will be trapped by the potential wall formed in front of the electrode [21, 22], which further increases the probability of the electron attachment process, leading to a higher charge density in that sheath.

Together, these plasma results are consistent with the processing results they produce. For the case of a sawtooth-up waveform, a qualitative comparison of the hydrogen and fluorinated species concentration close to each of the two electrodes with increasing H2 flow rate is presented in figure 5. Under the condition of no H2 injection, more intense power absorption occurs close to the powered electrode, experiencing the fast sheath expansion. Net etching processes are observed on both electrodes as there are no H2 molecules to scavenge the active fluorinated species. Once H2 is injected, the plasma switches to behaving like a more electronegative one (figure 4), a phenomenon observed but for which the explanation is not yet clear. The intense power absorption occurring close to the grounded electrode (experiencing fast sheath contraction) would result in a higher active fluorinated species concentration in front of the substrate. However, the injected H2 is still insufficient to scavenge these species, leading to either no deposition (figure 2(a)) or intense internal etching (figure 2(b)). The situation is simply reversed for a sawtooth-down waveform; due to a weaker electron power absorption, a lower fluorinated species concentration is present near the grounded electrode, easily scavenged by the available H2. The etching effect is much weaker, leading to either deposition (figure 2(a)) or at least the absence of net etching process (figure 2(b)) at low H2 flows.

With increasing H2 injection, the etching effect is gradually suppressed, and when the H2 flow rate is higher than 2 sccm, deposition processes can be observed on both electrodes (figure 2(b)). The resulting surface process is no longer limited by the presence of H2 but by the dissociation of SiF4. In this case, the more intense dissociation of SiF4 close to the grounded electrode will now lead to a higher deposition rate for this electrode (which previously observed a lower net deposition rate, figure 3).

In conclusion, we have experimentally shown that the use of sawtooth TVWs and a SiF6/H2/Ar gas mixture can result in controllably differing deposition or etching processes on each electrode in a CCP chamber. This is due to two effects: the multi-precursor nature of the deposition/etching process and the localized electron power absorption caused by the slope asymmetry effect of sawtooth TVWs. At low H2 flow rates, when processing identical a-Si:H layers but with opposite sawtooth TVWs, one can achieve a deposition process on the electrode where the weak electron power absorption occurs during the fast sheath expansion, and an etching process on the other electrode that experiencing the fast sheath contraction. Moreover, this deposition/etching balance on each electrode can be directly controlled by the H2 flow rate. At higher H2 flow rates, a deposition process is obtained on both electrodes. However, the discharge now operates in the drift-ambipolar heating mode (at the process conditions used in this work). As limited by the dissociation of SiF4, the relative net deposition rate on each electrode is now reversed. In short, this work encourages the prospect that one could choose a set of process conditions to achieve a wide variety of desired depositions on one electrode, while leaving the other electrode pristine.

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