Chemical sputtering by H₂⁺ and H₃⁺ ions during silicon deposition

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Chemical sputtering by $\text{H}_2^+$ and $\text{H}_3^+$ ions during silicon deposition

K. Landheer, W. J. Goedheer, I. Poulios, R. E. I. Schropp, and J. K. Rath

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Chemical sputtering by $H_2^+$ and $H_3^+$ ions during silicon deposition

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We investigated chemical sputtering of silicon films by $H_y^+$ ions (with $y$ being 2 and 3) in an asymmetric VHF Plasma Enhanced Chemical Vapor Deposition (PECVD) discharge in detail. In experiments with discharges created with pure $H_2$ inlet flows, we observed that more Si was etched from the powered than from the grounded electrode, and this resulted in a net deposition on the grounded electrode. With experimental input data from a power density series of discharges with pure $H_2$ inlet flows, we were able to model this process with a chemical sputtering mechanism. The obtained chemical sputtering yields were $(0.3–0.4) \pm 0.1$ Si atom per bombarding $H_2^+$ ion at the grounded electrode and at the powered electrode the yield ranged from $(0.4$ to $0.65) \pm 0.1$. Subsequently, we investigated the role of chemical sputtering during PECVD deposition with a series of silane fractions $S_F$ ($S_F(\%) = \left[SiH_4]/\left[H_2\right]^*$100) ranging from $S_F = 0\%$ to $20\%$. We experimentally observed that the $SiH_y^+$ flux is not proportional to $S_F$ but decreasing from $S_F = 3.4\%$ to $20\%$. This counterintuitive $SiH_y^+$ flux trend was partly explained by an increasing chemical sputtering rate with decreasing $S_F$ and partly by the reaction between $H_3^+$ and $SiH_4$ that forms $SiH_3^+$. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4960351]

I. INTRODUCTION

Hydrogenated micro-crystalline silicon ($\mu$-Si:H) and amorphous silicon (a-Si:H) layers are used in solar cells and are usually created by capacitively coupled Plasma Enhanced Chemical Vapor Deposition (cc PECVD). In a cc PECVD plasma, ions are formed that bombard the growing layer of the Si material. It is well known that ion bombardment from $SiH_2H_2$ PECVD discharges affects the bonding structure within the silicon network, 1,2 compactness, 3 uniformity, degree of hydrogenation 4 of the layer, and its interface with the substrate. 1 But chemical sputtering of Si by $H_2^+$ and $H_3^+$ (i.e., $H_y^+$) ions in a PECVD discharge has not been analyzed in detail before.

In an earlier publication, 5 we observed a counterintuitive trend: the $SiH_2^+$ flux was not proportional to the silane fraction ($S_F$) in the feedstock gas mixture. We also observed that for $S_F$ from 1.7% to 20%, the $H_2^+$ flux falls significantly and at low $S_F$ the $H_2^+$ bombardment deposits a large amount of energy per deposited Si atom (e.g., 29 eV at $S_F = 1.7\%$). Moreover, we measured a significant $SiH_2^+$ flux at $S_F = 0\%$.

In an effort to reveal possible causes for the $SiH_2^+$ flux trend, we hypothesized that etching through chemical sputtering by $H_2^+$ bombardment creates etch products that contribute to the $SiH_2^+$ flux at low $S_F$. We are not the first to attribute a role to hydrogenic ($H_2^+$) ions in the etching process. Leroy et al. 6 measured and modeled rf PECVD under similar deposition conditions (40 Pa and $S_F = 11\%$) and suggested that etching during deposition was mainly by $H_2^+$ ions, since the contribution of atomic hydrogen ($H$) etching as expected by the model of Abrefah and Olander 7 was negligible (<3%). However, their analysis focused on radicals in the discharge and not on ion bombardment. In this study, we compare experimental data with results from a 2D fluid model and a Monte Carlo model to develop a chemical sputtering model for PECVD discharges as well as to reach an understanding of the counterintuitive $SiH_y^+$ flux trend.

For a chemical sputtering process, the ions must be able to penetrate into the target material with a collision cascade and create strained Si–Si bonds in the film network. The minimal ion energy ($E_{\text{dam}}$) needed for these processes is about 20 eV for $H_y^+$ ions that are implanted in crystalline Si (c-Si). 9 The $H_3^+$ ion is the main component of the $H_3^+$ flux in our PECVD plasmas. The $H_3^+$ ion converts into either molecular and atomic hydrogen ($H_2 + H$) or only atomic hydrogen ($3H$) by dissociative recombination at the moment of impact. 11 Desorbing species are also formed near the ion penetration depth and this shows the chemical activity of the hydrogenic ions. 10 Atomic H diffusing through Si can break a weak Si–Si bond, it can passivate the Si dangling bonds formed, and it can recombine with another H atom and form molecular H3. Si–Si bond breaking reactions involved in atomic H etching have an activation energy of about 0.4 eV. 12 However, Wanka and Schubert 13 observed that the a-Si:H etch rate by atomic H, formed with a hot-tungsten filament, reduces for temperatures above room temperature. Two mechanisms can explain this observation: reduced atomic H surface coverage at elevated temperatures due to either enhanced atomic H recombination and desorption 14 or enhanced atomic H diffusion into the bulk. 7 The chemical

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sputtering rate of H⁺ ions is relatively constant from room temperature to 130 °C (Refs. 15 and 16) and this suggests that the atomic H surface coverage is not rate limiting for the chemical sputtering process in this temperature range. Physical ion sputtering of Si can be excluded because the ion bombardment energies in our SiH₄-H₂ VHF PECVD discharges remain below the threshold energy for physical sputtering. This threshold energy depends on the mass ratio of projectile and target atom and is about 50 eV for Ar⁺ ions⁸ that sputter Si. Therefore, it is not momentum transfer that removes etch products from the surface in the chemical sputtering process but thermal desorption.

It is important to realize that the chemical sputtering on both electrodes can be different. The process in which silicon is etched from the powered electrode and redeposited on the grounded electrode is known as chemical transport.¹⁷ In this process, the etch rate is lower than the gross deposition rate at the grounded electrode and at the powered electrode the etch rate is higher than the deposition rate. The net deposition rate on the grounded electrode can have several reasons, among others: a difference in the H⁺ ion flux between the powered and grounded electrode, a difference in temperature, and an ion energy dependent etch yield.

Recent theoretical studies by Heil et al.¹⁸ and Laffleur et al.¹⁹ have shown how an Electrical Asymmetry Effect (EAE) can be created in a geometrically symmetric reactor with a tailored waveform. This method is applied by Bruneau et al.²⁰ for the deposition of Si at low SF. In this study, we aim to further increase the understanding of the capacitive discharges at low SF that are excited with a single sinusoidal wave and this is also relevant for excitation by complex waveforms, as used for the EAE method. In this study, we used a reactor design similar to the GEC reference reactor.²¹ The deposition conditions used are in the regime of good quality a-Si:H as was confirmed by tests²² using the material created with SF of 1.7% as the passivation layer in flat silicon heterojunction (SHJ) solar cells.

II. EXPERIMENTAL

The parallel plate reactor and the plasma diagnostics used in the experiments are depicted in Fig. 1. The dimensions of our pillbox reactor are as follows: the radius of the powered electrode is 7.85 cm, the radius of the substrate electrode is 8.5 cm, and the separation between the electrodes is 2.7 cm. In between the powered electrode rim and the inner rim of the grounded guarding shield, a ceramic ring is present with a width of 1 cm. The rim of the grounded guarding shield is in contact with the wall of the reactor. The diameter of the reactor is 20 cm.

In order to test the chemical sputtering model in our VHF PECVD reactor and to determine the etch yield Y (number of Si atoms etched per impinging H⁺ ion), we performed two series of Si depositions on glass. We applied a pure H₂ plasma at power densities of 57, 114, and 171 mW cm⁻² in a reactor with Si on the electrodes and walls. This resulted in Si deposition on a strip of Corning glass substrate, mounted on the grounded electrode. The H₂ gas flow in these experiments was 60 sccm at 25 Pa. In the first series, the substrate temperature was 130 °C and in the second series the complete reactor was cooled down to room temperature.

The Si layers deposited on the glass on the grounded electrode were a-Si:H layers thinner than 100 nm. The Si layers on the powered electrode are directly deposited on the stainless steel showerhead electrode. Their crystallinity and hydrogenation are not monitored in situ and therefore unknown. The chemical sputtering etch yield depends on the crystallinity of the material, which is not taken into account in our chemical sputtering model. The Si layers on the powered electrode are most probably amorphous near the surface due to the intense ion bombardment.

The silane fraction series from SF₆ = 0% to 20% had the following plasma conditions: a gas pressure (p) of 25 Pa, a power density (Pₑ) of 57 mW cm⁻², and a substrate temperature (Tₛ) of 130 °C. At SF₆ = 20%, gas flows of 10 sccm SiH₄ and 50 sccm H₂ were used. We subsequently decreased SF₆ in our experiment by keeping the total flow at 60 sccm and reducing the SiH₄ flow in steps to 0 sccm. During processing, the gas pressure in the reactor was monitored with a Baratron pressure gauge and was maintained constant with a throttle valve between the reactor and pumps. The mass spectrometer is separately pumped and its pressure was kept below 5 × 10⁻⁴ Pa.

The Ion Energy Distributions (IEDs) of H₂⁺, H₃⁺, SiH₂⁺, SiH₃⁺, Si₂H₄⁺, and Si₃H₅⁺ in the SF₆ series were measured with a plasma analyzer. Fluid model and IED simulations were performed for the same ions, although in the simulation SiH₂⁺, SiH₃⁺, plus very small amounts of SiH⁺ and Si⁺ were put in a lump sum labelled SiHₓ⁺. The Si₂H₄⁺ (with y = 0–5) ions were put in the lump sum SiₓHᵧ⁺. In Section V, we model different reaction mechanisms for SiH₂⁺ and SiH₃⁺ and look at their contribution to the total SiHₓ⁺ flux at low SF₆.

The IED of a selected atomic mass unit (only singly ionized ions are expected) was measured by scanning an energy range with the Electrostatic Energy Analyzer (EEA) and...
keeping the quadrupole mass spectrometer (QMS) of the plasma analyzer steady at the selected mass. The energy resolution (FWHM) of the EEA is 2.55 eV and independent of the kinetic energy measured. Only ions that enter the plasma analyzer with an angle of incidence less than 15° are analyzed by the EEA. We label this measurement mode Ion Mass Spectrometry (IMS). Electrons are repelled and positive ions are attracted to the inlet of the plasma analyzer by the negative extractor voltage (−10 V) in IMS measurements. Before every measurement series, we optimized all lenses of the plasma analyzer for maximum transmission at 40 amu with an Ar plasma. Since the IEDs of the complete SF series are measured with constant transmission settings, the flux of the selected ion species can be compared between different SF. We measured a total ion flux of the order of $10^{19}$ ions m$^{-2}$ s$^{-1}$ with a retarding field energy analyzer for discharges with the same plasma conditions in an identical reactor. Our simulation results show the same order of magnitude for the total ion flux.

Near its orifice, the plasma analyzer has an ionization section to ionize neutrals and radicals with a mono-energetic electron beam. This device is active in the Residual Gas Analysis (RGA) measurement mode. Neutrals from the plasma can be measured in RGA mode: in this case, the ions from the plasma are repelled by a positive voltage of +60 V on the extractor. We verified in the IMS mode that no signal is detected when the extractor voltage is kept at +60 V. The silane depletion fraction $F_D$ is the fraction of SiH$_4$ that is consumed in plasma reactions. The measured $F_D$ is determined with RGA measurements and is the ratio of the loss in SiH$_2^+$ intensity as a consequence of switching on the plasma to the SiH$_2^+$ intensity without the plasma (i.e., in the presence of the gas mixture). Simultaneously, we measure the UV/VIS-light spectrum coming from the plasma halfway between the powered and grounded electrodes and monitor the power coupled into the discharge with a current-voltage (V−I) probe. The light spectrum is used to determine the Si* (288 nm) Optical Emission Spectroscopy (OES) peak intensity.

III. SIMULATIONS

A. Fluid model

We compared our experimental results with the modeling results of a self-consistent fluid model of the SiH$_4$−H$_2$ discharge. The 2-dimensional model of the cylindrically symmetric reactor, with the spatial dimensions $r$ and $z$, was built and described by Nienhuis et al. In the analysis presented here, the fluid model is used to compute an extensive set of time varying plasma parameters in the discharge. The following parameters have been modelled: electric potential, electron energy distribution function, electron density, and radical and ion densities (both positive and negative ions) as well as their fluxes to the electrodes. These quantities and distributions are used to explain the experimental ion bombardment trends and are used to calculate the Si* OES line intensity.

The fluid model simulates a-Si:H layer growth with a surface reaction probability $\beta$ and sticking coefficient $s$. For example, $\beta$ is 0.26 and $s$ is 0.09 for SiH$_3$. For Si$_n$H$_{2x+1}$ (x > 1) radicals, the same $\beta$ and $s$ are assumed. For SiH$_2$ on the other hand $\beta$ is 1 and $s$ is 0.7. All Si$_n$H$_{2x+1}^+$ ions bombarding the surface are assumed to contribute to the simulated deposition rate. This will result in an upper limit for the deposition rate as not all Si$_n$H$_{2x+1}^+$ ions stick to the surface; some ions may, for example, strip atomic H from a Si−H bond on the surface. The a-Si:H deposition rate is determined by dividing the number of deposited Si atoms by the Si atom density, being $5 \times 10^{25}$ m$^{-3}$ ($=5 \times 10^{19}$ m$^{-2}$ s$^{-1}$). Incident atomic H from the plasma abstracts a bonded H atom from the surface with a probability of 0.8 and subsequently desorbs as H$_2$. The chance that an incident H atom reflects is 0.2. In the simulations, the hydrogen content of the Si films is maintained at 10 at. % by adjusting the desorption of H$_2$.

The fluid model has restrictions in its applicability. It simulates collision-dominated PECVD discharges and therefore the gas pressure should be above 10 Pa. In the fluid model, the substrate temperature has only an effect on the gas density. The (surface) temperature is not influenced by the plasma or chemical reactions on the surface.

The model of Nienhuis et al. was extended in this research with hydrogen chemistry, such as the production of H$_3^+$ (H$_2^+$+H$_2$→H$_3^+$+H). Also electron energy dissipation processes have been added, among others the process H$_2$ + e$^-$ → H$_2$ + e$^-$ with radiative relaxation, that creates visible light emission from the plasma. However, etching or chemical sputtering was not included in the model, as this would require as yet unavailable data.

B. Monte Carlo model

A Monte Carlo model based on the null collision method is used to simulate the distribution of bombardment energies of H$_3^+$, H$_3^+$, SiH$_2^+$, and Si$_n$H$_{2x+1}^+$ ions on the electrodes. To simulate ion trajectories through the reactor, the Monte Carlo model uses the space and time dependent electric field and ion production, generated by the fluid model. Ions are released one at a time. The release time ($t_0$) and position ($z_0$) on the axis of the reactor ($r = 0$) are determined by a randomized drawing from the ion production distribution, $S(t, z)$, during one full rf period. After release, the ion can be accelerated by the electric field and it can collide with a neutral of the feedstock gas (SiH$_4$ or H$_2$). The time step used to advance the ions between collisions is taken equal to the time step in the fluid simulation, 1/256 of the rf period ($6.5 \times 10^{-11}$ s). A collision between two reactants can result in the following type of interactions: resonant charge exchange reactions, elastic collisions (using the hard sphere model, as recommended by Perrin et al.), and the production of different ion species. The ion continues its trajectory until it hits another neutral or one of the electrodes. At the moment the ion hits one of the electrodes, the impact energies and angles are recorded.

Simulated IEDs count only ions that impinge on the substrate surface at an incident angle less than 15°, in agreement with experimental conditions. However, all angles are considered in the computation of the ion flux and the ion energy...
flux. For the IEDs at the powered electrode we rely on the model, because only the dc self-bias $V_{DC}$ and the rf voltage amplitude ($V_{rf}$) are measured on the powered electrode. Since the kinetic energy of the ions in the sheath is higher than in the plasma bulk, reactions in the sheath can be endothermic and take place at a different rate than in the plasma bulk. For example, the dissociation of $H_3^+$ ($H_3^+ + H_2 \rightarrow H_2^+ + H_2 + H$) takes place in the sheath but not in the plasma bulk. IED modeling results are shown in Section 2 of the supplementary material.

C. The modeling of chemical sputtering

Chemical sputtering experiments with discharges created with a pure H$_2$ inlet flow were performed to find the etch yield ($Y$) on the electrodes. We use the diagram of Fig. 2 to tag the different silane flows and hydrogen fluxes involved in the chemical sputtering model. In our experiments, a glass substrate is mounted on the grounded electrode and a Si layer is present on the powered electrode. The H$_2$ plasma etches Si from the powered electrode and this creates a flow $\text{Si}_{\text{inlet},G} [\text{atoms s}^{-1}]$ of Si$_2$H$_x$ neutrals into the discharge. Part of the desorbed neutrals are dissociated and ionized in the discharge and form the gross deposition rate on the grounded ($r_{\text{gross},G} [\text{nm/h}]$) or powered electrode. Once Si deposits on the glass, it can also be etched away and this forms the flow $\text{Si}_{\text{inlet},P} [\text{atoms s}^{-1}]$. The term $r_{\text{net},G} [\text{nm/h}]$ is the net Si deposition rate on the glass, which is experimentally determined from the Si layer thickness and H$_2$ plasma exposure time. The amount of SiH$_4$ and Si$_2$H$_x$ created by the chemical sputtering at $P_{rf}$ = 57 mW cm$^{-2}$ is quantified with the SiH$_2^+$ and Si$_2$H$_4^+$ RGA signals.

The 2D fluid model computes the gross deposition rate $r_{\text{gross},G}$ (without etching) based on the amount of SiH$_4$ in the feedstock. Moreover, it computes the $H_2^+$ flux to the grounded ($\Gamma_{G,Hy^+}$) and powered ($\Gamma_{P,Hy^+}$) electrodes. The atomic H fluxes to the grounded ($G_{a,\text{flux}}$) and powered ($P_{a,\text{flux}}$) electrodes are also modeled and are used in the argumentation. Our chemical sputtering model is summarized in Equations (1) and (2) below and assumes that the Si etch rate is determined by the $H_2^+$ flux of ions with energies above 20 eV. The flow of Si atoms that are brought into the discharge by chemical sputtering on the grounded and powered electrodes can be calculated as follows:

\begin{align}
\text{Si}_{\text{inlet},G/P} &= Y_{G/P} [\text{atoms/ion}] \Gamma_{G/P,Hy^+} [\text{ions m}^{-2}\text{s}^{-1}] A_{G/P} [\text{m}^2], \\
\text{Si}_{\text{inlet}} &= \text{Si}_{\text{inlet},G} [\text{atoms s}^{-1}] + \text{Si}_{\text{inlet},P} [\text{atoms s}^{-1}],
\end{align}

where $Y_{G/P}$ is the yield, i.e., the number of Si atoms etched per incoming $H_2^+$ ion, on the grounded ($Y_G$) or powered ($Y_P$) electrode. $A_G$ and $A_P$ denote their area. $\text{Si}_{\text{inlet}}$ is thus the amount of Si atoms per second that is brought into the discharge. In the model, we assume that all etched Si atoms enter the discharge as SiH$_4$, and $\text{Si}_{\text{inlet}}$ is then converted to sccm SiH$_4$ and subsequently used to determine $r_{\text{gross},G}$ with the fluid model. The net deposition rate $r_{\text{net},G}$ on the glass substrate as a consequence of gross deposition ($r_{\text{gross},G}$) and etching by chemical sputtering ($r_{\text{etch},G}$) is modelled with the formulas

\begin{align}
r_{\text{etch},G} [\text{nm h}^{-1}] &= \frac{3.6 \times 10^3 [\text{s h}^{-1}]}{n_{Si} [\text{atoms m}^{-2}\text{nm}^{-1}]} \\
& \times Y_G [\text{atoms/ion}] \Gamma_{G,Hy^+} [\text{ions m}^{-2}\text{s}^{-1}], \\
r_{\text{net},G} [\text{nm h}^{-1}] &= r_{\text{gross},G} [\text{nm h}^{-1}] - r_{\text{etch},G} [\text{nm h}^{-1}],
\end{align}

where $n_{Si}$ is the Si atomic density of pure silicon, being $5 \times 10^{19} \text{m}^{-2} \text{nm}^{-1}$, and $3.6 \times 10^3 \text{s h}^{-1}$ converst per second into per hour. $r_{\text{gross},G}$ is calculated by the fluid model based on the equivalent SiH$_4$ inlet flow. Combining measured and computed quantities for two $P_{rf}$ settings gives sufficient information to obtain the values of $Y_G$ and $Y_P$. The starting point is the discharge at a power of 57 mW cm$^{-2}$, where we have additional information on the silane inflow from the RGA measurements.

IV. RESULTS

A. The chemical sputtering yield

In order to provide the chemical sputtering model with input data, we performed PECVD Si depositions on a glass substrate with only H$_2$ feedstock gas. We made series of Si depositions both at $T_s = 130^\circ C$ and at $T_s = 25^\circ C$ at three different $P_{rf}$ settings. Table 1 shows $r_{\text{net},G}$ of the two series. At $P_{rf} = 57 \text{ mW cm}^{-2}$, nothing was deposited on the glass. Therefore, we started the experiment with a 40 nm thick a-Si:H layer on glass to see if the layer is etched. The $P_{rf}$ series at $T_s = 25^\circ C$ shows only a slightly lower $r_{\text{net},G}$ than at $T_s = 130^\circ C$ for $P_{rf} = 114$ and 171 mW cm$^{-2}$.

For the computation of the etch yields $Y_G$ and $Y_P$ at $T_s = 130^\circ C$, we used three assumptions: $Y_G$ does not change in our $P_{rf}$ series since the $H_2^+$ ion energies do not increase a
energies, and $r_{net,G}$ is proportional to the SiH$_4$ inlet flow. In
With the Monte Carlo code (see supplementary material
that bombard the grounded electrode have energies between
and $V_{rf}$. When we put the experimental values in Eq.(3), we
only H$_2$ feedstock gas at $T_s$
Fig. 3, the measured H$_3^+$ ion energies at the grounded electrode at $P_{rf} = 171$ mW cm$^{-2}$ are comparable to the ion energies at $P_{rf} = 57$ mW cm$^{-2}$ at the powered electrode, we also made a calculation for the situation with $Y_G = 0.4$ at $P_{rf} = 171$ mW cm$^{-2}$ (last row of Table II). This resulted in $Y_P = 0.65$ at $P_{rf} = 171$ mW cm$^{-2}$, which is slightly higher than at $P_{rf} = 114$ mW cm$^{-2}$. It is expected that the chemical sputtering yield increases with higher H$_3^+$ ion energies for the range of energies investigated and therefore with increasing $P_{rf}$ (see supplementary material Section 1 for the complete computation of the chemical sputtering yields).

The chemical sputtering yield is not expected to vary with the H$_3^+$ influx, since $\Gamma_{G,H_y^+}$ and $\Gamma_{P,H_y^+}$ stay well below 10$^{20}$ ions m$^{-2}$ s$^{-1}$ in the etch experiments (see Table II). Roth$^{15}$ observed that for chemical sputtering of graphite by H$_3^+$ influxes above 10$^{21}$ ions m$^{-2}$ s$^{-1}$, the yield is decreasing, possibly related to a less efficient H passivation of dangling carbon bonds. Table II shows that the computed $\Gamma_{G,H_y^+}$ increases by a factor 1.9, but $\Gamma_{P,H_y^+}$ increases by a factor 2.7 at the powered electrode when increasing $P_{rf}$ from 57 to 171 mW cm$^{-2}$. Thus, increased etching at the powered electrode at higher $P_{rf}$ results in a higher $r_{net,G}$. This trend cannot be the result of atomic H etching alone, since $G_{s,flux}$ is slightly higher than $P_{s,flux}$ (see Table II). The powered electrode is not heated and is therefore significantly cooler than the grounded electrode at $T_s = 130^\circ$C. When the substrate was cooled down to room temperature, we observed the same trend: an increasing $r_{net,G}$ with increasing $P_{rf}$ (last column of Table II). Moreover, $r_{net,G}$ at $T_s = 25^\circ$C is of the same order of magnitude as at $T_s = 130^\circ$C, as is expected in the case of chemical sputtering.

### Table II. Modeling results at $p = 25$ Pa and $T_s = 130^\circ$C.

<table>
<thead>
<tr>
<th>$P_{rf}$ (mW cm$^{-2}$)</th>
<th>$\Gamma_{G,H_y^+}$ (m$^{-2}$ s$^{-1}$)</th>
<th>$\Gamma_{P,H_y^+}$ (m$^{-2}$ s$^{-1}$)</th>
<th>SiH$_4$ (sccm$^2$)</th>
<th>$Y_G$</th>
<th>$Y_P$</th>
<th>$r_{gross,G}$ (nm/h)</th>
<th>$r_{etch,G}$ (nm/h)</th>
<th>$r_{fact,G}$ (nm/h)</th>
<th>$G_{s,flux}$ (m$^{-2}$ s$^{-1}$)</th>
<th>$P_{s,flux}$ (m$^{-2}$ s$^{-1}$)</th>
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<td>0.35</td>
<td>0.3</td>
<td>0.40</td>
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<td>163</td>
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<td>1.0 $\times 10^{20}$</td>
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<td>$2.5 \times 10^{19}$</td>
<td>0.83</td>
<td>0.3</td>
<td>0.60</td>
<td>351</td>
<td>256</td>
<td>351</td>
<td>1.7 $\times 10^{20}$</td>
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<tr>
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<td>$3.3 \times 10^{19}$</td>
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<td>0.3</td>
<td>0.55</td>
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<td>300</td>
<td>437</td>
<td>2.1 $\times 10^{20}$</td>
<td>1.9 $\times 10^{20}$</td>
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<td>171</td>
<td>$1.4 \times 10^{19}$</td>
<td>$3.3 \times 10^{19}$</td>
<td>0.99</td>
<td>0.4</td>
<td>0.65</td>
<td>537</td>
<td>400</td>
<td>537</td>
<td>2.1 $\times 10^{20}$</td>
<td>1.9 $\times 10^{20}$</td>
</tr>
</tbody>
</table>

*aInflow of SiH$_4$ due to etching. The inflow of H$_2$ is kept at 60 sccm for all $P_{rf}$ applied.
B. Ion fluxes in the SF series

In Fig. 4, we show the simulated and measured SiH₃⁺ fluxes towards the grounded electrode in our SF series at \( P_{\text{rf}} = 57 \text{ mW cm}^{-2} \). The experimental SiH₃⁺ fluxes are not proportional to \( S_F \), whereas the fluid model computes an increasing SiH₃⁺ flux with increasing \( S_F \). The modelling results do not yet take chemical sputtering into account. The experimental fluxes displayed in Fig. 4 are computed by determining the area under the IEDs and normalizing the values with the area at \( S_F = 20\% \). The measured SiH₃⁺ and Si₂H₆⁺ fluxes are initially increasing with \( S_F \) up to \( S_F = 1.7\% \) or 3.4% and subsequently come down to the normalization point at \( S_F = 20\% \). The measured SiH₂⁺ IEDs consist predominantly of SiH₃⁺: the SiH₃⁺ flux is 3 times larger than the SiH₂⁺ flux at \( S_F = 20\% \). The normalized SiH₃⁺ flux has a maximum at low \( S_F \). This might be attributed to a reaction that creates SiH₃⁺: \( \text{H}^+ + \text{SiH}_3 \rightarrow \text{SiH}_3^+ + 2\text{H}_2 \). The central \( \text{H}_3^+ \) density is, namely, higher at \( S_F = 1.7\% \) than at \( S_F = 20\% \) and the central \( \text{H}_3^+ \) density is higher than the electron density (shown in Figs. 5 and 6). Also, the rate constant of this reaction is about one order higher in these discharges than the electron ionization rate constant for SiH₃⁺ formation. Therefore, this reaction can create a SiH₃⁺ flux that is not proportional to the silane fraction. This reaction and mechanisms that can be responsible for a higher SiH₃⁺ flux than SiH₂⁺ flux are further discussed in Section V B. Si₂H₄⁺ and Si₂H₃⁺ ions are formed by the electron ionization of Si₂H₄ or by one of the following three reactions: (1) \( \text{SiH}_2^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{H}_2 \), (2) \( \text{SiH}_2^+ + \text{SiH}_6 \rightarrow \text{SiH}_4^+ + \text{SiH}_3 \), and (3) \( \text{SiH}_3^+ + \text{SiH}_6 \rightarrow \text{SiH}_6^+ + \text{SiH}_4 \). There is some fluctuation in the Si₂H₆⁺ fluxes at \( S_F = 0\% \) and this is depicted with an error bar.

Drift to the electrodes is one of the mechanisms for a positive ion species (SiH₂⁺ and H₂⁺) to disappear from the discharge. The density of an ionic species in the bulk is determined by its production and loss rate. The ion fluxes are also determined by the central positive ion density, which is sustained by the negative charge in the plasma bulk. In the electronegative SiH₃H₂ discharge, the negative charge is composed of electrons and SiH₃⁻ ions. SiH₃⁻ ions are formed in the dissociative attachment reaction

\[
\text{SiH}_4 + e^- \rightarrow \text{SiH}_3^- + \text{H}.
\]  

Even at a low silane inflow, a considerable density of negative ions builds up at the discharge center. The negative charges are compensated by an equal amount of positive ions (SiH₂⁻ and H₂⁻) to ensure quasi-neutrality. Since the central negative charge density is predominantly built up by negative ions, these plasmas are called ion–ion plasmas. In an ion–ion plasma, the so-called ambipolar electric field is low, reducing the ion drift velocity. At \( S_F = 1.7\% \), the central \( \text{SiH}_3^- \) density is lower and more confined to the middle of the discharge than at \( S_F = 20\% \). To a lesser extent, the same is observed for the electron densities at \( S_F = 1.7\% \) and \( 20\% \). The simulated electron density distributions on the z-axis (\( r = 0 \)) of the reactor are displayed at \( S_F = 20\% \) in Fig. 5 and at \( S_F = 1.7\% \) in Fig. 6.

At \( S_F = 20\% \), the simulated SiH₃⁺ production rate and flux are roughly 4.5 times higher than at \( S_F = 1.7\% \), whereas the central SiH₃⁺ density at \( S_F = 20\% \) is 16 times higher than at \( S_F = 1.7\% \). On the other hand, the \( \text{H}_3^+ \) central density at \( S_F = 1.7\% \) (59 sccm H₂) is 1.7 times higher than at \( S_F = 20\% \) (50 sccm H₂). The \( \text{H}_3^+ \) flux to the electrodes is 4 times higher at \( S_F = 1.7\% \) than at \( S_F = 20\% \) and this is equal to the increase in the \( \text{H}_3^+ \) production rate. At \( S_F = 20\% \), the ambipolar electric field is lower than at \( S_F = 1.7\% \) and the \( \text{H}_3^+ \) density compensates the high \( \text{SiH}_3^- \) density to maintain charge neutrality and the \( \text{H}_3^+ \) ion does not readily leave the plasma bulk. The \( \text{H}_3^+ \) central density is significantly smaller than the \( \text{H}_3^+ \) central density: \( \text{H}_2^+ \) reacts to \( \text{H}_3^+ \). Fig. 7 shows that simulated and measured \( \text{H}_3^+ \) and \( \text{H}_4^+ \) fluxes are decreasing considerably with increasing \( S_F \) and the flux fall with increasing \( S_F \) steeper for \( \text{H}_3^+ \) than \( \text{H}_2^+ \). Fig. 7 also shows that the measured decrease in \( \text{H}_3^+ \) flux at the grounded electrode is much steeper than in simulations.

The simulated atomic H fluxes (\( \text{Ga,flux} \) and \( \text{Pa,flux} \)) increase with increasing \( S_F \): \( \text{Ga,flux} \) increases from 1.15 × 10¹⁰ m⁻² s⁻¹.
to $1.30 \times 10^{20} \text{ m}^{-2} \text{s}^{-1}$ for $S_F = 1.7\%$ to 20\%. $P_{a,\text{flux}}$ is slightly lower than $G_{a,\text{flux}}$ for all $S_F$ (e.g., $P_{a,\text{flux}}$ is $1.24 \times 10^{20} \text{ m}^{-2} \text{s}^{-1}$ at $S_F = 20\%$). The atomic H production rate due to H$_2$ dissociation is almost halved when $S_F$ increases from 1.7\% to 20\%. However, the electron density is more confined to the middle of the discharge at low $S_F$ and more H is formed by SiH$_4$ dissociation (e.g., reaction 4) at higher $S_F$ and therefore the H flux increases slightly with $S_F$.

C. Effect of chemical sputtering on the Si$_{x}$H$_{y}^{+}$ flux trend in the $S_F$ series

In Fig. 4, we observed that the experimental Si$_{x}$H$_{y}^{+}$ flux is not proportional to $S_F$ but decreased with increasing $S_F$. Here, we test if this Si$_{x}$H$_{y}^{+}$ flux trend can be explained with the chemical sputtering model. In simulations and measurements of the $S_F$ series, we see that the peaks of the H$_3^+$ IEDs on both electrodes (see supplementary material Section 2 A, Figs. S2–S4) are well above the threshold energy (E$_{\text{dam}}$ = 20 eV) for damage creation in c-Si by H$_3^+$ ions and therefore chemical sputtering is expected to occur on both electrodes. The measured H$_3^+$ peak position at the grounded electrode is around 28 ± 1 eV for all $S_F$, and with Eq. (3) we determined the experimental H$_3^+$ bombarding energy on the powered electrode to be 36 ± 1 eV ($V_{\text{DC,meas}} = -7 \pm 1 \text{ V}$ and $V_{\text{pl,meas}} = 30 \pm 0.5 \text{ V}$) for all $S_F$.

Now we include the contribution of chemical sputtering by H$_3^+$ ions on both electrodes to the modeled Si$_{x}$H$_{y}^{+}$ flux in the $S_F$ series (see Fig. 8). The sum of the Si$_{x}$H$_{y}^{+}$ flux created from the SiH$_4$ feedstock gas (Si$_{x}$H$_{y}^{+}$) and the SiH$_{3}^{+}$ flux as a result of H$_3^+$ chemical sputtering is labelled Si$_{x}$H$_{y}^{+}$ (corr). We modeled a discharge of 0.35 sccm SiH$_4$ and 60 sccm H$_2$ to determine the SiH$_{3}^{+}$ flux created with a pure H$_2$ inlet flow. The amount of SiH$_4$ created in the chemical sputtering process is proportional to the sum of the H$_3^+$ fluxes to the electrodes. Therefore, the amount of SiH$_{3}^{+}$ added by the correction at higher $S_F$ is a fraction of the SiH$_{3}^{+}$ in the discharge with 0.35 sccm SiH$_4$ and this is visible in Fig. 8.

The SiH$_{3}^{+}$ (corr) flux trend in Fig. 8 is slightly closer to the experimental SiH$_{3}^{+}$ trend (see Fig. 4). There is, however, still a significant difference between the simulated and measured Si$_{x}$H$_{y}^{+}$ flux trend and therefore we explore other mechanisms in Section V B. Chemical sputtering in the $S_F$ series does not significantly affect the deposition rate for $S_F > 1.7\%$. For $S_F \leq 1.7\%$, the deposition rate calculated by the fluid model is still close to the experimental value (see Fig. 9).

D. SiH$_4$ depletion fractions in the $S_F$ series

From the SiH$_3^+$ RGA signal (see Fig. 10), we derived that at $S_F = 0\%$ and $P_{\text{rf}} = 57 \text{ mW cm}^{-2}$, an amount equal to 0.35 sccm SiH$_4$ is added to the 60 sccm H$_2$ inlet flow. (This result is used in Section IV A.) To obtain this value, we assumed that the depletion fraction $F_D$ in this discharge is the same as for $S_F = 1.7\%$ (i.e., 1 sccm SiH$_4$), being $F_D = 0.39 \pm 0.02$. $F_D$ is determined experimentally: $F_D$ is the ratio of the loss in SiH$_2^+$ RGA signal as a consequence of switching on the plasma to the SiH$_2^+$ RGA signal without

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FIG. 6. Modeled time averaged electron density $n_e$ and ion densities of SiH$_2^+$, H$_3^+$, H$_2^+$, SiH$_4^{+}$ on the z-axis of the reactor at $S_F = 1.7\%$ as simulated by the fluid model. This discharge has a $V_{\text{DC}} = -28 \text{ V}$ and $V_{\text{pl,meas}} = 57 \text{ mW cm}^{-2}$.

FIG. 7. Simulated (Sim) H$_2^+$ and H$_3^+$ fluxes to the grounded and powered electrodes normalized to their values at $S_F = 20\%$. Measured (IMS) H$_2^+$ and H$_3^+$ fluxes to the grounded electrode (right-hand y scale) normalized to their value at $S_F = 20\%$.

FIG. 8. This graph shows the following modeled fluxes: the SiH$_{3}^{+}$ flux to the grounded electrode (SiH$_{3}^{+}$) as modeled without chemical sputtering, the H$_3^+$ ion flux to the grounded ($F_{\text{G,Hy}^+}$) and powered ($F_{\text{P,Hy}^+}$) electrode, and the result of the correction of the SiH$_{3}^{+}$ flux to the grounded electrode with the chemical sputtering model (SiH$_{3}^{+}$ (corr)).
the plasma (i.e., in the presence of the gas mixture). $F_D$ is the fraction of SiH$_4$ feedstock that is consumed in plasma reactions, and the remaining fraction is pumped away. In our simulations of the $S_F$ series, the residence time of the neutrals is 0.17 s for a total gas inlet flow of 60 sccm at 25 Pa.

$F_D$ is decreasing from $F_D = 0.45 \pm 0.01$ to 0.38 $\pm$ 0.02 for $S_F = 3.4\%$ to 20\% (see Fig. 9). At higher $S_F$, a lower percentage of the SiH$_4$ feedstock is consumed due to a lower electron temperature. At higher $S_F$, also more SiH$_3$H$_x$ molecules and radicals are formed, which are eventually pumped away. Therefore, the increase in the simulated deposition rate levels off for $S_F$ above 5%. On the other hand, $F_D$ at $S_F = 1.7\%$ is lower than at $S_F = 3.4\%$ since enhanced etching at low $S_F$ brings more SiH$_4$ back into the discharge and therefore it looks as if less SiH$_4$ is consumed. At $S_F = 0\%$, a clear Si* OES signal is measured (see supplementary material Section 3 C, Fig. S7), which is formed by chemically sputtered SiH$_4$. Fig. 10 shows that the SiH$_2^+$ and Si$_2$H$_4^+$ RGA signals that were measured with the plasma switched on are proportional to $S_F$, leading to an almost constant $F_D$. At $S_F = 0\%$, the signal clearly deviates from this proportionality to the SiH$_4$ inlet flow (i.e., 0 sccm SiH$_4$) and this is the result of chemical sputtering.

E. Control experiments and simulations

With a number of control experiments and simulations, we exclude some other mechanisms that can be considered responsible for the discrepancy between the simulated and experimental Si$_x$H$_y^+$ flux trend in the $S_F$ series. In particular, we address the possibility of physical sputtering and the difference between the simulated and measured $V_{DC}$ and $V_{rf}$ voltages.

1. Absence of physical sputtering

In this control experiment, we made IMS measurements of an Ar-SiH$_4$ dilution series. Here, the SiH$_3^+$ flux was proportional to the SiH$_4$ concentration in the Ar-SiH$_4$ feedstock gas mixture (see supplementary material Section 3 D, Fig. S8). When we applied a pure Ar plasma (60 sccm Ar, $p = 25$ Pa, $P_{rf} = 57$ mW cm$^{-2}$) in a reactor with a Si layer on the powered electrode, we did not detect a SiH$_3^+$ signal during IMS measurements. This confirms that for the plasma conditions used, the Ar ion energies are below the threshold energy for physical sputtering. However, as soon as we added a small amount of H$_2$ gas to the feedstock gas mixture, a significant SiH$_3^+$ signal was observed due to chemical sputtering.

2. The effect of an externally applied bias

In Section IV B, we showed experimental and simulated H$_3^+$ and Si$_2$H$_4^+$ flux trends and their density profiles. The ion-ion plasmas of the $S_F$ series are rigid in the sheath and bulk in the sense that the ion density distributions resist deformation by the rf electric field and an externally applied dc voltage that is added to $V_{DC}$. The sheath is formed by an almost immobile ion density profile and an oscillating electron density profile, whereas the bulk ion–ion plasma only reacts to the average electric field. In Fig. 11, the broadness and central alignment of the average potential profile and SiH$_3^-$ ion density at $S_F = 1.7\%$ and 20\% are compared. At low $S_F$, the $n_e$ and SiH$_3^-$ density are more confined to the middle of the reactor and this results in a narrower plateau of the potential profile. The dc self-bias shifts the $n_e$ and SiH$_3^-$ density slightly towards the grounded electrode ($z = 27$ mm).

The sheath at the powered electrode is about 2 mm wider than at the grounded electrode.

We investigated the changes when the simulated $V_{DC}$ is pinned at the experimentally determined $V_{DC} = -7$ V by an externally applied bias for $S_F = 1.7\%$ and 20\% (see Fig. 11). The discharge becomes more symmetric and the plasma potential increases with about $7 \pm 1$ V. The externally applied bias voltage introduces a small DC current through the discharge that affects the ion fluxes only a little bit. Therefore, it can be concluded that the ion fluxes from the simulated discharge ($V_{DC} = -29$ V and $V_{rf} = 81$ V at $S_F = 20\%$) represent the ion fluxes of the experimental discharge ($V_{DC} = -7$ V and $V_{rf} = 62$ V at $S_F = 20\%$) in spite of the different $V_{DC}$ and $V_{rf}$. This phenomenon is also experimentally observed in Fig. S6 of the supplementary material, which shows the effect of an externally applied bias of +69 V on the SiH$_3^+$ IEDs of the $S_F$ series.
In the chemical sputtering process, a collision cascade of a H$_y^+$ ion inside the Si layer creates strained or broken Si–Si bonds. Strained bonds are readily broken and Si dangling bonds are passivated by the ubiquitous atomic H in the growth zone that is supplied by the plasma. This mechanism forms loosely bound reaction products that are thermally desorbed. Thus, in the chemical sputtering process, the H$_y^+$ ions enhance the atomic H etching process.

The H$_y^+$ flux in our experiments consists of 90% H$_3^+$ ions and the rest is H$_2^+$ (the amount of H$^+$ is negligible). Mitchell et al.\textsuperscript{11} found that the thermalized H$_3^+$ ion is converted into 3 H or H$_2 +$ H at the moment of impact due to dissociative recombination.\textsuperscript{11,26,33} In this way, the H$_3^+$ ion brings not only energy to break the Si-Si bond (2.3 eV) but also atomic H to passivate the Si dangling bonds and to form a stable desorption product. The formation of the Si-H bond releases a few eV as thermal energy\textsuperscript{9} (the amount of energy depends on the Si-H bond configuration) and this is usually more than the SiH$_4$ desorption energy:\textsuperscript{34} $E_{\text{des}} = 1.8 \pm 0.1$ eV. The desorption product is SiH$_2$(x:2).

The H$_y^+$ ions bombarding the two electrodes in the Prf series (Section IV A) have energies well above $E_{\text{dam}} = 20$ eV. In our chemical sputtering model, we assumed that theetch yield increases with the H$_y^+$ bombardment energy and found $Y_G = (0.3–0.4) \pm 0.1$ and $Y_P = (0.4 \pm 0.66) \pm 0.1$ for Prf from 57 to 171 mW cm$^{-2}$. In studies with carbon targets, chemical sputtering of carbon by impinging H$_y^+$ ions in an extreme ultraviolet (EUV) induced H$_2$ plasma and a microwave (surface wave discharge) H$_2$ plasma at low pressure and low bias voltage\textsuperscript{35} with a yield of 0.5 C atom per impinging H$_y^+$ ion has been reported. It is also similar to the 0.6 C atom per impinging Ar$^+$ ion reported by Hopf et al.\textsuperscript{36} achieved with a 20 eV Ar$^+$ beam in combination with an abundant supply of atomic hydrogen.\textsuperscript{36} The yields we found for silicon are of the same order as these values for chemical sputtering of carbon.

A study by Balden and Roth\textsuperscript{16} on c-Si etching with monoenergetic D$_3^+$ ion beams for T$_e$ ranging from 25$^\circ$C to 827$^\circ$C revealed that the etch yield for c-Si by a 20 eV D$_3^+$ beam has a pronounced maximum around 130$^\circ$C, being 0.015 Si atom per impinging D$_3^+$ ion. This temperature maximum in the yield has not been reported for atomic H produced with a tungsten filament.\textsuperscript{13} Since the Si etch yield of the 20 eV D$_3^+$ beam is much lower than one should expect from chemical sputtering, Balden and Roth suggested that $E_{\text{dam}}$ is about 30 eV for c-Si. Then, the results confirm that etching of D$_3^+$ with ion energies below $E_{\text{dam}}$ is similar to atomic H etching: the etch yield of atomic H etching\textsuperscript{6,7} at 130$^\circ$C is about 0.015. It should be noted that the atomic H etch yield is much larger than the chemical sputtering etch yield, and the H$_y^+$ fluxes are only one order of magnitude lower than the atomic H fluxes in the Prf and Sf series presented.

The relative substrate temperature independence of the chemical sputtering mechanism reported by Balden and Roth\textsuperscript{30} and Roth\textsuperscript{15} for chemical sputtering of hydrogenated carbon matches our experimental results. In our Prf series (Section IV A), the net deposition rate is only reduced by 26% when the substrate temperature is lowered from 130$^\circ$C to room temperature at Prf$=114$ mW cm$^{-2}$. Moreover, the plasma heats the substrate only a few $^\circ$C and therefore this effect is neglected in the analysis.

A model for H$_y^+$ chemical sputtering during Si deposition by a SiH$_4$-H$_2$ cc PECVD discharge has not been presented before, but the mechanism has been used before. Vepřek and Mareček\textsuperscript{37} report chemical transport by chemical sputtering of c-Si by a PECVD H$_2$ plasma at 13 Pa which results in a deposition rate in the order of 10 nm/h on a heated glass substrate. The atmospheric-pressure plasma enhanced chemical transport (APECT) method described by Ohmi et al.\textsuperscript{38} applies chemical sputtering. This method uses an H$_2$–He cc PECVD discharge at atmospheric pressure to deposit a poly-crystalline Si film by chemical sputtering, but they do not report the ion energies or species involved. Otobe et al.\textsuperscript{14} report an a-Si:H etch rate in the order of 200 nm/h for etching with a H$_2$ PECVD discharge at $T_e = 150^\circ$C, $P_{\text{rf}} = 180$ mW cm$^{-2}$, and p = 27 Pa. The etch rate for c-Si etching is a factor 10 lower under the same plasma conditions. An etch rate of 200 nm/h matches the etch rates we found in the Prf series (see $r_{\text{etch},G}$ in Table II) with similar plasma parameters.

### B. Ion flux trends in the Sf series

The measured SiH$_3^+$, SiH$_3^+$, SiH$_4^+$, and SiH$_5^+$ fluxes in our Sf series decreased for Sf = 3.4%–20%. This trend is in good agreement with the Si$_x$H$_y^+$ flux trends observed by Horvath and Gallagher\textsuperscript{39} in their Sf series, but this trend is not reproduced by our fluid model (see Fig. 4). H$_n^+$ chemical sputtering of Si by a Si$_x$H$_2$(x:2) neutral discharge at low Sf as we learned from the RGA signals in Fig. 10 and the Si$^+$ OES signal (Fig. S7) at Sf = 0% and can partly explain the measured Si$_x$H$_y^+$ flux trends (see Fig. 8). Changes in the plasma parameters of the Sf series as a cause of the decreasing Si$_x$H$_y^+$ flux must be excluded. Although the rate constant for ionization decreases from Sf = 1.7% to 20%, it is too little (62% in the electron temperature range of interest) to...
compensate for the decrease in SiH₄ density due to the lower S₁ and therefore unlikely to occur. Finally, Allen observe a decreasing SiH₃ flux from 1.7% to 20%.

The high SiH₃⁺-to-SiH₂⁺-flux-ratios measured might provide a clue for the enhanced SiH₂⁺ flux at low S₁. We observe a decreasing SiH₃⁺-to-SiH₂⁺-flux-ratio from 7 to 3 for S₁ = 1.7% to 20%. The ratio of the ionization cross sections for SiH₃⁺ and SiH₂⁺ formation is 0.72 at an electron energy of 15 eV.⁴⁰ The latter ratio is only gradually increasing up to 0.83 at 70 eV electron energy and therefore does not strongly depend on S₁. Thus, we considered other reaction mechanisms. First, Turban et al.⁴¹ and Perrin et al.⁴² show that it is likely that a SiH₃⁺ ion picks up an H atom in a reaction with SiH₄ in the bulk, for example, with reaction 5 below. Second, one could suggest that SiH₂⁺ recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below. Third, one could suggest that SiH₂⁺-ions recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below. Third, one could suggest that SiH₂⁺-ions recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below. Third, one could suggest that SiH₂⁺-ions recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below. Third, one could suggest that SiH₂⁺-ions recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below. Third, one could suggest that SiH₂⁺-ions recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below. Third, one could suggest that SiH₂⁺-ions recombines more easily with SiH₃⁺ in the plasma bulk than SiH₃⁺, but actually the opposite is true: Reents and Mandich⁴² found that SiH₂⁺-ion picks up an H atom in a reaction with SiH₃⁺-ion. This reaction is much more likely to occur in the plasma bulk than in the bulk, for example, with reaction 5 below.

VI. CONCLUSIONS

We observed that the experimental SiH₃⁺ flux is not proportional to S₁ for SiH₄-H₂ discharges with silane fractions ranging from S₁ = 0% to 20%. In addition, we experimentally observed that the H₃⁺ flux decreases more than eleven times from S₁ = 1.7% to 20%. This brought us to the hypothesis of Si etching by chemical sputtering with H₃⁺ ions. This etching mechanism has a rate proportional to the H₃⁺ ion flux and therefore brings more Si into the discharge at low S₁.

We found chemical sputtering of silicon films by H₃⁺ ions in an asymmetric VHF PECVD discharge. A Prf series of discharges with pure H₂ inlet flow resulted in chemical transport of Si from the powered electrode to the substrate. Modelling showed that in this Prf series the flux of H₃⁺ ions to the powered electrode was larger than to the grounded electrode, whereas the atomic H flux to the powered electrode was smaller than to the grounded electrode. Moreover, a control experiment (supplementary material Section 3 A) showed that the major part of the SiH₄⁺ signal during IMS measurements is formed by Si etched from the powered electrode. With our chemical sputtering model, we determined an etch yield (Si atoms etched per bombarding H₃⁺ ion) at the grounded electrode of Yₚ = (0.3–0.4) ± 0.1 and at the powered electrode the etch yield varied from Yₚ = (0.4 to 0.65) ± 0.1 for Prf = 57–171 mW cm⁻². These yields are of the same order of magnitude as yield values reported in the literature for chemical sputtering of hydrogenated carbon by H⁺ ions.

With mass resolved ion bombardment measurements and numerical modeling, we gained a good understanding of the ion densities, energies, and fluxes towards the electrodes in the S₁ series. We observed that the H₃⁺ bombardment energies at both electrodes are well above E₀ = 20 eV in our S₁ series. The chemical sputtering mechanism, however, cannot completely explain the difference between the modeled and measured SiH₃⁺ flux trends. Splitting the SiH₃⁺ lump sum in the fluid model and the addition of the reaction between H₃⁺ and SiH₄ that creates SiH₃⁺ made the difference at low S₁ smaller.

In an asymmetric discharge, the deposition rate on the grounded electrode of YG is much smaller than to the powered electrode. Moreover, the atomic H flux to the powered electrode was smaller than to the grounded electrode. With our chemical sputtering model, we determined an etch yield (Si atoms etched per bombarding H⁺ ion) at the grounded electrode of Yₚ = (0.3–0.4) ± 0.1 and at the powered electrode the etch yield varied from Yₚ = (0.4 to 0.65) ± 0.1 for Prf = 57–171 mW cm⁻². These yields are of the same order of magnitude as yield values reported in the literature for chemical sputtering of hydrogenated carbon by H⁺ ions.

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In an asymmetric discharge, the deposition rate on the grounded electrode of YG is much smaller than to the powered electrode. Moreover, the atomic H flux to the powered electrode was smaller than to the grounded electrode. With our chemical sputtering model, we determined an etch yield (Si atoms etched per bombarding H⁺ ion) at the grounded electrode of Yₚ = (0.3–0.4) ± 0.1 and at the powered electrode the etch yield varied from Yₚ = (0.4 to 0.65) ± 0.1 for Prf = 57–171 mW cm⁻². These yields are of the same order of magnitude as yield values reported in the literature for chemical sputtering of hydrogenated carbon by H⁺ ions.
by chemical sputtering of Si from the cathode. By tuning the 
\( \text{H}_2^+ \) ion bombardment fluxes and energies with discharge 
power and gas pressure, this process can be optimized. 
Starting a deposition with a pure \( \text{H}_2 \) plasma allows to create 
a thin \( \mu\text{-Si}:\text{H} \) seed layer on an amorphous substrate, such as 
glass, by chemical transport. This seed layer can subsequently 
be used for high rate \( \mu\text{-Si}:\text{H} \) layer growth with a 
reduced or absent incubation layer.\(^{44}\) Knowledge of the 
chemical sputter mechanism of Si by \( \text{H}_2^+ \) ions can be an 
asset for industry that uses cc PECVD plasmas at low \( \text{SF}_6 \) 
(and even with only \( \text{H}_2 \) feedstock gas) to deposit \( \text{a-Si:H} \), 
\( \mu\text{-Si}:\text{H} \) or poly-crystalline Si.

**SUPPLEMENTARY MATERIAL**

See supplementary material file for Figs. S1–S8. The supplementary material consists of the following sections: (1) Complete computation of the chemical sputtering yield, (2) modeling \( \text{SiH}_x^3 \) IEDs with the Monte Carlo code in the 
\( S_P \) series, (3) extra control experiments, titled: (A) “Powered 
electrode with and without a Si layer,” (B) “exclusion of 
etching by electrons,” (C) “\( \text{Si}^* \) OES signal in the \( S_P \) series,” 
and (D) “absence of physical sputtering.”

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**APPENDIX: LIST OF FREQUENTLY USED VARIABLES**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{\text{G/P}} )</td>
<td>( m^2 )</td>
<td>Surface area of the substrate holder ( (A_{\text{G}} = 227 , \text{cm}^2) ) or powered electrode ( (A_{\text{P}} = 194 , \text{cm}^2) )</td>
</tr>
<tr>
<td>( E_p )</td>
<td>( eV/ion )</td>
<td>Peak position of the ( \text{H}_2^+ ) IED at the powered electrode</td>
</tr>
<tr>
<td>( \Gamma_{\text{G/P,\text{H}_2^+}, \text{i}} )</td>
<td>( \text{ions} , m^{-2} , s^{-1} )</td>
<td>( \text{H}_2^+ ) ion flux to the substrate holder/powered electrode</td>
</tr>
<tr>
<td>( \text{H}_2^+ )</td>
<td>( \text{n/a} )</td>
<td>Name for the group of ( \text{H}_2^+ ) plus ( \text{H}<em>2^+ ) ions ( (n</em>{\text{H}_2^+} = 5 \times 10^{19} , \text{m}^{-2} , \text{s}^{-1}) )</td>
</tr>
<tr>
<td>( n_{\text{Si}} )</td>
<td>( \text{m}^{-2} , \text{nm}^{-1} )</td>
<td>( \text{Si} ) atomic density of pure silicon ( (n_{\text{Si}} = 5 \times 10^{19} , \text{m}^{-2} , \text{s}^{-1}) )</td>
</tr>
<tr>
<td>( P_{\text{rf}} )</td>
<td>( \text{mW cm}^{-2} )</td>
<td>Coupled power density divided by the ( \text{surface area of the powered electrode} ) ( (A_{\text{P}}) )</td>
</tr>
<tr>
<td>( \tau_{\text{etch,G}} )</td>
<td>( \text{nm/h} )</td>
<td>Gross Si etch rate from the substrate holder ( (i.e., \text{on the surface area} \ A_{\text{G}}) )</td>
</tr>
<tr>
<td>( \tau_{\text{grow,G}} )</td>
<td>( \text{nm/h} )</td>
<td>Gross Si deposition rate on the substrate holder ( (i.e., \text{on the surface area} \ A_{\text{G}}) )</td>
</tr>
<tr>
<td>( \tau_{\text{net,G}} )</td>
<td>( \text{nm/h} )</td>
<td>Net Si deposition rate on the substrate holder ( (i.e., \text{on the surface area} \ A_{\text{G}}) )</td>
</tr>
<tr>
<td>( \text{Si}_{\text{inlet, P}} )</td>
<td>( \text{atoms s}^{-1} )</td>
<td>Gross flow of Si atoms from the powered electrode due to chemical sputtering ( (i.e., \text{on the surface area} \ A_{\text{G}}) )</td>
</tr>
<tr>
<td>( \text{Si}_{\text{inlet, G}} )</td>
<td>( \text{atoms s}^{-1} )</td>
<td>Gross flow of Si atoms from the substrate (holder) due to chemical sputtering</td>
</tr>
<tr>
<td>( \text{Si}_{\text{inlet}} )</td>
<td>( \text{atoms s}^{-1} )</td>
<td>Total flow of Si atoms brought into the discharge by chemical sputtering ( (1 , \text{scm} , \text{SiH}_4 = 4.48 \times 10^{17} , \text{Si atoms s}^{-1}) )</td>
</tr>
<tr>
<td>( Y_{\text{G/P}} )</td>
<td>( \text{atoms/ion} )</td>
<td>Chemical sputtering etch yield: Si atoms etched per bombarding ( \text{H}_2^+ ) ion</td>
</tr>
</tbody>
</table>

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