Chemical sputtering by H\textsuperscript{2} + and H\textsuperscript{3} + ions during silicon deposition

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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) ± 0.1 Si atom per bombarding H$_y^+$ ion at the grounded electrode and at the powered electrode the yield ranged from (0.4 to 0.65) ± 0.1. Subsequently, we investigated the role of chemical sputtering during PECVD deposition with a series of silane fractions S$_F$ (S$_F$(%) = [SiH$_4$]/[H$_2$]*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 (μc-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$_4$–H$_2$ PECVD discharges affects the bonding structure within the silicon network, compactness, uniformity, degree of hydrogenation of the layer, and its interface with the substrate. 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, we observed a counterintuitive trend: the SiH$_y^+$ 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$_3^+$ 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$_3^+$ flux at S$_F$ = 0%.

In an effort to reveal possible causes for the SiH$_y^+$ flux trend, we hypothesized that etching through chemical sputtering by H$_y^+$ bombardment creates etch products that contribute to the SiH$_y^+$ flux at low S$_F$. We are not the first to attribute a role to hydrogenic (H$_y^+$) ions in the etching process. Leroy et al. 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$_y^+$ ions, since the contribution of atomic hydrogen (H) etching as expected by the model of Abrefah and Olander 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). The H$_3^+$ ion is the main component of the H$_y^+$ flux in our PECVD plasmas. The H$_3^+$ ion converts into either molecular and atomic hydrogen (H$_2$ + H) or only atomic hydrogen (3 H) by dissociative recombination at the moment of impact. Desorbing species are also formed near the ion penetration depth and this shows the chemical activity of the hydrogenic ions. 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 H$_2$. Si–Si bond breaking reactions involved in atomic H etching have an activation energy of about 0.4 eV. However, Wanka and Schubert 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 or enhanced atomic H diffusion into the bulk. The chemical
sputtering rate of \( H_y^+ \) ions is relatively constant from room temperature to 130 °C (Ref. 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 SiH\(_4\)-H\(_2\) 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\(^+\) ions\(^8\) 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.\(^1\) 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 \( H_y^+ \) 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.\(^1\) and Lafleur et al.\(^1\) 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.\(^2\) for the deposition of Si at low \( S_F \). In this study, we aim to further increase the understanding of the capacitive discharges at low \( S_F \) 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.\(^3\) The deposition conditions used are in the regime of good quality a-Si:H as was confirmed by tests\(^4\) using the material created with \( S_F = 1.7\% \) 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 \( H_y^+ \) ion), we performed two series of Si depositions on glass. We applied a pure H\(_2\) 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 H\(_2\) 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 \textit{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 \( S_F = 0\% \) to 20\% had the following plasma conditions: a gas pressure (\( p \)) of 25 Pa, a power density (\( P_{\text{rd}} \)) of 57 mW cm\(^{-2}\), and a substrate temperature (\( T_s \)) of 130 °C. At \( S_F = 20\% \), gas flows of 10 sccm SiH\(_4\) and 50 sccm H\(_2\) were used. We subsequently decreased \( S_F \) in our experiment by keeping the total flow at 60 sccm and reducing the SiH\(_4\) 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 H\(_2^+\), H\(_3^+\), SiH\(_2^+\), SiH\(_3^+\), Si\(_2\)H\(_4^+\), and Si\(_3\)H\(_5^+\) in the \( S_F \) series were measured with a plasma analyzer. Fluid model and IED simulations were performed for the same ions, although in the simulation SiH\(_2^+\), SiH\(_3^+\), plus very small amounts of SiH\(_4^+\) and Si\(_2^+\) were put in a lump sum labelled SiHy\(_y^+\). The SiHy\(_y^+\) (with \( y = 0-5 \)) ions were put in the lump sum SiHy\(_y^+\). In Section V, we model different reaction mechanisms for SiH\(_2^+\) and SiH\(_3^+\) and look at their contribution to the total SiHy\(_y^+\) flux at low \( S_F \).

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 S_F series are measured with constant transmission settings, the flux of the selected ion species can be compared between different S_F. 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.25 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_2: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.25 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.26,27

The fluid model25 simulates a-Si:H layer growth with a surface reaction probability β and sticking coefficient s. For example, β is 0.26 and s is 0.09 for SiH_3. For Si_H_{2x+1}^+ (x > 1) radicals, the same β and s are assumed. For SiH_2 on the other hand β is 1 and s is 0.7. All Si_H_{2y}^+ 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_H_{2y}^+ 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,24 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.25 was extended in this research with hydrogen chemistry, such as the production of H_3^+ (H_2^+ + H_2 → H_3^+ + H).28 Also electron energy dissipation processes have been added, among others the process H_2 + e^- → H_2,^+ + 2H + e^- with radiative relaxation, that creates visible light emission from the plasma.29 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 method30 is used to simulate the distribution of bombardment energies of H_2^+, H_3^+, SiH_2^+, and Si_H_{2x}^+ 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,28,31 elastic collisions (using the hard sphere model, as recommended by Perrin et al.32), 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 H₂ 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 H₂ plasma etches Si from the powered electrode and this creates a flow \( Si_{inlet,P} \) of \( SiH_2^+ \) on the grounded electrode (or powered electrode). The \( Si_{inlet,G} \) of \( SiH_2^+ \) is the amount of SiH₄ and \( Si_2H_6 \) created by the chemical sputtering at \( Prf \). Table I shows \( r_{net,G} \) of the two series. At \( Prf \), the dissociation of \( H_3^+ \) takes place in the sheath but not in the plasma bulk. IED modeling results are shown in Section 2 of the supplementary material.

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

where \( Y_{G,P} \) is the yield, i.e., the number of Si atoms etched per impinging \( H_3^+ \) ion, on the grounded \((Y_G)\) or powered \((Y_P)\) electrode. \( A_G \) and \( A_P \) denote their area. \( Si_{inlet} \) is the amount of Si atoms per second that is brought into the discharge by chemical sputtering on the grounded and powered electrodes can be calculated as follows:

\[
\begin{align}
\text{Si}_{\text{inlet},G} &= \frac{130}{2} \text{nm h}^{-1}, \\
\text{Si}_{\text{inlet},P} &= 3.6 \times 10^{3} \text{sh}^{-1} \frac{n_{Si}[\text{atoms]} \times m^{-2} \text{nm}^{-1}}{Y_G[\text{atoms/ion} \times \Gamma_{G,Hy^+}[\text{ions m}^{-2}s^{-1}]],
\end{align}
\]

where \( n_{Si} \) is the Si atomic density of pure silicon, being \( 5 \times 10^{19} \text{ m}^{-2} \text{ nm}^{-1} \) and \( 3.6 \times 10^{3} \text{ sh}^{-1} \) converges per second into per hour. \( r_{net,G} \) is calculated by the fluid model based on the equivalent SiH₄ inlet flow. Combining measured and computed quantities for the \( P_{rf} \) 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 H₂ feedstock gas. We made series of Si depositions both at \( T_e = 130 \text{ °C} \) and at \( T_e = 25 \text{ °C} \) at three different \( P_{rf} \). Table I shows \( r_{net,G} \) 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 \( T_e = 25 \text{ °C} \) shows only a slightly lower \( r_{net,G} \) than at \( T_e = 130 \text{ °C} \) for \( P_{rf} = 114 \text{ and 171 mW cm}^{-2} \).

For the computation of the etch yields \( Y_G \) and \( Y_P \) at \( T_e = 130 \text{ °C} \), we used three assumptions: \( Y_G \) does not change in our \( P_{rf} \) series since the \( H_3^+ \) ion energies do not increase a
TABLE I. Experimental results for H₂ plasma etching at 25 Pa.

<table>
<thead>
<tr>
<th>P₁f (mW cm⁻²)</th>
<th>r_net,G</th>
<th>Tₛ = 130°C (nm/h)</th>
<th>r_net,G</th>
<th>Tₛ = 25°C (nm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>-30⁴</td>
<td></td>
<td>0⁴</td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>+95</td>
<td></td>
<td>+70</td>
<td></td>
</tr>
<tr>
<td>171</td>
<td>+137</td>
<td></td>
<td>+132</td>
<td></td>
</tr>
</tbody>
</table>

⁴Determined by starting with a 40 nm thick a-Si:H layer on glass. Due to the H₂ plasma treatment the a-Si:H layer may become more crystalline.

lot (see Fig. 3), Y_P can increase for higher H⁺ ion bombardment energies, and r_gross,G is proportional to the SiH₄ inlet flow. In Fig. 3, the measured H⁺ IEDs of the P₁f series created with only H₂ feedstock gas at Tₛ = 130°C are shown: all H⁺ ions that bombard the grounded electrode have energies between 20 and 40 eV and thus contribute to the chemical sputtering. With the Monte Carlo code (see supplementary material Section 2), we found that the position of the peak in the H⁺ IED at the grounded electrode (V_pl) can be calculated with the measured V_DC and the plasma potential (V_pl)

\[ \text{E}_P [\text{eV/ion}] = 0.98 (|\text{V}_{\text{DC}}| + \text{V}_{\text{pl}}). \]  

(3)

The experimental V_pl for a given P₁f is roughly equal to the H⁺ IED peak position at the grounded electrode. The inset table of Fig. 3 shows the experimental V_pl, V_DC, E_P, and V rf. When we put the experimental values in Eq. (3), we find E_P at 34, 53, and 72 eV for P₁f = 57, 114, and 171 mW cm⁻², respectively.

With the equations and assumptions presented above, we calculated the etch yields Y_G and Y_P of the P₁f series (see Table II). The starting point is the discharge at P₁f = 57 mW cm⁻², where RGA measurements showed that chemical sputtering introduces a flow of Si atoms into the discharge that is equivalent to 0.35 sccm SiH₄ (see Section IV D). With an inlet flow of 0.35 sccm SiH₄, the fluid model computed r_gross,G = 133 nm/h and the tabulated \( \Gamma_{G,\text{Hy}⁺} \) and \( \Gamma_{P,\text{Hy}⁺} \) fluxes at P₁f = 57 mW cm⁻². With the net deposition rate, r_net,G, of Table I, using Eq. (2b), the rate becomes: r_etch,G = 163 nm/h. This value is used to calculate Y_G with Eq. (2a); Y_G = 0.3. Y_P is then the only unknown left in Eq. (1); Y_P = 0.40. Now Y_G is kept fixed at 0.3 in the Y_P computations for P₁f = 114 and 171 mW cm⁻². By using the measured r_net,G and Y_G = 0.3, we obtained the gross deposition rate and found a higher value than obtained for 0.35 sccm SiH₄, showing that chemical sputtering at higher P₁f created a larger equivalent SiH₄ inflow (i.e., Si_inlet in Eq. (1)). The fluid model was therefore rerun with an inflow of 1 sccm SiH₄ and 60 sccm H₂ to compensate for possible changes in the ion fluxes, resulting in the tabulated values. Since H⁺ ion energies at the grounded electrode at P₁f = 171 mW cm⁻² are comparable to the ion energies at P₁f = 57 mW cm⁻² at the powered electrode, we also made a calculation for the situation with Y_G = 0.4 at P₁f = 171 mW cm⁻² (last row of Table II). This resulted in Y_P = 0.65 at P₁f = 171 mW cm⁻², which is slightly higher than at P₁f = 114 mW cm⁻². It is expected that the chemical sputtering yield increases with higher H⁺ ion energies for the range of energies investigated and therefore with increasing P₁f (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⁺ flux, since \( \Gamma_{G,\text{Hy}⁺} \) and \( \Gamma_{P,\text{Hy}⁺} \) stay well below \( 10^{20} \) ions m⁻² s⁻¹ in the etch experiments (see Table II). Roth⁵ observed that for chemical sputtering of graphite by H⁺ fluxes 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 \( \Gamma_{G,\text{Hy}⁺} \) increases by a factor 1.9, but \( \Gamma_{P,\text{Hy}⁺} \) increases by a factor 2.7 at the powered electrode when increasing P₁f from 57 to 171 mW cm⁻². Thus, increased etching at the powered electrode higher P₁f results in a higher r_net,G. This trend cannot be the result of atomic H etching alone, since \( G_{a,\text{flux}} \) is slightly higher than \( P_{a,\text{flux}} \) (see Table II). The powered electrode is not heated and is therefore significantly cooler than the grounded electrode at Tₛ = 130°C. When the substrate was cooled down to room temperature, we observed the same trend: an increasing r_net,G with increasing P₁f (last column of Table II). Moreover, r_net,G at Tₛ = 25°C is of the same order of magnitude as at Tₛ = 130°C, as is expected in the case of chemical sputtering.

TABLE II. Modeling results at p = 25 Pa and Tₛ = 130°C.

<table>
<thead>
<tr>
<th>P₁f (mW cm⁻²)</th>
<th>( \Gamma_{G,\text{Hy}⁺} ) (m⁻² s⁻¹)</th>
<th>( \Gamma_{P,\text{Hy}⁺} ) (m⁻² s⁻¹)</th>
<th>SiH₄ (sccm)</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_a,flux (m⁻² s⁻¹)</th>
<th>P_a,flux (m⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>( 8.0 \times 10^{19} )</td>
<td>( 1.3 \times 10^{19} )</td>
<td>0.35</td>
<td>0.3</td>
<td>0.40</td>
<td>133</td>
<td>163</td>
<td>-30</td>
<td>( 1.1 \times 10^{20} )</td>
<td>( 1.0 \times 10^{20} )</td>
</tr>
<tr>
<td>114</td>
<td>( 1.2 \times 10^{19} )</td>
<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>+95</td>
<td>( 1.7 \times 10^{20} )</td>
<td>( 1.6 \times 10^{20} )</td>
</tr>
<tr>
<td>171</td>
<td>( 1.4 \times 10^{19} )</td>
<td>( 3.3 \times 10^{19} )</td>
<td>0.99</td>
<td>0.3</td>
<td>0.55</td>
<td>437</td>
<td>300</td>
<td>+137</td>
<td>( 2.1 \times 10^{20} )</td>
<td>( 1.9 \times 10^{20} )</td>
</tr>
</tbody>
</table>

⁴Inflow of SiH₄ due to etching. The inflow of H₂ is kept at 60 sccm for all P₁f applied.
constant for SiH₃ 

Also, the rate constant of this reaction is about one order 

ues with the area at SF 

determining the area under the IEDs and normalizing the val-

omal point at SF 

results do not yet take chemical sputtering into account. The 


electronegative SiH₄-H₂ discharge, the negative charge is 

sustained by the negative charge in the plasma bulk. In the 

create a SiH₃ 

This reaction and mechanisms that can be responsible 

formation. Therefore, this reaction can 

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 (SiH⁺ and H⁺) 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 SF = 1.7%, the cen-

tral SiH₃⁻ density is lower and more confined to the middle 

of the discharge than at SF = 20%. To a lesser extent, the 

same is observed for the electron densities at SF = 1.7% and 

20%. The simulated ion and electron density distributions 

on the z-axis (r = 0) of the reactor are displayed at SF = 20% 

in Fig. 5 and at SF = 1.7% in Fig. 6. 

At SF = 20%, the simulated SiH₄⁺ production rate and 

flux are roughly 4.5 times higher than at SF = 1.7%, whereas 

the central SiH₅⁺ density at SF = 20% is 16 times higher 

than at SF = 1.7%. On the other hand, the H₂⁺ central 

density at SF = 1.7% (59 sccm H₂) is 1.7 times higher than at 

SF = 20% (50 sccm H₂). The H₂⁺ flux to the electrodes is 

4 times higher at SF = 1.7% than at SF = 20% and this is equal 

to the increase in the H₂⁺ production rate. At SF = 20%, the 

ambipolar electric field is lower than at SF = 1.7%: the H₂⁺ 

density compensates the high SiH⁺ density to maintain 

charge neutrality and therefore the H₂⁺ ion does not readily 

leave the plasma bulk. The H₂⁺ central density is signifi-

cantly smaller than the H⁺ central density: H₂⁺ reacts to 

H⁺. Fig. 7 shows that simulated and measured H₂⁺ and H⁺ 

fluxes are decreasing considerably with increasing SF and 

the flux fall with increasing SF is steeper for H⁺ than H₂⁺. 

Fig. 7 also shows that the measured decrease in H₂⁺ flux 

at the grounded electrode is much steeper than in simulations. 

The simulated atomic H fluxes (G_a,flux and P_a,flux) increase 

with increasing SF: G_a,flux increases from 1.15 × 10²⁰ m⁻² s⁻¹
to $1.30 \times 10^{20}$ m$^{-2}$ s$^{-1}$ for $S_F = 1.7\%$ to 20%. $P_{a,\text{flux}}$ is slightly lower than $C_{a,\text{flux}}$ for all $S_F$ (e.g., $P_{a,\text{flux}}$ is $1.24 \times 10^{20}$ m$^{-2}$ 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$^{22+}$ 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 ($V_{\text{DC,meas}} = -7 \pm 1$ V and $V_{\text{pl,meas}} = 30 \pm 0.5$ V) for all $S_F$.

Now we include the contribution of chemical sputtering by H$_3^+$ ions on both electrodes to the modeled SiH$_y^+$ flux in the $S_F$ series (see Fig. 8). The sum of the SiH$_y^+$ flux created from the SiH$_4$ feedstock gas (SiH$_y^+$) and the SiH$_y^+$ flux as a result of H$_3^+$ chemical sputtering is labelled SiH$_y^+$ (corr). We modeled a discharge of 0.35 sccm SiH$_4$ and 60 sccm H$_2$ to determine the SiH$_y^+$ 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$_y^+$ added by the correction at higher $S_F$ is a fraction of the SiH$_y^+$ in the discharge with 0.35 sccm SiH$_4$ and this is visible in Fig. 8.

The SiH$_y^+$ (corr) flux trend in Fig. 8 is slightly closer to the experimental SiH$_y^+$ 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 $P_{\text{rf}} = 57$ 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
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.

\[ F_D = 0.45 \pm 0.01 \text{ to } 0.38 \pm 0.02 \text{ for } S_F = 3.4\% \text{ to } 20\% \text{ (see Fig. 9).} \]

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 Si\(_{\text{ix}}\)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.

![Fig. 10](image)

**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 \( V_{\text{DC}} \) and \( V_{\text{rf}} \) 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, \( p = 25 \text{ Pa}, P_{\text{rf}} = 57 \text{ mW cm}^{-2} \)) 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 SiH\(_4^+\) 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 \( V_{\text{DC}} \). 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 (\( z = 27 \text{ mm} \)). The sheath at the powered electrode is about 2 mm wider than at the grounded electrode.

We investigated the changes when the simulated \( V_{\text{DC}} \) is pinned at the experimentally determined \( V_{\text{DC}} = -7 \text{ V} \) 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 ± 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 (\( V_{\text{DC}} = -29 \text{ V} \) and \( V_{\text{rf}} = 81 \text{ V} \) at \( S_F = 20\% \)) represent the ion fluxes of the experimental discharge (\( V_{\text{DC}} = -7 \text{ V} \) and \( V_{\text{rf}} = 62 \text{ V} \) at \( S_F = 20\% \)) in spite of the different \( V_{\text{DC}} \) and \( V_{\text{rf}} \). 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.

![Fig. 11](image)
A. Chemical sputtering

In the chemical sputtering process, a collision cascade of a H$_3^+$ 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$_3^+$ ions enhance the atomic H etching process.

The H$_3^+$ 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 Si$_2$H$_4$ and Si$_2$H$_4$$_2$.

The H$_3^+$ 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 the etch yield increases with the H$_3^+$ 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$_3^+$ 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$_3^+$ 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.

B. Ion flux trends in the S$_p$ series

The measured SiH$_3^+$, SiH$_4^+$, Si$_2$H$_4^+$, and SiH$_6^+$ fluxes in our S$_p$ series decreased for S$_p = 3.4\%$–20\%. This trend is in good agreement with the Si$_2$H$_4^+$ flux trends observed by Horvath and Gallagher\textsuperscript{39} in their S$_p$ series, but this trend is not reproduced by our fluid model (see Fig. 4). H$_3^+$ chemical sputtering of Si brings Si$_2$H$_2$$_2$$_2$ neutral into the discharge at low S$_p$ as we learned from the RGA signals in Fig. 10 and the Si$^+$ OES signal (Fig. S7) at S$_p = 0\%$ and can partly explain the measured Si$_2$H$_4^+$ flux trends (see Fig. 8). Changes in the plasma parameters of the S$_p$ series as a cause of the decreasing Si$_2$H$_4^+$ flux must be excluded. Although the rate constant for ionization decreases from S$_p = 1.7\%$ to 20\%, it is too little (62% in the electron temperature range of interest) to
compensate for the decrease in SiH$_4$ density due to the lower S$_F$. In addition, the central n$_e$ increases slightly and is less confined to the middle of the discharge when S$_F$ increases from 1.7% to 20%.

The high SiH$_3^+$-to-SiH$_2^+$-flux-ratios measured might provide a clue for the enhanced Si$_x$H$_y^+$ flux at low S$_F$. We observe a decreasing SiH$_3^+$-to-SiH$_2^+$-flux-ratio from 7 to 3 for S$_F = 1.7\%$ to 20%. The ratio of the ionization cross sections for SiH$_3^+$ and SiH$_2^+$ 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 S$_F$. Thus, we considered other reaction mechanisms. First, Turban et al.41 and Perrin et al.32 show that it is likely that a SiH$_3^+$ ion picks up an H atom in a reaction with SiH$_4$ in the bulk, for example, with reaction 5 below. Second, one could suggest that SiH$_2^+$ recombines more easily with SiH$_2^+$ in the plasma bulk than SiH$_3^+$, but actually the opposite is true: Reents and Mandich42 found below. Third, the endothermic reaction of SiH$_2^+$ with D$_2$ reported by Allen et al.33 can be considered. Thus, SiH$_2^+$ that collides in the sheath with H$_2$ can create SiH$_3^+$. However, the mean free path of this reaction is 40 mm at 25 Pa and therefore unlikely to occur. Finally, Allen et al.43 and Perrin et al.32 mention reactions 6 and 7

$$\text{SiH}_2^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{SiH}_3^+, \quad (5)$$
$$\text{H}_2^+ + \text{SiH}_4 \rightarrow \text{SiH}_2^+ + 2\text{H}_2, \quad (6)$$
$$\text{H}_2^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{H}_2 + \text{H} \quad (7)$$

At low S$_F$, especially reaction 6 becomes dominant. To simulate the effect of reactions 5–7, the SiH$_2^+$ and SiH$_3^+$ ions were treated as separate species in the fluid model. This resulted in a higher SiH$_y^+$ flux and the maximum in the SiH$_y^+$ flux shifted to a lower S$_F$ (compare SiH$_4^+$ (G,ls) and SiH$_y^+$ (G,ss)) in Fig. 12. We found a 100% increase of the SiH$_y^+$ flux at S$_F = 1.7\%$ and a 25% increase at S$_F = 20\%$. The new SiH$_y^+$ (G,ss) flux contributed about 30% to the a-Si:H growth rate at S$_F = 1.7\%$. The simulated SiH$_3^+$-to-SiH$_2^+$-flux-ratio ranged from 3.1 to 4.2 for S$_F = 1.7\%$ to 20%. We also observed that the decrease in the normalized H$_3^+$ flux with increasing S$_F$ became much steeper and therefore more in agreement with the measured trend (see Fig. 7). The Si created by the chemical sputtering process was not added to the SiH$_4$ inlet flow in the simulations of Fig. 12. With this addition, the maximum in the Si$_x$H$_y^+$ flux trend will shift slightly to a lower S$_F$, but there is still a significant difference between the measured and simulated Si$_x$H$_y^+$ flux trend at low S$_F$. A sensitivity study of the rate constants of reactions 5–7 is recommended for further analysis.

VI. CONCLUSIONS

We observed that the experimental Si$_x$H$_y^+$ flux is not proportional to S$_F$ for SiH$_4$-H$_2$ discharges with silane fractions ranging from S$_F = 0\%$ to 20%. In addition, we experimentally observed that the H$_3^+$ flux decreases more than eleven times from S$_F = 1.7\%$ to 20%. This brought us to the hypothesis of Si etching by chemical sputtering with H$_3^+$ ions. This etching mechanism has a rate proportional to the H$_3^+$ ion flux and therefore brings more Si into the discharge at low S$_F$.

We found chemical sputtering of silicon films by H$_3^+$ ions in an asymmetric VHF PECVD discharge. A Prf series of discharges with pure H$_2$ 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 H$_3^+$ 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 SiH$_4^+$ 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 H$_3^+$ ion) at the grounded electrode of $Y_{G} = (0.3–0.4) \pm 0.1$ and at the powered electrode the etch yield varied from $Y_{P} = (0.4$ to 0.65) $\pm 0.1$ for $P_{ef} = 57–171 \text{ mW cm}^{-2}$. These yields are of the same order of magnitude as yield values reported in the literature for chemical sputtering of hydrogenated carbon by H$_3^+$ 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 S$_F$ series. We observed that the H$_y^+$ bombardment energies at both electrodes are well above $E_{diam} = 20 \text{ eV}$ in our S$_F$ series. The chemical sputtering mechanism, however, cannot completely explain the difference between the modeled and measured Si$_x$H$_y^+$ flux trends. Splitting the SiH$_4^+$ lump sum in the fluid model and the addition of the reaction between H$_3^+$ and SiH$_4$ that creates SiH$_3^+$ made the difference at low S$_F$ smaller.

In an asymmetric discharge, the deposition rate on the grounded electrode at low S$_F$ can be significantly enhanced.
by chemical sputtering of Si from the cathode. By tuning the H$_{y}^{+}$ ion bombardment fluxes and energies with discharge power and gas pressure, this process can be optimized. Starting a deposition with a pure H$_2$ plasma allows to create a thin µc-Si:H seed layer on an amorphous substrate, such as glass, by chemical transport. This seed layer can subsequently be used for high rate µc-Si layer growth with a reduced or absent incubation layer. Knowledge of the chemical sputter mechanism of Si by H$_{y}^{+}$ ions can be an asset for industry that uses cc PECVD plasmas at low SF$_6$ (and even with only H$_2$ feedstock gas) to deposit a-Si:H, µc-Si:H or poly-crystalline Si.

**SUPPLEMENTARY MATERIAL**

See supplementary material file for Figs. S1–S8. The authors thank P. Dingemans for technical assistance. This research is part of the FLASH Perspectief program, supported by the Dutch Technology Foundation STW, which is part of the Dutch Organization for Scientific Research (NWO). The authors thank P. Dingemans for technical assistance.

**APPENDIX: LIST OF FREQUENTLY USED VARIABLES**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$A_{G/P}$</td>
<td>m$^2$</td>
<td>Surface area of the substrate holder ($A_{G} = 227$ cm$^2$) and powered electrode ($A_{P} = 194$ cm$^2$)</td>
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<tr>
<td>$E_{P}$</td>
<td>eV/ion</td>
<td>Peak position of the H$_{y}^{+}$ IED at the powered electrode</td>
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<tr>
<td>$\Gamma_{G/P, H^y+}$</td>
<td>ions m$^{-2}$ s$^{-1}$</td>
<td>H$_{y}^{+}$ ion flux to the substrate holder/powered electrode</td>
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<td>$n_{Si}$</td>
<td>m$^{-2}$ nm$^{-1}$</td>
<td>Si atomic density of pure silicon ($n_{Si} = 5 \times 10^{19}$ m$^{-3}$)</td>
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<tr>
<td>$P_{r}$</td>
<td>mW cm$^{-2}$</td>
<td>Coupled power density divided by the surface area of the powered electrode ($A_{P}$)</td>
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<tr>
<td>$r_{etch,G}$</td>
<td>nm/h</td>
<td>Gross Si etch rate from the substrate holder (i.e., on the surface area $A_{G}$)</td>
</tr>
<tr>
<td>$r_{gross,G}$</td>
<td>nm/h</td>
<td>Gross Si deposition rate on the substrate holder (i.e., on the surface area $A_{G}$)</td>
</tr>
<tr>
<td>$r_{net,G}$</td>
<td>nm/h</td>
<td>Net Si deposition rate on the substrate holder (i.e., on the surface area $A_{G}$)</td>
</tr>
<tr>
<td>$S_{inlet,P}$</td>
<td>atoms s$^{-1}$</td>
<td>Gross flow of Si atoms from the powered electrode due to chemical sputtering</td>
</tr>
<tr>
<td>$S_{inlet, G}$</td>
<td>atoms s$^{-1}$</td>
<td>Gross flow of Si atoms from the substrate holder due to chemical sputtering</td>
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<tr>
<td>$S_{inlet}$</td>
<td>atoms s$^{-1}$</td>
<td>Total flow of Si atoms brought into the discharge by chemical sputtering (1 sccm SiH$_4$ = 4.48 $\times$ 10$^{17}$ Si atoms s$^{-1}$)</td>
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<tr>
<td>$Y_{G/P}$</td>
<td>atoms/ion</td>
<td>Chemical sputtering etch yield: Si atoms etched per bombarding H$_{y}^{+}$ ion</td>
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