Evaluation of the Electrical Asymmetry Effect by spectroscopic measurements of capacitively coupled discharges and silicon thin film depositions

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\textbf{A B S T R A C T}

A capacitively coupled hydrogen diluted silane discharge operated at pressures above 500 Pa and driven by a combination of 13.56 MHz and 27.12 MHz is investigated by infrared laser absorption spectroscopy. Adjusting the phase angle between the two applied frequencies enables the control of the discharge symmetry via the Electrical Asymmetry Effect (EAE). The absorption measurements prove that the degree of dissociation of SiH$_4$ and, thus, the radical flux remains approximately constant, independently of the phase angle. Furthermore, the results show that the DC self-bias can be adjusted by tuning the phase, so that the sheath voltages change. Thus, the ion properties at the electrodes can be controlled via the EAE. This has an effect on the deposition of thin films, which are grown on glass substrates at various phase angles and analyzed using Raman spectrometry: Reducing the ion energy at the substrate leads to a decrease of the amorphous fraction in the predominantly microcrystalline film.

\textbf{1. Introduction}

In the manufacturing of various high-tech products such as glass coatings or thin film solar cells, the deposition of thin films on large area substrates is required. Here, plasma enhanced chemical vapor deposition (PECVD) is a common method, because the energy of the radicals and ions produced in the chemically rich gas phase can be controlled, thereby reducing the harmful thermal impact on sensitive materials [1]. In particular, capacitively coupled radio frequency (CCRF) discharges are widely used, as this discharge type allows for a very uniform treatment of plain surfaces [2]. Both the general quality and the specific physical properties of the thin film are mainly determined by the properties of the chemically reactive radicals and ions reaching the layer growing on the substrate surface. Hence, methods of controlling the flux ratio of the ions and radicals as well as methods of controlling the total fluxes and incident energies of radicals and ions are highly desired.

Recently, many studies demonstrated that a collisional discharge regime, i.e. the operation of the CCRF discharge at relatively high pressures of several hundred Pascal, is beneficial for the deposition of thin silicon films [3–6]. This can be attributed to the fact that the ion energy is strongly reduced due to the ion mean free path being much shorter than the width of the sheath region, where the ions are accelerated towards the surface by the rf oscillating electric field. Thus, damaging of the growing film by highly energetic ion bombardment is avoided. However, in general any change in global control parameters such as the applied voltage amplitude or the gas pressure affects both the energy and the flux of ions reaching the electrodes. Hence, there is no method of separate control of the flux and mean energy of the ions arriving at the electrodes in capacitive single-frequency plasmas [7].

The Electrical Asymmetry Effect (EAE) [3,4,8–14] provides a simple means of independent control of ion energy and ion flux by applying a dual-frequency voltage waveform

\begin{equation}
\phi_\text{in}(t) = \phi_\text{hf} \cos(\omega t + \theta) + \phi_\text{lf} \cos(2\omega t)
\end{equation}


\[\text{(1)}\]

to the powered electrode. $\phi_\text{lf}$ and $\phi_\text{hf}$ are the amplitudes of the fundamental angular frequency ($\omega$) and its second harmonic (2$\omega$), respectively. Adjusting the phase angle, $\theta$, between the two frequencies allows for...
the control of the symmetry of the voltage waveform. Accordingly, the global extremum of $\phi(t)$ and, thereby, the DC self-bias developing in the CCRF discharge can be controlled by tuning $\theta$ [8–13]. This affects the sheath voltages, which, in turn, are most important for the ion energy at the electrodes. Therefore, the symmetry control via the EAE results in a convenient control of the mean ion energy independently of the ion flux [8,9,11,14].

A very similar approach called voltage waveform tailoring (VWT) [15–22] is based on the application of multiple synchronized frequencies to the capacitively coupled plasma, thereby enhancing the control range [15,23,24]. Johnson et al. have demonstrated that this effect is indeed useful for the optimization of CCRF discharges for thin film deposition applications [19–21]. However, this approach is associated with practical problems, as the matching of more than two subsequent frequencies is technically challenging and has not been achieved yet. Nevertheless, these studies show that the control of the voltage waveform translates into a control of the film morphology in PECVD applications [22]. Fundamentally even more important, gaining insight into the specific role of the fluxes and energies of radicals and ions might be possible using the EAE or VWT, respectively.

The focus of this paper is to emphasize the decoupling between the radical fluxes and the ion properties using the EAE at high pressures and to show how the ion energy control via the EAE affects the properties of microcrystalline silicon thin film depositions. The experimental setup and, in particular, the spectroscopic methods used to investigate the plasma and the deposited films, respectively, are explained in the next section. The results are presented and discussed in section three. Finally, we summarize our findings in the fourth section.

2. Experimental setup

The basic setup of the CCRF parallel plate discharge used in this work has been described in detail elsewhere [12–14]. In brief, a plasma is operated in the 14 mm gap between the quadratic powered electrode with a surface area of 1600 cm$^2$ and the grounded counter-electrode. The temperature of both electrodes can be set individually and is maintained constant. The feed gas consisting of H$_2$ with a small admixture of SiH$_4$ flows into the chamber through the showerhead system implemented into the powered electrode. A voltage waveform according to Eq. (1) is produced by two synchronized rf generators. Each of the two frequencies has its own matching branch, and is blocked from the other matching branch by a low or high pass filter, respectively. The amplitudes of both frequencies, the phase angle, and the DC self-bias are determined from high voltage probe measurements after a calibration procedure [9].

The dissociation of the SiH$_4$ feed gas is measured by infrared laser absorption spectroscopy (IRLAS, see Fig. 1). By sweeping the current, a lead salt laser diode, which is kept at a constant temperature within a liquid nitrogen dewar, is tuned in the spectral range around 2230 cm$^{-1}$ (or 4484 nm) corresponding to the R branch of the $\nu_1$ vibration band of the SiH$_4$ molecule. A monochromator with a grating blazed at 4750 nm is used to select one of the multiple modes, which the diode emits simultaneously. The overall laser mode light intensity is then split into three components. A fraction of 25% is detected behind a reference cell filled with N$_2$O gas to find absolute spectral positions [25], while a fraction of 25% passes an etalon to visualize relative spectral changes. The analysis of both signals, which are measured by capacitively coupled HgCdTe detectors, allows for the determination of the absolute wavelength scale. The remaining 50% of the beam is coupled into the discharge chamber.

After a double path through the plasma chamber, the laser signal is measured by a directly coupled detector. The length of the laser beam path within the H$_2$/SiH$_4$ chamber is about 2.83 cm = 166 cm. Accordingly, the region of a homogeneous plasma adjacent to the powered electrode with an edge length of 40 cm, where dissociation takes place, corresponds to approximately 50% of the total absorption length. From these measurements, the absorbance, $A'$, can be obtained as

$$A' = -\ln\left(\frac{I}{I_0}\right). \quad (2)$$

Here, $I$ and $I_0$ are the intensities in the presence and absence of absorption, respectively. Four absorption lines are investigated, which are spectrally located at 2230.211 cm$^{-1}$, 2230.249 cm$^{-1}$, 2230.338 cm$^{-1}$, and 2230.374 cm$^{-1}$, respectively. These lines can be assigned to transitions from $J=8$ states to $J=7$ states of the $^{28}$SiH$_4$ isotope according to the outcome of simulations [26]. The absorbance is directly proportional to the density of the absorbing medium. Hence, in the following the reduction of the absorbance is used as a measure for the reduction in the SiH$_4$ density, i.e. for the increase in the dissociation of the SiH$_4$ feed gas molecule.

Thin film depositions, which have been grown on 10 x 10 cm$^2$ glass substrates placed centrally on top of the grounded electrode, are analyzed by means of Raman spectrometry. A HeNe laser emitting at 632.8 nm is focused on the film by a microscope lens. It has been assured that the incident laser power does not cause any irreversible damage, e.g. phase changes, to the deposited film [27]. The Raman shift, i.e. the difference in the wavenumbers of the incident and scattered light, has been calibrated by the examination of a monocrystalline silicon probe. In addition, a Dektak profilometer is used to estimate the film thickness and deposition rate, respectively, by moving the needle across a film edge, which is produced by a clamp that covers a small part of the glass substrate during the deposition process. Other diagnostic techniques such as Fourier transform infrared (FTIR) spectroscopy [28,29] would further improve the film characterization. However, such

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**Fig. 1.** Sketch of the IRLAS system and the discharge setup. OAPM: off-axis parabolic mirror, M: mirror, G: grating, BS: beam splitter, E: etalon, RGC: reference gas cell, Det: detector, hvp: high voltage probe.
measurements were not possible in the frame of this study and remain as a future topic.

3. Results

Fig. 2 shows the absorbance in single-frequency CCRF discharges operated at either 13.56 MHz or 27.12 MHz. All values are normalized by the absorbance without plasma, i.e. by the case of negligible dissociation. The error bars represent the statistical error due to deviations among the four absorption lines investigated in this work. The absorbance decreases as a function of the applied voltage amplitude at both frequencies. This is due to the fact that the energy contents of the plasma electrons increase and, subsequently, more energy is available for electron impact dissociation processes. Also, a higher driving frequency enhances the dissociation at the same voltage amplitude due to the more efficient electron heating [7,30–32]. It should be noted that the minimum normalized absorbance at high applied voltage amplitudes is about 22% (see Fig. 2(a)). This means that the SiH₄ molecules are dissociated after entering the plasma volume through the showerhead electrode, thereby reducing the flow of SiH₄ out of the plasma volume, as well. Without further gas phase reactions, the degree of dissociation in the volume surrounding the plasma remains the same as at the plasma boundary. Furthermore, the plasma might partially extend into the volume around the interelectrode volume. Altogether, the degree of dissociation in the plasma volume is equal to or slightly larger than the measured relative decrease of the absorbance.

The dependence of the absorbance and, accordingly, of the dissociation on the power applied to the discharge is approximately independent of the applied frequency (see Fig. 2(b)). The graph is based on the same data set as Fig. 2(a), whereas an increase in the power is assigned to an increase in the voltage amplitude. It should be noted that the same generator output power and, assuming equal power efficiencies of the matching networks, the same applied power leads to a smaller voltage at higher frequencies, because the plasma density and, accordingly, the discharge current increase. Therefore, the frequency dependence of the voltage (electron energy gain) and the current (number of electrons) compensate each other in the overall dissociation rate, leading to an applied frequency independent dissociation at equal applied power. Therefore, the degree of dissociation depends only on the available power per molecule [33,34]. This has been discussed in great detail (see, e.g., [35–38] and references therein).

By applying the synchronized combination of both frequencies, the EAE allows for controlling the discharge symmetry by tuning the phase angle, θ. As shown in Fig. 3, the absorbance and, accordingly, the dissociation remain almost constant for all θ. Here, the temperature of the powered electrode is kept at T_pow = 80 °C, while the temperature of the grounded electrode is set to 80 °C (equal temperatures, T_pow = T_grnd) or 200 °C (same temperatures as used in deposition processes below). The measurement results at three different applied voltage amplitudes are depicted, whereas the individual voltage amplitudes of the low (13.56 MHz) and high (27.12 MHz) frequency component of the voltage waveform are kept identical, i.e. $\phi_y = \phi_y$ in Eq. (1). It can be observed again, that the absorbance will decrease and the degree of dissociation will increase, if the applied voltage amplitude is increased. Furthermore, by comparing the three curves we note that the absorbance is lower and the dissociation is higher at higher electrode temperatures, respectively. Again, this is due to the fact that the neutral gas density is lower at higher temperatures, so that the energy available per molecule is larger at constant power [35–38]. Also, enhanced diffusion fluxes at higher gas temperatures [39] as well as surface reactions might play a role. The mean gas temperature can be estimated to be 140 °C and 80 °C, respectively. Thus, the difference in the dissociation due to a change in the mean temperature by about 60 °C (16%) can be compensated by a change in the applied voltage amplitude of about 20 V (20%).

Again, the finding of an almost equal dissociation for all phase angles can be understood by the power absorption of the plasma electrons. As discussed in [10], the temporally and spatially averaged power absorbed by the electrons within the plasma volume and within one period of the fundamental frequency is approximately independent of the choice of $\theta$, because the peak-to-peak voltage amplitude depends only very weakly on the phase angle. Thus, tuning $\theta$ changes the individual sheath voltages and, thereby, the power absorbed by the electrons and ions adjacent to each electrode, whereas the total electron heating and, subsequently, the overall absorbance and dissociation remain basically unaffected. This behavior provides the general basis for the control of the ion energy separately from the fluxes of both ions and radicals by adjusting $\theta$.

![Fig. 2. Normalized absorbance in single-frequency discharges operated at 13.56 MHz or 27.12 MHz as a function of (a) the applied voltage amplitude and (b) the generator output power. The discharge conditions are 500 Pa, 1000 sccm H₂ with 5 sccm SiH₄, $T_{pow} = T_{grnd} = 50 ^{\circ}C$.](image)

![Fig. 3. Normalized absorbance in electrically asymmetric dual-frequency discharges driven by the combination of 13.56 MHz and 27.12 MHz as a function of the phase angle. The discharge conditions are 900 Pa, 1000 sccm H₂ with 5 sccm SiH₄. For other parameters see graph and text.](image)
Based on the independence of the radical generation from the phase angle verified by the IRLAS measurements shown above, the ion energy via the EAE [8,9,11,14] can be used to optimize the ion impact energy for thin film deposition processing applications of CCRF discharges. We evaluate the effect of this control on silicon depositions by analyzing thin films grown in an electrically asymmetric hydrogen diluted silane plasma, keeping all quantities constant except for the phase angle and the DC self-bias. Three different choices of the phase angle are examined and compared to a standard case of a film, which is deposited using only 13.56 MHz as driving frequency with the same total voltage amplitude as in the dual-frequency cases (see Table 1). In the dual-frequency cases, the sum of the output power of the rf generators is typically around 800 W; it is varied by ±8% to maintain the same voltage amplitudes for all θ. The generator power in the single-frequency case is 625 W. Fig. 4 shows the Raman spectroscopic measurements of thin films grown on glass substrates using the EAE.

The strongest Raman scattering signal occurs at about 521 cm⁻¹. This peak corresponds to the crystalline phase. The left shoulder of the maximum shows a decreasing slope for larger distances from the peak and smoothly drops to a value of 0.12 at about 430 cm⁻¹. This means that there is only a small amorphous fraction in the phase composition. Hence, the structure of the hydrogenated silicon film is dominantly microcrystalline (μc-Si:H) [40–42]. This is most likely due to the fact that the silane admixture of only 1% to the hydrogen flow is very small and, therefore, the ratio of the fluxes of atomic hydrogen and silicon containing radicals such as SiH, SiH₂, Si₂H₅, and, dominantly [43], SiH₃ is large. Accordingly, the surface coverage with hydrogen during the deposition process is high. This leads to a good material quality [42,61], because atomic hydrogen plays an important role in the radical kinetics on the surface, as the surface diffusion length of reactive radicals is mainly determined by the surface coverage with hydrogen [27,41,42,64].

Comparing the Raman spectra of films deposited in CCRF discharges with different electrical asymmetries, i.e. using the EAE with different phase angles, it can be inferred that the normalized spectrum stays about the same except for the left shoulder of the peak structure. The center of the varying spectral interval is at about 480 cm⁻¹, so that the change can be associated with a decreasing or increasing fraction of the amorphous phase incorporated into the grown layer [40–42]. Furthermore, the full width half maximum of the peak at 521 cm⁻¹ is slightly smaller in the θ = 0° case compared to the other conditions, indicating an improved crystalline phase [45]. Tuning the phase angle in a way that the DC self-bias vanishes (here θ = 32°) results in the same discharge symmetry and applied voltage amplitude as in the standard single-frequency case, so that the resulting films reveal almost identical properties, as expected.

A phase angle of θ = 0° results in a strongly negative DC self-bias (see Table 1). Accordingly, the mean sheath voltage is much larger at the powered side compared to the grounded one. This leads to a smaller ion energy at the substrate, which is placed on the grounded electrode, leading to the growth of a more crystalline film. On the other hand, at θ = 90° the DC self-bias is strongly positive, the time averaged voltage drop across the grounded electrode sheath is relatively large, and the ion energy at the substrate is comparatively high, leading to the growth of a more amorphous film. Thus, the change in the material properties, that are indicated by the changes in the Raman scattering spectrum, can be understood by the ion energy impact on the growing film. It should be noted that direct measurements of the ion energy are hardly possible in chemically reactive (and especially in deposition forming) discharges. It has been demonstrated before [14] in pure hydrogen discharges under otherwise similar conditions, that the EAE allows for a separate control of ion energy and ion flux.

The ions arriving at the substrate certainly contribute to the deposition directly [27], but they also alter the entire deposition process in a manifold of ways: First of all, the bombardment of the surface by energetic ions leads to defect formation [42]. These defects are the basis for incubation zones of amorphous phase film growth [41] and, hence, result in a decrease of the crystalline fraction. Accordingly, the decomposition into smaller grains deteriorates the electronic properties of the film [46]. Furthermore, ions with a high kinetic energy are able to dissociate into reactive radicals upon impact [27] or penetrate into the subsurface layer, i.e. the topmost few monolayers of the film. The ion kinetic energy is transferred to the surface, where bonds are broken and, in particular, the physisorbed layer is efficiently removed [27]. This, in turn, decreases the mobility, i.e. the ability of surface diffusion, of the chemically reactive radicals (such as SiH₃). Thus, finding the energetically most favorable, crystalline structure becomes less probable [40,42].

Accordingly, it can be concluded by the analysis of test depositions in combination with the separate control of the radical and ion properties via the EAE found in the IRLAS measurements, that the film phase composition is directly linked to the energy impact of the ions, i.e. a higher ion energy is associated with a less crystalline film. This correlation is in agreement with earlier work (see, e.g. [40,44,47,48] and references therein) and means that the EAE is very useful for the improvement of deposition processes [19], as it allows for a convenient control of the ion energy. For instance, in the production of thin film solar cells, both a crystalline and an amorphous structure have to be deposited in order to manufacture a tandem solar cell [49]. The growth of an amorphous film is typically fast and simple, whereas the crystalline part is very sensitive to changes in the discharge conditions, e.g. the dilution of silane in hydrogen, and runs at lower deposition rates [1,27,6,49].

The determination of the film thickness presented in Table 1 is possible only with an uncertainty of about 10% due to the poor quality of the film edge, which is obtained by partially covering the glass substrate during the deposition process. Nevertheless, it can be argued that the measured data does not indicate a change in the resulting film thickness.

### Table 1

<table>
<thead>
<tr>
<th>Case</th>
<th>$\delta$ [V]</th>
<th>$\delta$ [V]</th>
<th>$\varphi$ [V]</th>
<th>Film thickness [nm]</th>
<th>Deposition rate [A/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single frequency</td>
<td>325</td>
<td>0</td>
<td>1</td>
<td>403 ± 31</td>
<td>2.24 ± 0.17</td>
</tr>
<tr>
<td>EAE, $\theta \approx 0^\circ$</td>
<td>200</td>
<td>125</td>
<td>62</td>
<td>392 ± 58</td>
<td>2.18 ± 0.32</td>
</tr>
<tr>
<td>EAE, $\theta \approx 32^\circ$</td>
<td>200</td>
<td>125</td>
<td>0</td>
<td>433 ± 37</td>
<td>2.41 ± 0.21</td>
</tr>
<tr>
<td>EAE, $\theta \approx 90^\circ$</td>
<td>200</td>
<td>125</td>
<td>58</td>
<td>410 ± 32</td>
<td>2.28 ± 0.18</td>
</tr>
</tbody>
</table>

Fig. 4. Raman spectra of thin films deposited in electrically asymmetric discharges. The standard case obtained in a single frequency (sf) discharge is shown, as well. The set of conditions is: 500 Pa, 1000 sccm H₂, 10 sccm SiH₄, $\delta$ + $\delta$ = 325 V (see Table 1), $T_{ess}$ = 200 °C, $T_{pri}$ = 80 °C, 30 minute deposition time.
Accordingly, the deposition rate is about the same for all cases. The value of approximately 0.22 nm/s is within the typical range of deposition rates for hydrogenated microcrystalline silicon films [41,42,6,47,49]. We note that the deposition rate could be enhanced by choosing higher driving frequencies [6,32,50]. The deposition of a more crystalline film at equal growth rate can be converted into the deposition of a film with equal phase composition at higher growth rate due to the strong coupling of crystallinity and deposition rate [42,6,49]. Therefore, the deposition time and costs in applications might benefit from the opportunity of depositing μ-Si:H films with unchanged properties faster via the EAE [3]. Furthermore, it might be possible to account for any drifts in the process conditions such as the reactor wall conditions [51], which lead to an unwanted variance of the film phase composition, by adjusting the phase angle. Certainly, the control of the lateral plasma homogeneity and deposition uniformity is another major issue [32]. Preliminary studies have shown, that the uniformity remains comparable to the single-frequency case at 13.56 MHz when adding a 27.12 MHz component [3,4]. This needs to be investigated in more detail in future studies on electrically asymmetric capacitive discharges.

A comparison of the properties of films, that have been grown using the EAE using different phase angles and ion energy settings, is hardly possible under slightly different conditions involving higher fluxes of SiH₄. As exemplarily shown in Fig. 5, this is due to the fact that in most cases the film peels off after the deposition process in the presence of a strongly positive DC self-bias, i.e. high ion energy, conditions. Note that the absolute values of the DC self-bias at θ ≈ 0° and θ ≈ 90° differ from each other due to the additional asymmetry caused by the asymmetric distribution of dust particles [12] agglomerating in high pressure silane containing plasmas. For most positive DC self-bias values, the ion energy at the substrate is large. Then, the film does not stick to the glass surface and becomes decomposed into flakes, so that a detailed analysis, e.g. via Raman spectroscopy, is precluded. (Based on the discharge conditions, we can only roughly estimate the film thickness to be of the order of a micrometer.) However, the reduced film adhesion might be explained by the film stress due to its bombardment with energetic ions. Therefore, the result itself (see photographs shown in Fig. 5) is illustrative and shows that high ion energies, which can be prevented by tuning the phase angle, potentially cause severe problems in thin film deposition processes.

4. Conclusions

In summary, the Electrical Asymmetry Effect is investigated experimentally in geometrically symmetric (parallel plate) capacitively coupled radio frequency discharges operated in hydrogen diluted silane at relatively high pressures, i.e. under discharge conditions relevant for PECVD applications such as silicon thin film solar cell manufacturing. The dissociation of SiH₄ within the plasma volume is determined by absorption spectroscopy and the resulting films are analyzed using Raman spectrometry.

It is found that the degree of dissociation is approximately constant for all phase angles, θ, and electrically induced discharge asymmetries, respectively. Therefore, the flux of radicals is expected to be independent of θ, whereas the ion energy is known to change as a function of θ. Hence, the EAE provides an opportunity of investigating the role of the ions for the silicon thin film deposition process. The Raman spectra reveal an increase of the amorphous fraction in the dominantly microcrystalline silicon thin films with increasing θ and, accordingly, with increasing ion energy. At the same time, the deposition rate stays about the same, because the fluxes of chemically reactive radicals and ions are independent of the discharge asymmetry under these conditions.

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