

# Control of the ion-energy distribution and measurement of ion currents with a non-sinusoidal substrate bias

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**Abstract**— Hydrogenated amorphous silicon (a-Si:H) can be deposited at high growth rates (up to 10 nm/s) via Expanding Thermal Plasma Chemical Vapor Deposition (ETP-CVD). However, high deposition temperatures (~400°C) are necessary to obtain solar-grade material suitable for solar cell applications at these high growth rates. These high temperatures degrade the properties of the previously deposited p-layer in solar-cell structures. An alternative way to supply energy to the surface is by ion bombardment. Positive ions in the plasma are accelerated towards the growing film in a controlled fashion by applying a special waveform to the substrate. In this way the deposition temperature might be lowered while maintaining the material quality.

Preliminary tests indicate that the ion energy can be controlled in the ETP-CVD system while obtaining a narrow ion energy distribution function (IEDF). An additional benefit of this setup is that it can be used to measure ion currents. Knowledge about the ion current is desired, as not only the ion energy, but also the ion-to-radical ratio is important for the interpretation of ion bombardment studies.

Preliminary results of the ion current measurements show that the addition of hydrogen to the argon plasma in the arc drastically reduces the ion density. The addition of silane reduces the ion density further.

**Keywords**— ETP-CVD, hydrogenated amorphous silicon, ion bombardment

## I. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) solar cells are a promising alternative to crystalline solar cells available today. Whereas the efficiency obtained with these cells is lower than for crystalline silicon solar cells, they can be produced at significantly lower costs. For the deposition of thin layers of a-Si:H a wide range of deposition methods can be used. The most common method to deposit a-Si:H layers is by capacitively coupled RF-PECVD, in which a sinusoidal voltage bias is applied between two electrode plates, one of which acts as a substrate holder. The silane (SiH<sub>4</sub>) gas injected

in the space between the plates is ionized and a SiH<sub>4</sub> plasma is created. The plasma is a complex mixture of radicals and ions, with radicals as the main film precursors and ions interacting with the growing film.

The deposition method utilized for the work presented in this paper is called expanding thermal plasma chemical vapor deposition (ETP-CVD). This method has been developed in the Equilibrium and Transport in Plasmas group at the Eindhoven University of Technology. High deposition rates of up to 10 nm/s for a-Si:H thin films have been demonstrated, compared to growth rates of ~1-2 Å/s obtained with conventional RF-PECVD methods [1]. A schematic representation of the reactor is shown in Fig. 1.

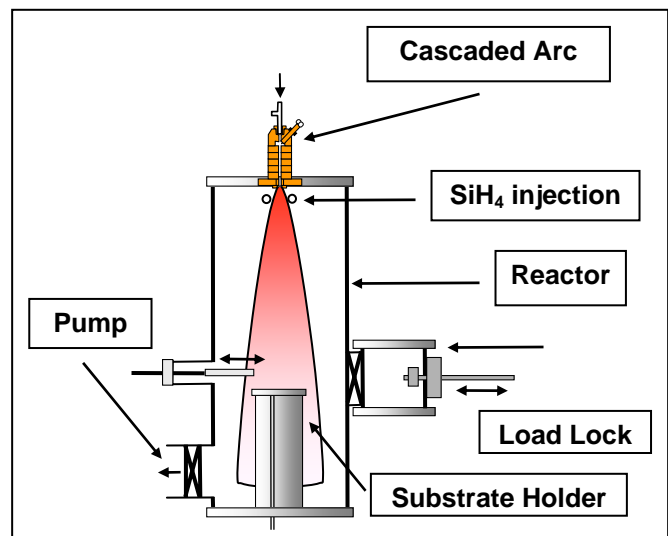


Fig. 1: Schematic drawing of the ETP-CVD reactor. The plasma is created in the arc and expands into the reactor due to the lower pressure

For this deposition method an Ar-H<sub>2</sub> plasma is created in the arc, where the gases are injected into a 2.5 mm diameter tube surrounded by six isolated copper plates. A DC-discharge

is sustained between three cathodes and the grounded copper plate located at the end of the arc. While the arc operates at pressures of 0.2 to 0.5 bar, a pressure of about 0.2 mbar is maintained in the reaction chamber by two stacked root blowers during depositions. Due to the large pressure difference, the plasma expands supersonically into the reactor. After a stationary shock a few centimeters after the nozzle, the plasma continues to expand subsonically.

The precursor gas  $\text{SiH}_4$  is injected into the plasma beam via an injection ring located a few centimeters below the nozzle. When traveling towards the substrate, the  $\text{SiH}_4$  will react with the atomic hydrogen created in the Ar- $\text{H}_2$ -plasma. Hydrogen is abstracted from the silane molecule forming silyl-radicals ( $\text{SiH}_3$ ), the dominant growth radical responsible for 90% of the film growth [2]. The distance between the injection ring where the  $\text{SiH}_4$  is injected and the substrate holder is 43 cm. Due to the remote nature of the plasma, one can change plasma parameters without directly affecting substrate conditions and vice versa. The nature of the reactive species in the plasma depends only on the arc conditions [6].

Ion bombardment in ETP is induced only by the low self-bias of the substrate holder due to the potential difference between the plasma and the grounded substrate holder, leading to a typical ion energy  $< 2$  eV. Initially, this absence of direct interaction between high energy ions and the growing film was assumed to be an advantage of the ETP-CVD method, as damaging processes such as sputtering could be excluded [6]. However, it was found that high deposition temperatures of  $\sim 300$ - $400$  °C are needed to obtain solar-grade material [3],[4],[9]. At lower temperatures of  $< 300$  °C, the thermally activated migration of silyl radicals on the film surface is too slow compared to the molecular flux of silyl radicals to the film surface, and voids are incorporated in the material [4]. At high temperatures, the silyl radicals migrate fast enough to reach an energetically favorable site on the film surface and a smooth and dense film is obtained.

Solar-grade material can indeed be deposited at lower temperatures with conventional RF-PECVD-methods (where plasma source and substrate are not separated and thus the growing film is constantly bombarded with energetic ions). Therefore it seems that ion bombardment plays an important role in the deposition of a-Si:H films. Due to the lack of intrinsic ion bombardment, ETP is an ideal method to study the effect of controlled ion bombardment on the deposited material.

It is assumed that bombardment with low-energy ions (from a few eV to maybe 50 eV [5]) enhances the surface diffusion of silyl radicals on the substrate surface. Ideally ion bombardment would improve silyl migration in the same way as thermal energy does and thus the deposition temperature could be lowered without altering the material properties significantly.

Research on controlled ion bombardment has been reported previously (e.g., Ref. [3]). For this bombardment, a simple sinusoidal RF-signal with a frequency of 13.56 MHz is applied to the substrate. Denser a-Si:H films have been

obtained under ion bombardment, due to a decrease in the void fraction incorporated in the film [7][11]. With this kind of biasing, a broad ion-energy distribution (IEDF) is obtained, as can be seen in a schematic drawing in Fig. 2 [7],[10], with two peaks at both ends of the spectrum. Numerous interactions between ions and the growing film have been reported in the literature, ranging from low-energy supply to  $\text{SiH}_3$ -radicals at the film surface, enhancing the surface migration, to surface and bulk atom displacement and even sputtering at high-ion energies [5], [8].

This wide range of possible interactions of ions with the film shows that control of the ion energy is crucial for the interpretation of the results. When the effect of different ion energies is known, it is possible to limit the interaction between ions and the growing film to ion energies associated to improved silyl surface migration, or improved material properties in general.

An additional problem that could be solved with controlled ion bombardment is the presence of ionic clusters in the growth flux, especially at high reactor pressures. These charged clusters have a sticking coefficient of about 1 and thus do not migrate on the film surface after impact. Material deposited with a growth flux containing a considerable amount of clusters has a larger void fraction and is therefore less dense. Controlled ion bombardment could accelerate these ionic clusters towards the substrate surface, causing them to break up upon impact [1].

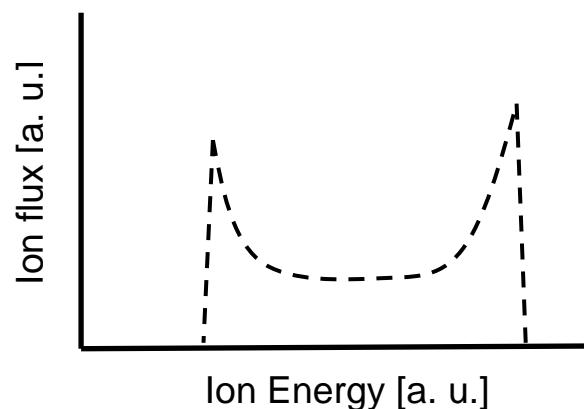


Fig. 2: Schematic representation of the ion energy distribution for an RF-biased substrate in a remote plasma.

In this paper, we will describe a setup enabling us to control the ion energy, limiting it to a narrow peak that can be shifted in the IEDF. In this way, we will be able to investigate the effect of different ion energies on the material properties. The aim of this project is to deposit solar-grade material using controlled ion bombardment at low deposition temperatures.

## II. EXPERIMENTAL

The setup installed in our ETP-CVD reactor to control the IEDF has been previously described by Wang *et al.* [7] and has been adapted. Wang *et al.* developed a setup to control the ion energy in ion etching processes and to increase the aspect

ratio of etched features in a remote plasma setup (helicon plasma etch tool). Although our intended application of thin-film deposition with controlled ion bombardment is very different from etching processes, the principle of controlling the IEDF remains the same for all remote plasmas with low ion energy close to the substrate.

Sinusoidal RF-substrate biasing in remote plasmas with collision-less sheaths typically yields a bimodal IEDF, as shown in Fig. 2. If the sheath transit time of the ions is much shorter than the RF cycle, the ions quickly transit the sheath. Thus the ion energy depends on the phase of the sinusoidal signal when the ion enters the sheath. Since the voltage change is slowest close to the minimum and maximum voltages, more ions cross the sheath during these phases of the biasing which explains the two peaks in the IEDF spectrum. The center of the bimodal distribution is located at the mean sheath voltage,  $V_s$ . Since the IEDF depends on the ion mass, one obtains a different IEDF for every type of ion present in the plasma [10].

A constant substrate voltage allows all ions to be accelerated by the same potential difference, resulting in a narrow IEDF with a single peak at a specific energy. However, glass or other insulating materials are often used as substrate material. A constant potential on such a substrate would result in charge accumulating on the substrate and thus the substrate bias will change. Therefore the applied waveform must fulfill two criteria:

- (1) The substrate must be discharged regularly, and
- (2) The charge buildup in the substrate must be counteracted.

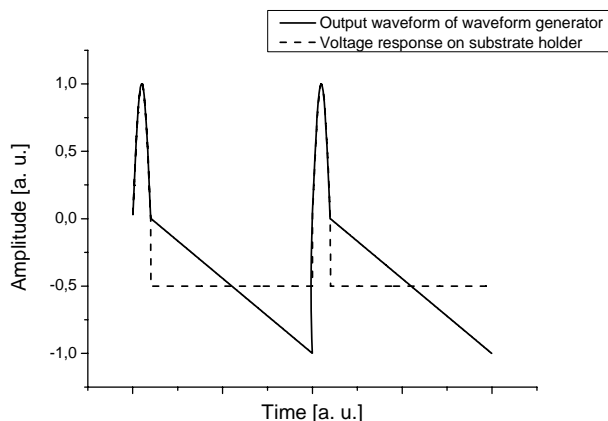


Fig. 3: Schematic representation of the pulse-shaped bias applied to the substrate holder (solid line) and the response on the substrate holder under a remote plasma

These requirements lead to the waveform shown by the solid line in Fig. 3. It consists of a ramp-section and a pulse-section. During the ramp-section the voltage output of the applied signal is constantly lowered to balance exactly the buildup of charge on the substrate holder (which is related to the positive ion flux). Discharging of the substrate occurs during the short positive peak, allowing electrons in the

plasma to neutralize the positive charge in the substrate. Since the mobility of the electrons in the plasma is much larger than the mobility of the positive ions, the pulse section can be made much shorter than the ramp section while maintaining the current balance. The resulting, flat potential at the substrate holder is schematically shown by the dashed line in Fig. 3.

The setup used to create this waveform can be seen in Fig. 4. The non-sinusoidal wave is created by an arbitrary waveform generator (Agilent 33250A). A broadband amplifier (Amplifier Research 150A250) with an amplification range from 10 kHz up to 250 MHz is used to control the signal amplitude. In principle, this setup enables us to operate in a frequency range for the non-sinusoidal wave from 200 kHz up to 8 MHz (the limit of the arbitrary waveform generator).

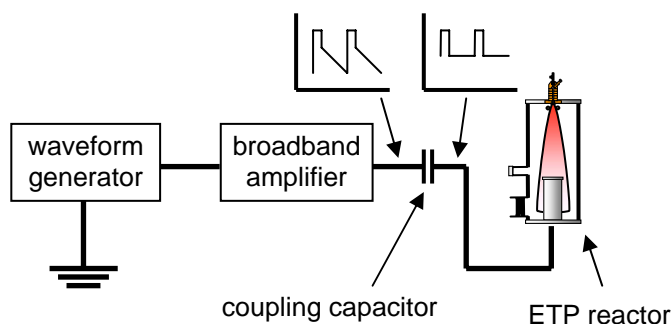


Fig. 4: Schematic representation of the of the pulse bias setup with its major components. Also depicted is the applied signal to the left and the response on the substrate holder exposed to a remote plasma.

In between the amplifier and the substrate holder, a coupling capacitor is installed, which serves two purposes:

- (1) It serves as a measurement device. On the amplifier side, the output of the amplifier can be measured, whereas on the substrate side the voltage on the substrate can be measured [7].
- (2) It ensures that there is no DC offset in the signal. Therefore the same amount of charge discharges the substrate that has previously charged it.

When the pulse-shaped bias is applied, the response of the system to the signal can contain oscillations due to resonances in the electronic circuit formed by the reactor and all components in it. Most of these resonances have a low amplitude or are located in a frequency range not utilized for this application, except one oscillation located at  $\sim 400$  kHz. This oscillation is the result of a capacitive coupling between the biased substrate holder and the heating elements located in the chuck with a capacitance of 0.2 nF. The heating elements are connected via the power line in series to an RF-filter with an inductance of  $\sim 1$  mH. This parallel connection of capacitor and inductance leads to a resonance frequency of 400 kHz.

An oscillation with this frequency can be seen in Fig. 5 in the solid line. The presence of this oscillation would lead to a

non-constant substrate potential between the pulses and thus a spreading of the IEDF.

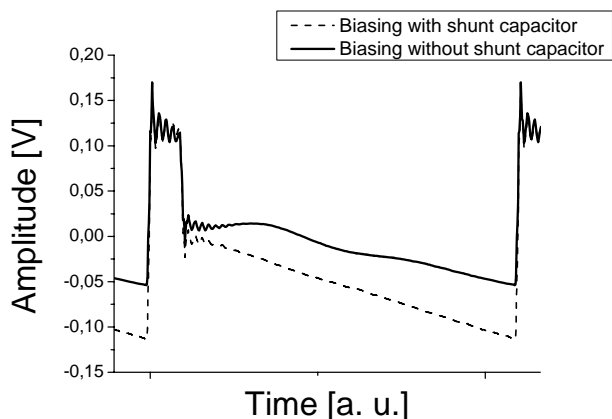


Fig. 5: Solid line: voltage signal measured at the coupling capacitor with an oscillation of  $\sim 400$  kHz. Dashed line: The same measurement with a shunt capacitor installed between the RF filter and ground.

This resonance can be damped by shunting the power line with a large capacitance (in our case 5 nF), creating a low impedance path for oscillations to ground. The resulting biasing on the substrate holder can be seen in Fig. 5 in the dashed line. The slope of the ramp section is constant (the high frequency oscillations at the beginning and at the pulse are a measurement artifact), presumably resulting in a narrow IEDF.

In addition to substrate biasing with controlled ion energy discussed above, the pulse bias setup can also be used to measure the ion flux arriving at the substrate, from which the ion density in the plasma can be deduced. The ion flux can be calculated from the slope of the waveform and the capacitance of the coupling capacitor. The ion flux is an important parameter when analyzing ion bombardment experiments. Not only the ion energy influences the type of interaction between ions and surface, but also the ion-to-radical ratio impinging on the substrate. As an example, Hamers *et al.* found a reduction in nanosized voids for ion energies of  $> 5$  eV *per deposited silicon atom* [11]. Additionally, the effect of different gas settings on the ion flux can be investigated.

### III. RESULTS

Several measurements were carried out utilizing the pulse-shaped substrate bias as a method to measure ion currents. For this measurement, the waveform described above is applied to the substrate holder and then the frequency is tuned until a constant potential between two pulses is obtained at the substrate holder. The ion current can be deduced from the slope of the applied waveform.

In a first series of measurements, the ion current was measured as a function of  $H_2$  injected in the arc. This

measurement was carried for four different Ar flows: 400, 670, 800 and 1000 sccm. The results of these measurements can be seen in Fig. 6. For all four Ar flows, one can clearly see a minimum in ion current. For higher Ar flows, the minimum in the ion current is found at higher  $H_2$  flows. It shifts from  $\sim 80$  sccm  $H_2$  for 400 sccm Ar to  $\sim 130$  sccm for 1000 sccm Ar. Also the minimum ion current is reduced at lower Ar flows.

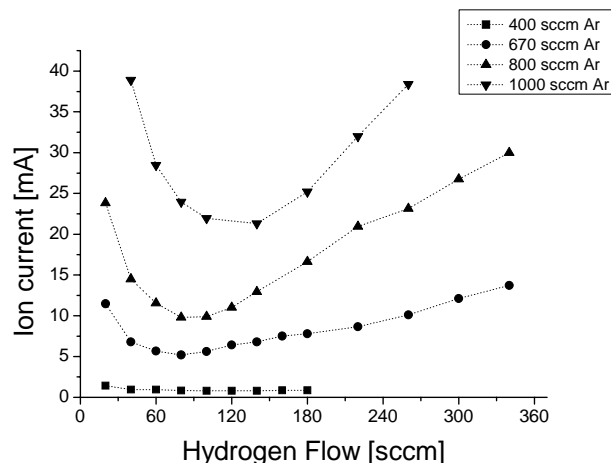
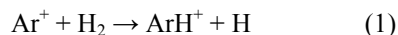
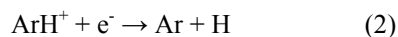


Fig. 6: Ion current as function of  $H_2$  flow for different Ar flows.

The occurrence of a minimum ion current can be explained by two competing mechanisms. In a pure Ar plasma, the injection of  $H_2$  in the plasma leads to a charge transfer reaction [1]:



This reaction is followed by a dissociative recombination reaction:



As a result, atomic hydrogen is created and the ion density is lowered.

The increase in ion current at higher pressures can be explained by an increase in pressure in the arc and the reactor with increasing hydrogen flow. This pressure increase can be seen in Fig. 7. As the pressure in both parts of the deposition system increases, the plasma beam diameter is lowered. Consequently a larger percentage of the ions emanating from the arc arrive at the substrate holder, leading to a larger current measured with this technique. This trend only increases the ion density arriving at the substrate holder, the ion density in the arc is not necessarily increased. However, it can not be excluded that at higher  $H_2$  flows, different ions (e.g.,  $H^+$  or  $H_2^+$ ) are created in the plasma, which would lead to an actual increase of the ion density emanating from the arc.

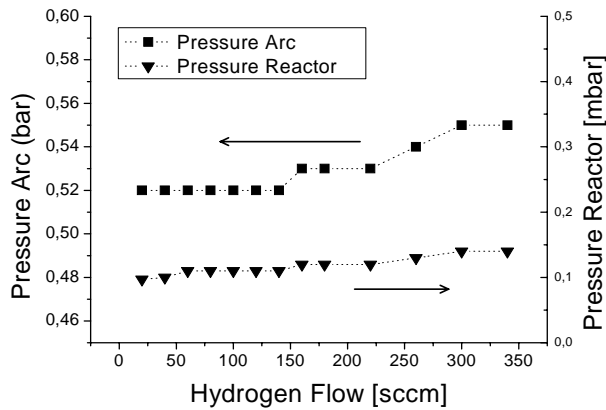


Fig. 7: Pressure in the arc and the reactor of the ETP-CVD setup for different H<sub>2</sub> flows in the arc. The Ar flow was held constant at 670 sccm

The dependence of the ion current on the SiH<sub>4</sub>-flow was investigated in a separate measurement series. The Ar-flow was set to 670 sccm and two series were measured for two different H<sub>2</sub> flows, 80 and 200 sccm. The SiH<sub>4</sub> flow was varied between 0 and 250 sccm.

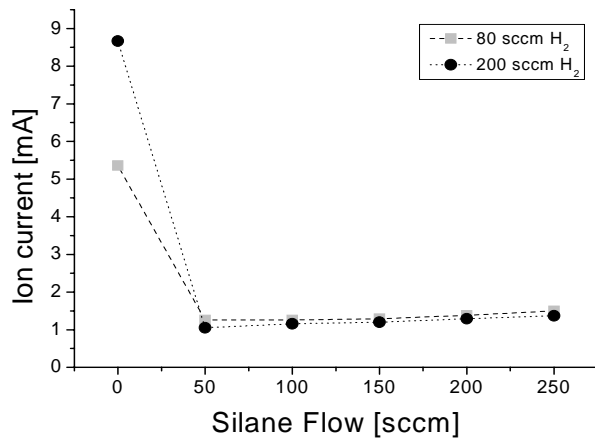
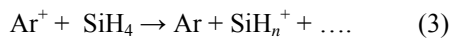


Fig. 8: Ion current as function of SiH<sub>4</sub> flow for two different hydrogen flows

As can be seen in Fig. 8, the ion density drastically decreases already at very low SiH<sub>4</sub> flows. A further increase in the SiH<sub>4</sub> flow does not reduce the ion current further; instead we observe a slight increase which can probably be attributed to an increase in reactor pressure.

The reduction in ion current at low SiH<sub>4</sub> flows is possibly due to a reaction between remaining Ar<sup>+</sup>-ions that did not react with hydrogen according to (1), and SiH<sub>4</sub>-molecules



where  $n \geq 3$ . SiH<sub>n</sub><sup>+</sup> is then neutralized by an electron, leading to the formation of SiH<sub>m</sub> where  $m \geq 2$ . As a result, the ion density in the plasma is quenched. Since this reaction is very effective, a small amount of SiH<sub>4</sub> is enough to react with the

majority of the remaining Ar<sup>+</sup> ions and an increase in SiH<sub>4</sub> flow does not reduce the ion current further. This observation will be investigated further with other analysis methods (e. g. Langmuir probe measurements) in the future.

Although there are no significant differences in ion current for the two different H<sub>2</sub> flows, this does *not* mean that the materials obtained would have the same properties. The influence of the H<sub>2</sub> flow on certain material properties at a fixed Ar and SiH<sub>4</sub> flow has indeed been shown by Kessels *et al.* [12].

#### IV. CONCLUSION

A setup to control the ion energy distribution function has been introduced, based on a similar setup designed for a different application. Control over the ion energy will enable us to study the effect of different ion energies on the material independently in future experiments.

Ion current measurements have been carried out for different gas flow settings. For several different argon flow settings, a minimum in ion current has been observed when the hydrogen flow in the arc is varied. This was attributed to two competing effects, a charge recombination due to a dissociative reaction between Ar ions, H<sub>2</sub> molecules and electrons, and an increase in reactor an arc pressure due to increased gas flows. Low flows of SiH<sub>4</sub> injected into the plasma beam are sufficient to reduce the ion current significantly, increased SiH<sub>4</sub> flows do not reduce the ion current further.

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