

# Detection of powder formation in SiH<sub>4</sub>/H<sub>2</sub> glow discharges

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**Abstract.** Time-resolved self-bias voltage measurements and spatiotemporal resolved optical emission spectroscopy were used in order to monitor particle formation and instabilities in the initial stage of 13.56 MHz SiH<sub>4</sub>/H<sub>2</sub>. The effect of total gas pressure on the particles formation and the time required for the plasma to reach steady state was investigated. Both techniques were very sensitive in monitoring the nucleation and coagulation phase of particles formation. The characteristic times required for reaching steady state were similar for both techniques indicating that electrical properties and chemical kinetics are affected in a similar way from particle formation. The increase of pressure resulted in a significant shortening of the instability period and this can be a significant advantage in the deposition of device grade silicon thin films.

## 1. Introduction

Plasma enhanced chemical vapour deposition (PECVD) using radio frequency (RF) capacitively coupled silane/hydrogen (SiH<sub>4</sub>/H<sub>2</sub>) discharges, is the most common technique, that is used to produce hydrogenated microcrystalline (μc-Si:H) and amorphous (a-Si:H) silicon. These materials are currently applied on single, tandem and multi-junction solar cells and modules for more effective use of solar spectrum [1]. There are still several issues and technological aspects related to these devices that are under investigation for their efficiency improvement and the reduction of cost [2]. More precisely, the increase of the μc-Si:H growth rate while maintain or even improve the film quality is crucial. The increase of the SiH<sub>4</sub>/H<sub>2</sub> gas pressure and the so called high-pressure depletion method is the most promising technique, which can reach the goal of high deposition rates and device grade materials [3]. On the other hand, pressure raise will enhance the powder formation in the discharge which in turn can affect the film quality or the process costs due to the necessity of larger reactor cleaning times between depositions [4]. Gases residence time in the plasma and electron/ion-molecule, molecule-molecule collision frequencies will increase with pressure favoring secondary gas phase reactions, nucleation of clusters and dust formation.

Particles formation in SiH<sub>4</sub> plasmas has been the subject of investigation for several studies that can be found in the literature [5], [6], [7], [8]. The mechanism of clusters nucleation, coagulation and agglomeration has been monitored by different plasma diagnostics [9], [10], [11], [12], [13], theory and simulations [14], [15], [16]. However, all these studies are focused on low pressure, pure SiH<sub>4</sub> or SiH<sub>4</sub> – Ar discharges, which are not typically used for μc-Si:H films deposition. Molecular hydrogen

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that is used in mixtures with SiH<sub>4</sub> for the formation  $\mu\text{c-Si:H}$  is a reactive gas and can significantly alter the mechanism of particle formation.

In the present work, we focused on the effect of the total SiH<sub>4</sub>/H<sub>2</sub> pressure on the initial electrical and chemical instabilities that are induced by the nucleation and coagulation of silicon clusters. The investigation was carried out at typical conditions of  $\mu\text{c-Si:H}$  film growth. Time resolved electrical and optical plasma diagnostics were implemented and the characteristic times for instabilities ignition and steady state conditions were monitored. Spatio-temporal optical measurements were also used to follow changes on the electron heating mechanisms during the nucleation phase. The increase of pressure resulted in significant drop of the time that is required to reach steady state plasma conditions and this can be an important advantage for the material properties as it will minimize the undesirable incubation layer [17].

## 2. Experimental

A capacitively coupled, ultrahigh vacuum ( $10^{-8}$  Torr base vacuum) reactor, with parallel plate electrodes was used in this work [18]. The gas was fed into the plasma through a showerhead electrode. The process pressure was monitored by a capacitance manometer and was controlled via a throttle valve. All experiments were performed at room temperature with an excitation frequency of 13.56 MHz and interelectrode space of 15 mm. The total gas flow rate was 150 sccm, with SiH<sub>4</sub> input concentration of 4%, while the chamber pressure was varied from 0.5 to 4 Torr (table 1).

**Table 1.** Experimental conditions.

	Set 1	Set 2
Electrode gap	15 mm	15 mm
Total gas flow	150 sccm	150 sccm
SiH <sub>4</sub> concentration	4%	0%
Discharge Power	11 W	11 W
Substrate Temperature	30 °C	30 °C
Chamber Pressure	0.5 – 4 Torr	0.5 – 4 Torr

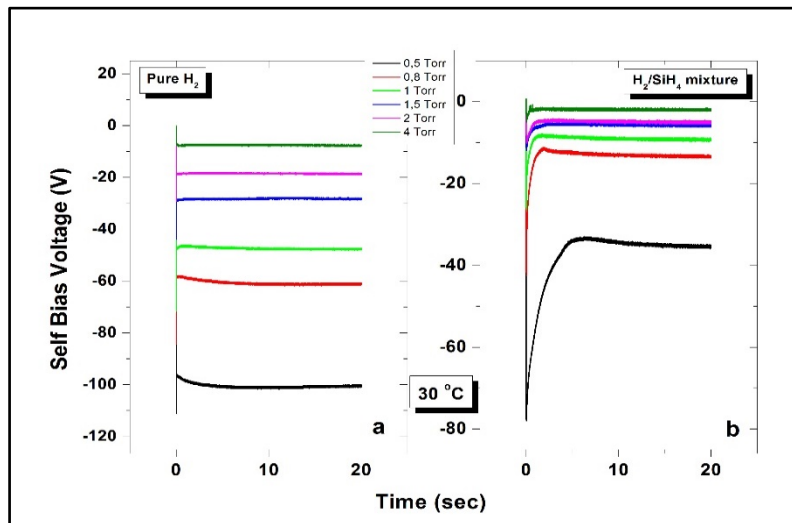
The amount of RF power dissipated in the discharge was calculated by using the transmission ABCD matrix method [19], after measuring the voltage and current waveforms and their relative phase difference outside the reactor. For all the experimental conditions that are presented here, the real power dissipated to the plasma was fixed to 11 W.

Plasma imaging and spatiotemporal emission profiles of  $\alpha$ -balmer, b-balmer and SiH ( $A^2\Delta-X^2\Pi$ ) lines were measured according to the method described in [20], [21] by using an iCCD detector (Andor, iStar734) and the proper interference filters. Self-bias voltage was measured by a handmade low-pass filter attached to the RF electrode.

## 3. Results and discussion

Figure 1 shows the time evolution of the self-bias voltage ( $V_{dc}$ ) as a function of time for (a) the pristine Hydrogen and (b) SiH<sub>4</sub>/H<sub>2</sub> discharges. Different gas pressures ( $P$ ) from 0.5 to 4 Torr are also plotted for each case and as we can observe  $V_{dc}$  values become less negative with pressure for both H<sub>2</sub> and SiH<sub>4</sub>/H<sub>2</sub> plasmas. This is typical behaviour in RF capacitively coupled asymmetric sheaths, where previous studies have shown that  $V_{dc}$  will scale linearly with  $P^{-1/2}$  due to the plasma confinement and the drop of the electron temperature [22], [23]. In addition,  $V_{dc}$  is less negative in SiH<sub>4</sub>/H<sub>2</sub> compared to pure H<sub>2</sub> discharges for the same pressure again due to the lower electron temperature that is expected in the SiH<sub>4</sub>-containing mixture.

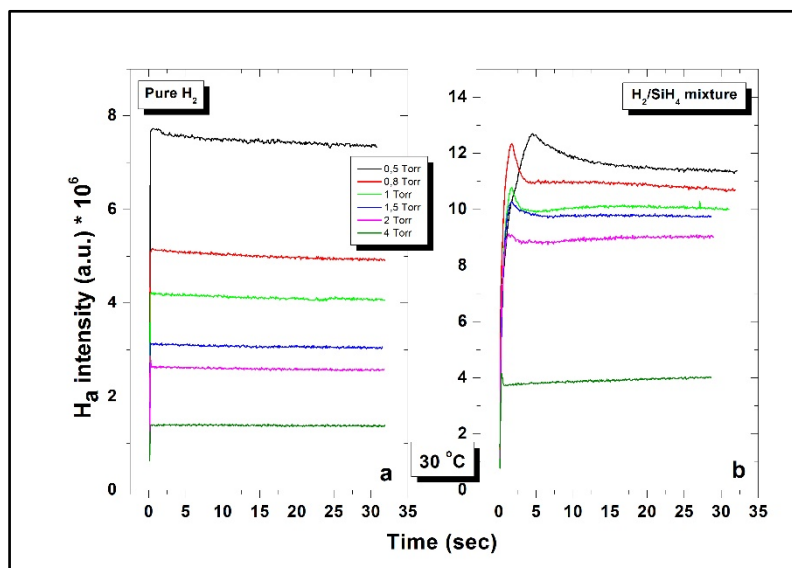
As for the time evolution of the  $V_{dc}$ , in pure Hydrogen it reaches a steady state value few ms after plasma ignition. On the other, hand, for the SiH<sub>4</sub>/H<sub>2</sub> mixture  $V_{dc}$  gets the most negative value few ms



**Figure 1.** Time evolution of the self-bias voltage for several values of chamber pressure for the cases of pristine  $\text{H}_2$  (a) and  $\text{SiH}_4/\text{H}_2$  (b) discharges.

after plasma is on and then decreases in absolute value asymptotically. It is worth noticing that the time required reaching steady state is of the order of seconds and becomes shorter with pressure increase. Similar variation of  $V_{dc}$  values have been reported [8], [12], [24] in  $\text{SiH}_4\text{-Ar}$  and  $\text{SiH}_4\text{-H}_2$  plasmas and are related to the first two stages of dust formation i.e the nucleation and coagulation of clusters.

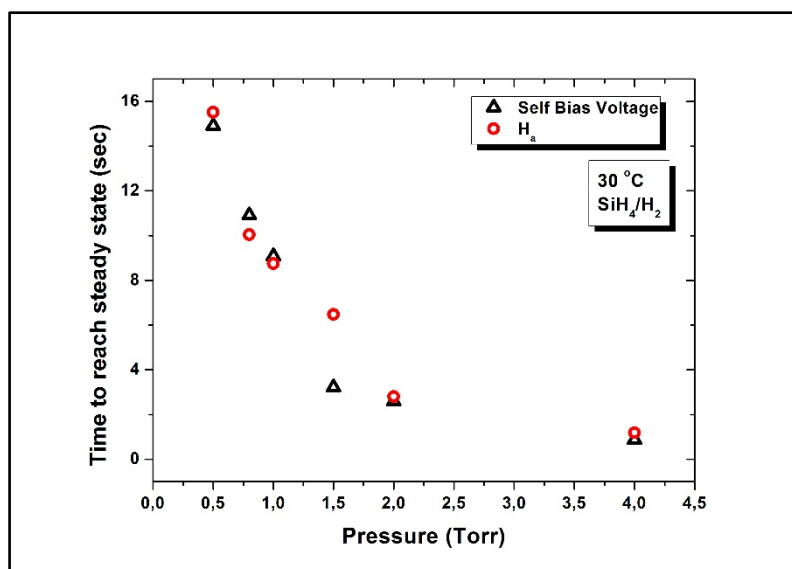
Figure 2 presents the time evolution of the  $\text{H}_\alpha$  line intensity in the case of pristine Hydrogen (a) and  $\text{SiH}_4/\text{H}_2$  mixture (b) for different values of total pressure. The increase of pressure results in a drop of  $\text{H}_\alpha$  emission intensity for both  $\text{H}_2$  and  $\text{SiH}_4/\text{H}_2$  mixture and this is related to the drop of electron temperature with pressure, which in turn affects all the high energy electron – molecule collision processes. Moreover, as in the case of  $V_{dc}$  the emission intensity in pure hydrogen plasma increases



**Figure 2.** Emission intensity of  $\text{H}_\alpha$  line for several values of chamber pressure for the cases of pristine  $\text{H}_2$  (a) and  $\text{SiH}_4/\text{H}_2$  (b) discharges.

very fast and stabilizes few msec after the plasma ignition. In  $\text{SiH}_4\text{-H}_2$  discharges,  $\text{H}_\alpha$  emission intensity increases also rapidly immediately after plasma ignition and continues to rise in a slower rate for the next few sec. The duration of this second stage becomes shorter with pressure and is followed by a slow drop of  $\text{H}_\alpha$  emission intensity until steady state conditions are reached. The slower rate rise of emission intensity in the second stage should be attributed to an increase in electron temperature during the particle nucleation phase in order to compensate the charge loss due to the electron attachment [7]. On the other hand, the slight drop of  $\text{H}_\alpha$  emission intensity and the subsequent stabilization reflects the coagulation phase which is followed by decrease of both electron density and temperature until steady state is reached [14].

Figure 3 shows the time required for the plasma to reach state conditions ( $t_{st}$ ) as a function of the  $\text{SiH}_4/\text{H}_2$  total gas pressure. The characteristic times were calculated from the temporally resolved  $V_{dc}$  and  $\text{H}_\alpha$  emission intensity measurements and there is almost no difference between the estimated times for stabilization. Finally, the increase of pressure results in significant drop of the  $t_{st}$ . This can be attributed to the enhancement of chemical kinetics and can be an important advantage for the material properties as it will minimize undesirable incubation layer, which is caused by process instabilities during the film initial growth [17].



**Figure 3.** Time to reach steady state in self-bias voltage (3a) and  $\text{H}_\alpha$  emission line (3b).

#### 4. Conclusions

Self-bias voltage and time-resolved optical emission spectroscopy (OES) were used to detect particles formation in  $\text{SiH}_4/\text{H}_2$  discharges and instabilities during the initial plasma stage. It was shown that both techniques are very sensitive to particle detection and can be used to monitor nucleation and coagulation stage of particles formation. In dust free conditions (pure  $\text{H}_2$ ) we observe that self-bias voltage as well as  $\text{H}_\alpha$  intensity stabilized few msec after plasma ignition. In the  $\text{SiH}_4/\text{H}_2$  discharges, the time required for plasma to reach steady state conditions is of the order of seconds. Both techniques lead to similar values of  $t_{st}$  indicating that plasma electrical properties and chemical kinetics are affected in a similar way from the formation of particles. The increase of pressure results in a significant drop of the time required for process steady state conditions and this can be considered as an important advantage that favors the growth of good quality silicon thin films under high pressure conditions.

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