

# PECVD of hydrogenated silicon thin films from $\text{SiH}_4 + \text{H}_2 + \text{Si}_2\text{H}_6$ mixtures

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## Abstract

The effect of small addition of disilane on highly diluted silane in hydrogen discharges for the deposition of microcrystalline silicon thin films has been investigated. A spectacular six times enhancement of the film growth rate has been recorded by introducing 0.6% disilane in the mixture at very low power densities. It is clarified that the observed increase is not a result of the higher concentration of silicon atoms in the gas feed but it can rather be attributed to the increase of silane dissociation caused by the addition of disilane and to the enhanced contribution of higher radicals to the film growth. The effect of the small addition of disilane on the film growth along with the rationalistic use of the silicon precursors need to be further examined as a solution for rapid deposition of microcrystalline silicon layers.

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**Keywords:** Microcrystalline silicon; Disilane; PECVD; Glow discharge; Silane

## 1. Introduction

The deposition of microcrystalline silicon thin films ( $\mu\text{c-Si:H}$ ) at higher growth rates is a very important issue for the mass production of completely microcrystalline single junction cells as well as tandem structures consisting of an a-Si:H top cell and a  $\mu\text{c-Si:H}$  bottom cell [1].

The excitation frequency increase (VHF-glow discharge technique) [2] and the total gas pressure increase (high pressure depletion technique) [3] of highly diluted  $\text{SiH}_4$  in  $\text{H}_2$  discharges, have both been proposed to be advantageous for the increase of  $\mu\text{c-Si:H}$  deposition rate. An alternative approach that has not been considered yet in the case of  $\mu\text{c-Si:H}$  deposition is the use of alternative or modified source gas. More precisely, if one considers the hopeful results reported for a-Si:H deposition rate [4], the use of disilane as gas precursor instead of or in combination with silane appears to be worth examining since the requirements for deposition rate enhancement are more stringent in the case of  $\mu\text{c-Si:H}$  [5].

In this direction, we report a systematic study of the effect of a small addition of  $\text{Si}_2\text{H}_6$  on the properties of

highly diluted  $\text{SiH}_4$  in  $\text{H}_2$  discharges. Namely, two kinds of experiments were performed: (a)  $\text{Si}_2\text{H}_6$  fraction in the  $\text{SiH}_4/\text{H}_2$  mixture was maintained constant at 0.3 and 0.6% while varying  $\text{SiH}_4$  partial pressure from 6 to 9%; and (b)  $\text{SiH}_4$  fraction in the mixture was kept constant at 6% while  $\text{Si}_2\text{H}_6$  fraction was varying from 0 to 0.6%.

## 2. Experimental

The experiments were performed in a capacitively coupled ultrahigh vacuum (UHV) parallel plate reactor having a base vacuum of  $10^{-9}$  mbar. The reactor is equipped with four quartz windows suitable for recording spatially resolved emission profiles. The 90-mm diameter grounded electrode is mounted on a linear motion feedthrough, allowing for continuous variation of the interelectrode spacing (in this work the electrode separation was fixed at 15 mm). The total flow rate was kept constant in this series of experiments at 100 sccm while the total pressure was adjusted independently via a downstream throttle valve controller.

The power actually consumed in the discharge and the discharge impedance, were determined using Fourier transform voltage and current analysis as described in detail elsewhere [6]. The  $\mu\text{c-Si:H}$  films were grown on Corning 7059 at a substrate temperature of 250 °C and

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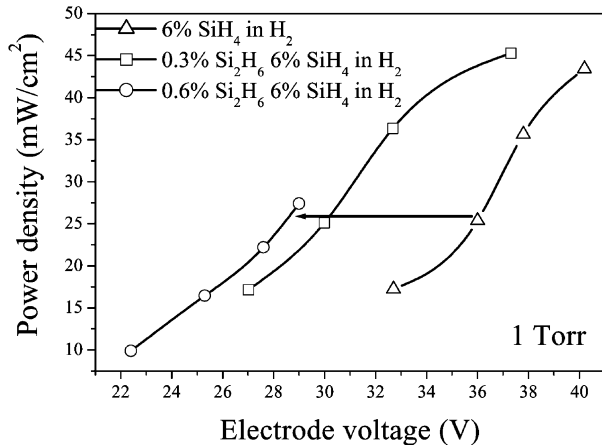


Fig. 1. Power dissipation as a function of electrode voltage amplitude for the gas mixtures of 6% SiH<sub>4</sub> in H<sub>2</sub>, 0.3% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub> in H<sub>2</sub> and 0.6% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub> in H<sub>2</sub> and the total gas pressure of 1 Torr.

their deposition rate were measured in situ using laser reflectance interferometry. All the measurements were performed in dust free conditions as monitored using a laser light scattering technique.

### 3. Results and discussion

In order to investigate the effect of small addition of Si<sub>2</sub>H<sub>6</sub> on the film growth rate, we performed different sets of electrical measurements in 6% SiH<sub>4</sub> in H<sub>2</sub>, 0.3% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub>/H<sub>2</sub> and 0.6% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub>/H<sub>2</sub> discharges. The excitation frequency was 27.12 MHz and the total gas pressure was 1 Torr. Fig. 1 shows the variation of the power consumed in the discharge as a function of the applied voltage for the above-mentioned gas mixtures. The successive addition of Si<sub>2</sub>H<sub>6</sub> to SiH<sub>4</sub>/H<sub>2</sub> discharges leads to an enhancement of the power dissipation for the same applied voltage. Thus, in order to maintain the same power consumption, a drop of the electrode potential is required (solid line, Fig. 1). This drop is due to the introduction of Si<sub>2</sub>H<sub>6</sub>, a gas with lower ionisation threshold and higher cross-sections compared to SiH<sub>4</sub> and H<sub>2</sub> [7]. The fact that even in so small concentrations Si<sub>2</sub>H<sub>6</sub> can affect the power dissipation and the electrical properties of the discharge indicates that an analogous strong influence on the gas phase chemistry and the film growth rate can be expected.

In Fig. 2 is presented the variation of the deposition rate as a function of the power consumed in the three previously mentioned gas mixtures. The increase of power leads to an enhancement of the film growth rate which is much more important in the 0.6% Si<sub>2</sub>H<sub>6</sub> case. Indeed, in the cases of 6% SiH<sub>4</sub> in H<sub>2</sub> and 0.3% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub> in H<sub>2</sub> the increase of power from 25 to 43 mW/cm<sup>2</sup> leads to approximately 40% increase of the

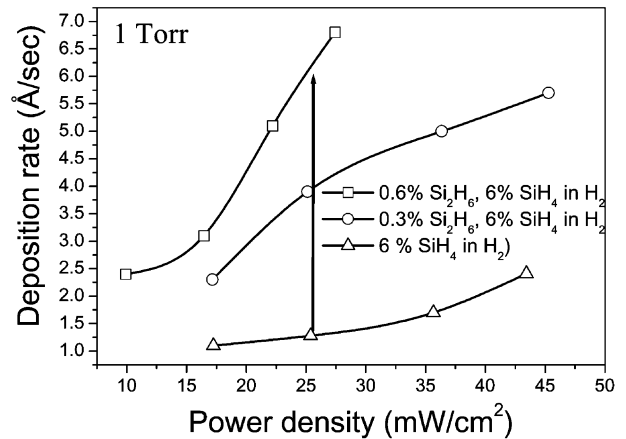


Fig. 2. Deposition rate as a function of the power consumed in 6% SiH<sub>4</sub> in H<sub>2</sub>, 0.3% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub> in H<sub>2</sub> and 0.6% Si<sub>2</sub>H<sub>6</sub>/6% SiH<sub>4</sub> in H<sub>2</sub> discharges. Solid line indicates film growth rates obtained in constant power conditions.

film growth rate while in the case of 0.6% Si<sub>2</sub>H<sub>6</sub>, a smaller increase of the power density (10–27 mW/cm<sup>2</sup>) increases the deposition rate by approximately 65%. In addition, if one compares the effect of disilane addition under conditions of constant power dissipation (solid line, Fig. 2) a spectacular 90% increase of the deposition rate is observed. Finally, in the 0.6% Si<sub>2</sub>H<sub>6</sub> case the deposition rate reaches the value of 7 Å/s, a very impressive result considering the very low power level (27 mW/cm<sup>2</sup>).

In order to clarify, if the enhancement of the deposition rate is a result of the higher total concentration of Si atoms in the reactor or is due to the different physicochemical properties and the gas phase chemistry of Si<sub>2</sub>H<sub>6</sub>, the concentration of Si atoms in the reactor was modified by increasing the fraction of SiH<sub>4</sub> in the gas mixture. The influence of this increase on the

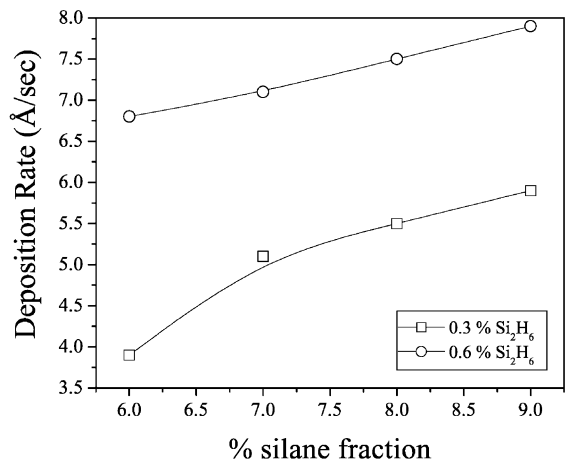


Fig. 3. Deposition rate as a function of silane partial pressure in the two cases of small disilane addition of 0.3% and 0.6% Si<sub>2</sub>H<sub>6</sub>.

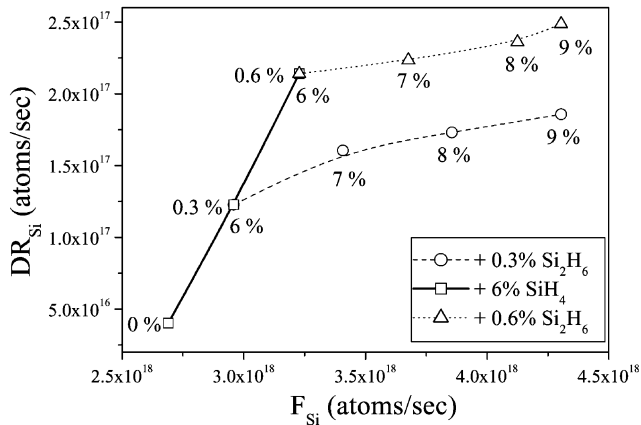


Fig. 4. Silicon atom film incorporation rate as a function of the silicon atom feed rate in the reactor chamber for the case of small Si<sub>2</sub>H<sub>6</sub> addition and for the case of increase of silane partial pressure.

deposition rate was investigated for the two cases of 0.3% Si<sub>2</sub>H<sub>6</sub> in H<sub>2</sub> and 0.6% Si<sub>2</sub>H<sub>6</sub> in H<sub>2</sub> and is presented in Fig. 3. The frequency and the total gas pressure were as in the previous case maintained at 27.12 MHz and 1 Torr, respectively, while the power actually consumed in the discharge was about the same and equal to 27 mW/cm<sup>2</sup> in all the experiments. It is observed that the increase of silane fraction in the gas mixture from 6 to 9% results in an enhancement of the deposition rate that is more pronounced (34 vs. 14%) for the 0.3% Si<sub>2</sub>H<sub>6</sub> compared to the 0.6% Si<sub>2</sub>H<sub>6</sub> case. However, this enhancement is much weaker compared to the one that has been observed before by increasing the Si<sub>2</sub>H<sub>6</sub> content under conditions of constant power dissipation (Fig. 2).

This becomes clearer if one examines both cases in what concerns the rate by which silicon atoms are fed in the reactor and the rate by which silicon atoms are incorporated in the growing film. These figures are presented in Fig. 4 where the deposition efficiency is plotted. The rate that silicon atoms are fed in the reactor  $DR_{Si}$  and the rate of silicon atom film incorporation  $F_{Si}$  are calculated according to Ref. [8]. The results presented in Fig. 4 show that a small increase of the silicon atoms feed rate caused by the increase of Si<sub>2</sub>H<sub>6</sub> fraction (solid line) leads to a rapid increase of the number of silicon atoms contributing to the film growth. The slope of the line reveals that approximately 40% of the Si atoms that are initially present in the discharge are finally incorporated in the film. This is significantly high if one considers that for the case of SiH<sub>4</sub>/H<sub>2</sub> discharges and in conditions of high growth rates the deposition efficiency does not exceed 25% [8]. However, if the increase of the rate that silicon atoms are fed into the chamber is done by increasing the fraction of SiH<sub>4</sub> in the gas mixture, this is not followed by an analogous enhancement of the rate of film incorporation of silicon atoms (Fig. 4, dash and dot line). Moreover,

the addition of SiH<sub>4</sub> is followed by a drop of the deposition efficiency, which in both cases (0.3% and 0.6% Si<sub>2</sub>H<sub>6</sub>) becomes less than 10%. Thus, the small addition of Si<sub>2</sub>H<sub>6</sub> in SiH<sub>4</sub>/H<sub>2</sub> mixtures is a much more rationalistic way to improve the film growth rate compared to the increase of silane partial pressure.

It has thus been clarified that the beneficial effect of Si<sub>2</sub>H<sub>6</sub> addition to the film growth rate is not related to the increase of the concentration of Si atoms in the reactor and it must be related to other phenomena. Although further investigation is required for a complete understanding, the presence of disilane in the discharge leads to an increase of the electron density and thus favors the dissociation of SiH<sub>4</sub> [5], as indicated by the decrease of the excitation voltage that is required for maintaining the same power level. Silane dissociation is otherwise favored also by the enhancement of secondary reactions. This enhancement of the gas phase reactivity and the production of higher radicals that can contribute to the film growth by offering more than one silicon atom to the growing film network, can be an additional reason. Whatever is the case, the quite high deposition rate in combination to the fact that the films deposited with small Si<sub>2</sub>H<sub>6</sub> addition, are microcrystalline or on the onset of microcrystallinity, leads to the candidacy of Si<sub>2</sub>H<sub>6</sub> for deposition rate enhancement in device fabrication.

#### 4. Conclusions

The PECVD process of microcrystalline silicon thin films from SiH<sub>4</sub>/Si<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> mixtures has been investigated. The small addition of Si<sub>2</sub>H<sub>6</sub> in the SiH<sub>4</sub>/H<sub>2</sub> discharges was found to increase the power consumption significantly thus indicating that even in small concentrations it can seriously affect gas phase processes.

The increase of the Si<sub>2</sub>H<sub>6</sub> fraction from 0 to 0.6% under constant power dissipation results in a spectacular increase of the deposition rate by more than six times. This increase has been proved as not induced by the increase of silicon atom density in the reactor and has been attributed to the possible increase of silane dissociation caused by the increase in electron density and to the enhanced contribution of higher radicals to the film growth.

Finally, the observed high film growth rates in combination to the rationalistic consumption of the silicon precursors indicate that Si<sub>2</sub>H<sub>6</sub> must be further considered for the production of single or multi junction solar cells containing microcrystalline silicon layers.

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