# Input silane concentration effect on the a-Si:H to μc-Si:H transition width

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## Abstract

In this work the microstructure transition width from amorphous to microcrystalline silicon is discussed. It is shown that the width of the transition depends on the input silane concentration level and indirectly on the silane depletion level. The higher the input silane concentration and depletion, the wider the transition. Experimental results are then compared to an analytical model and good agreement is obtained with a semi-empirical approach that takes into account the effect of the silane density in the plasma on the electron density.

*Key words:* silicon thin film, silane-hydrogen discharge, microstructure transition

## 1 Introduction

Microcrystalline silicon is a composite material embedding silicon nanocrystals in an amorphous matrix that has attracted much research effort in the field of thin film silicon [1]. Used as a photoactive material, it can be integrated as bottom cell in a tandem structure with an amorphous silicon top cell, lifting efficiencies of micromorph cells well above 10 % [2]. Used as carrier channel in thin film field effect transistors, it increases by several orders of magnitude the carrier mobility compared to amorphous silicon [3]. The properties of the microcrystalline material change depending on the specific

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application: in photovoltaics the amorphous matrix plays an important and not yet fully understood role of passivating grain boundaries and reducing defect densities [1,4]. The best material is obtained within the transition region from amorphous to highly microcrystalline and knowledge of the variation of the crystalline fraction with respect to input silane concentration or any other process parameter like the RF power is thus critical; in thin film transistor technology instead, materials with higher crystallinity fractions are used, because of the larger carrier mobility [3]. Yet even if the required characteristics of the microcrystalline material are known for a specific application, the parameters in which microcrystalline silicon is deposited may vary considerably depending on such parameters as RF driving frequency [5], silane concentration in hydrogen [6] or the deposition rate [7]. As a result, the relationship between deposition conditions and properties of microcrystalline material is only partially understood. In this paper the transition from amorphous to highly microcrystalline silicon is studied in different deposition conditions. It is shown that the transition and in particular its width as a function of input silane concentration can be characterized and explained using a recently published model [8]. Silane depletion in the reactor chamber, together with the input silane concentration are shown to be two relevant physical parameters determining the width of the transition region.

## 2 Experimental details

Microcrystalline silicon layers were deposited by very high frequency (VHF) plasma-enhanced chemical vapor deposition (PECVD) at 40.68 MHz in an industrial KAI-S type reactor based on the Plasma-Box concept [9], using silane and hydrogen as gas precursors. Substrate temperature was 180C in all depositions. The samples were deposited in different conditions of total gas pressure, input silane concentration and silane depletion as resumed in Tab. 1. The RF power input was kept constant within each series, but was adjusted to have the different Before the deposition of the layers studied in this paper, a highly microcrystalline layer was deposited on glass in order to avoid amorphous incubation layers [10]. The crystalline fraction of the layers was analyzed by micro-Raman spectroscopy [11].

## 3 Experimental results

Raman crystallinity fractions of silicon intrinsic layers deposited in the transition region are plotted as a function of silane concentration in Fig. 1. In all deposition regimes, silane concentration was varied changing silane input

flow and keeping constant total flow. As summarized in Tab. 1, the curves were obtained in different conditions of total gas pressure ranging from 1.2 to 3.5 mbar. Total gas flows were 1.3 slm at 1.2 mbar and 1.6 slm at 3.5 mbar in the low silane concentration deposition regimes and about 0.2 slm in the high silane concentration deposition regimes (marked in the figures with the acronym HD, standing for high silane depletion). As has been shown recently, it is possible to obtain microcrystalline silicon at very high silane concentrations, provided the silane dissociation rate and/or the residence time of the gas particles in the deposition chamber are sufficiently high [6]. This can be achieved by reducing the total gas flow through the deposition chamber at a fixed pressure. Thus, decreasing the hydrogen flow, the total flow was reduced from 1.3 slm to 0.21 slm at 1.2 mbar, implying necessarily an increase of silane concentration. However, the crystallinity of the layer does not change significantly as the reduction of hydrogen molecules in the input flow is offset by a higher dissociation in the plasma due to the longer gas residence time in the plasma. This leads to similar conditions of silane to hydrogen precursor flows to the substrate, which has been shown to be the determining factor for microcrystalline growth [8]. The widths of the transition curve obtained in the low and high silane concentration regimes are strikingly different (see Fig. 1). At low silane concentration, transition widths are significantly narrower than at high silane concentrations. For instance, for the case at 1.2 mbar it can be clearly seen that reducing the hydrogen flow (i.e. increasing silane concentration) widens the transition width approximately by a factor of 5. As an inset in Fig. 1, the relationship between average silane concentration (measured at 50 % Raman crystallinity) and transition width (measured from 10 % crystallinity to 70 % crystallinity) is shown in the six studied cases. This shows that the higher the input silane concentration $c$, the wider is the transition from amorphous to highly microcrystalline silicon material until it reaches a plateau. As a result, the film microstructure uniformity is less sensitive to $c$ variation, in time and/or in space, at high silane concentration in large area reactors that could rise from improper gas distribution or pumping. This is because the transition width discussed in the present work determines the tolerance in silane input concentration to maintain the plasma conditions concomitant with the deposition of transition material.

Despite the wide range of deposition parameters used, it is possible to relate the differences in the width of the amorphous to highly microcrystalline transitions to differences in input silane concentrations and silane depletion conditions in the plasma. As a rough estimate of silane depletion it is possible to evaluate the ratio between the deposition rate $R$ and the maximum possible deposition rate $R_{\max}$ reached if all silicon atoms contained in the input gas flow are deposited uniformly on the reactor walls and substrate [6]:

$$R_{\max} = \frac{0.0962 \cdot \Phi_{SiH_4}}{A} \qquad (1)$$

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$\Phi_{\mathrm{SiH_4}}$ is the silane input flow expressed in sccm, $A$ is the internal area facing the plasma of the KAI-S Plasma-Box. As a result, different points on the transition curve in Fig. 1 have different deposition rates $R$ and maximum deposition rates $R_{\mathrm{max}}$, because the input silane flow $\Phi_{\mathrm{SiH_4}}$ was varied to change silane concentration. The relationship between deposition rates and depletion $D$ is given by the following expression assuming uniform thickness over the reactor walls, and incorporation of all silane radicals formed in the plasma into growing film:

$$\eta = \frac{R}{R_{\mathrm{max}}} = \frac{D}{1 + (1 - D) \cdot c} \tag{2}$$

For small silane concentration $c$, $\eta$ and $D$ roughly coincide. For the two deposition regimes with high silane concentration, the silane depletion fraction reaches $D \approx 0.8$ and is significantly increased compared to the low silane concentration deposition regimes where $D \approx 0.4$. This is mainly due to the smaller total flows and therefore longer gas residence time. For higher pressures (typically above 2 mbar) polysilane and powder formation becomes critical and thus a measurement in high depletion conditions at 3.5 mbar has been avoided in this study.

## 4  Theoretical Model

The experimental observations made in the previous section can be understood following a model published recently [8]. In this model it is shown that the transition from amorphous to microcrystalline growth is more correctly described with the silane concentration in the plasma, $c_{\mathrm{p}}$, instead of the input silane concentration, $c$. These two parameters are related by the fractional silane depletion, $D$, according to the following expression:

$$c_{\mathrm{p}} = c \cdot (1 - D). \tag{3}$$

Microcrystalline material is obtained for values of $c_{\mathrm{p}}$ lower than about 1 %. As a result, microcrystalline silicon can be deposited at high initial silane concentrations provided that the silane depletion in the plasma is sufficiently large so that the flux ratio of atomic hydrogen to silane radical remains higher than 40 as reported by Dingemans *et al* for a substrate temperature of 200 °C [12]. The transitions displayed in Fig. 1 are obtained as a function of silane concentration $c$ while keeping all other parameters constant. Intuitively, the variation of only the silane concentration should correspond to a vertical trajectory in the $(D, c)$ plane of Fig. 2 (dashed line, $\partial D / \partial c = 0$). Therefore, the overlay between this vertical line and the microstructure transition zone,

defined between two iso-$c_p$ curves (grey zone), leads to a monotonic increase of the transition width as a function of the input silane concentration as shown by the dashed line in Fig. 3. This intuitive approach is in agreement with the experiment at low silane concentrations. However, it fails to fit the data and largely overestimates the transition width at high silane concentration.

Measurement of the silane depletion by infrared absorption spectroscopy as a function of the input silane concentration [8] presented in Fig. 4 shows that, as opposed to the intuitive approach ($\partial D/\partial c = 0$), the silane depletion fraction decreases while increasing the silane concentration. This optical measurement is independently confirmed by calculating $D$ from Eq. 1 at different silane concentrations. This is probably due to the fact that the silane density in the plasma and electron density are correlated because of electron attachment to $SiH_4$ [13] as suggested in Fig. 5 by the variation of the relative electron density with silane density deduced from previous time-resolved optical emission spectroscopy measurements [14]. Therefore, the slope of $c(D)$ should be negative as shown in Fig. 2 (solid line, $\partial D/\partial c = -0.14 < 0$) and not infinite as in the intuitive case. This is because the silane density in the plasma, i.e. $c_p$, varies while crossing the microstructure transition zone, hence, the electron density is not constant while varying the input silane concentration. The resulting estimation of the transition width by using $\partial D/\partial c = -0.14$ for all conditions (solid line in Fig. 2) predicts a maximum before stabilizing to about 6 - 7 %, which is in very good agreement with the experimental results as shown in Fig. 3.

## 5   Conclusions

The transition from amorphous to microcrystalline silicon thin film deposited in a large area parallel plate reactor was studied. It was shown that the transition width from amorphous to microcrystalline depends strongly on the silane depletion level and the initial silane concentration. In the low silane concentration and depletion regime, the transition could be as sharp as a fraction of a percent in silane concentration, but in the high silane concentration and depletion regime it reaches more than 5 % with a maximum in width for an input silane concentration of about 20-30 %. It has been shown that a simple model, originally developed to link the plasma composition $c_p$ to the radical flux ratio towards the growing film surface, could be extended to explain the transition width as a function of silane concentration in different silane depletion conditions. However, it has necessitated the addition of dependence between electron density and silane concentration in the plasma.

## Acknowledgements

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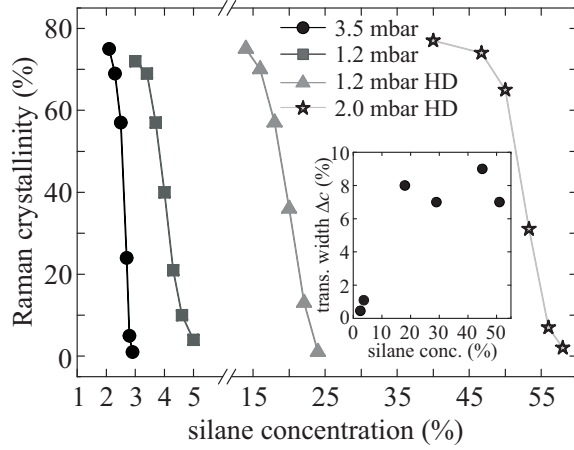| $c$ % | total flow (slm) | $p$ (mbar) | $P_{RF}$ (W) |
|---|---|---|---|
| $\sim 2.5$ | 1.6 | 3.5 | 450 |
| $\sim 4$ | 1.3 | 1.2 | 400 |
| $\sim 20$ | 0.21 | 1.2 | 400 |
| $\sim 29$ | 0.23 | 1.5 | 450 |
| $\sim 45$ | 0.16 | 1.8 | 500 |
| $\sim 50$ | 0.15 | 2.0 | 530 |

Table 1

Fig. 1. Raman crystallinity as a function of input silane concentration in four of the six deposition regimes studied. The inset presents the transition width as a function of the input silane concentration.
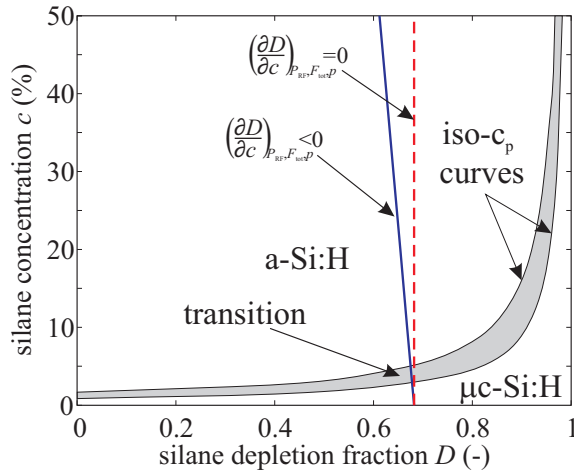


Fig. 2. Amorphous and microcrystalline silicon deposition region in the $(D, c)$ space with the two discussed dependencies of the silane depletion on the input silane concentration.
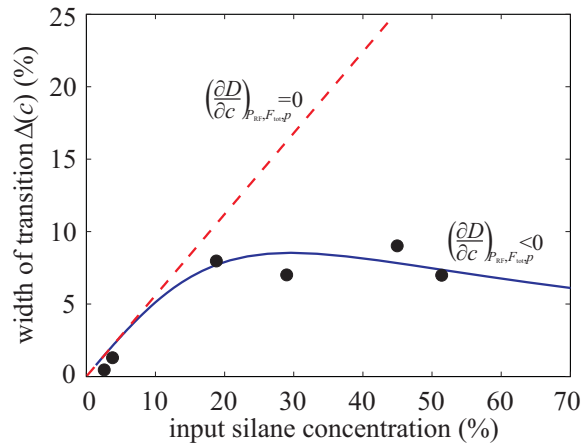
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Fig. 3. Width of the transition as a function of the input silane concentration from the data plotted in Fig. 1 with the two models.
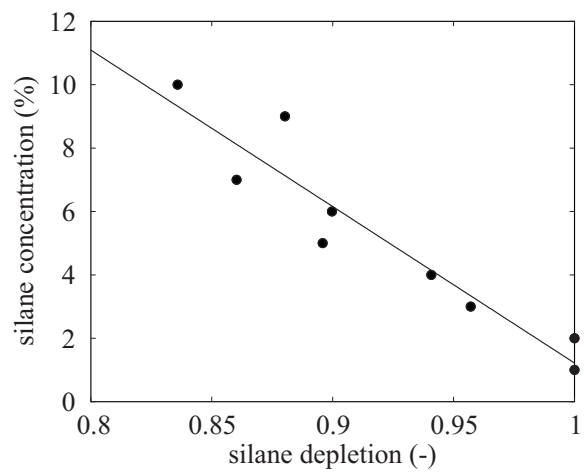


Fig. 4. Induced dependence of the silane depletion measured by FTIR spectroscopy on its input concentration (data taken from [8]).
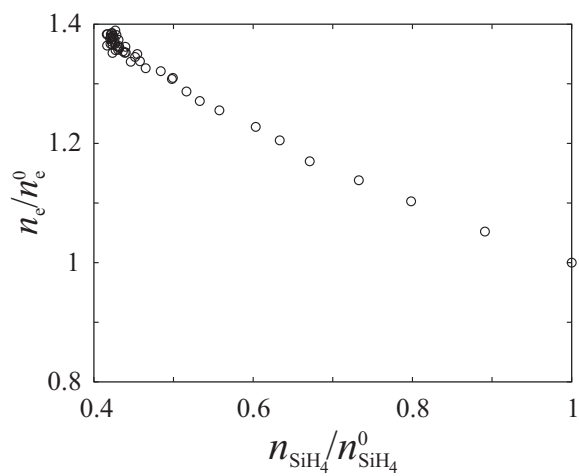
Fig. 5. Relative electron density variation with relative silane density measured by time-resolved optical emission spectroscopy. $n_e$ and $n_{SiH_4}$ are the electron and silane density in the plasma and $n_e^0$ and $n_{SiH_4}^0$ are the electron and silane density at plasma ignition (data taken from [14]).