Study of the microstructure transition width from amorphous to microcrystalline silicon as a function of the input silane concentration

B. Strahm[a,b], A. Feltrin[a], G. Bugnon[a], F. Meillaud-Sculati[a], C. Ballif[a], A.A. Howling[b] & Ch. Hollenstein[b]

[a]Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering IMT, Photovoltaics and thin film electronics laboratory, Breguet 2, CH-2000 Neuchâtel, Switzerland.
[b]Ecole Polytechnique Fédérale de Lausanne (EPFL), Centre de Recherches en Physique des Plasmas, CH-1015 Lausanne, Switzerland.

ABSTRACT

Amorphous and microcrystalline silicon have been proven to be very interesting for low cost thin film photovoltaic devices. Usually these two materials are deposited using the same large area plasma-enhanced chemical vapor deposition reactors from silane and hydrogen gases. The transition from amorphous deposition regime to microcrystalline deposition regime is generally done by reducing the silane concentration in the input gas flow and the optimum deposition parameters to achieve high performance device stands just at the transition between the two microstructures. In the present work, a study of the transition width from amorphous to microcrystalline silicon is presented as a function of the input silane concentration. It is shown that the higher the input silane concentration, the wider is the microstructure transition. As a consequence, the process is less sensitive to fluctuations of the silane concentration when silane concentrations higher than 10 % are used and better uniformity and reproducibility can be then achieved.

amorphous silicon, microcrystalline silicon, microstructure transition, PECVD

1. INTRODUCTION

Thin film silicon is one of the technologies proven to be capable to reduce the cost of photovoltaic electricity compared to the conventional first generation based on crystalline silicon. Silicon films are generally deposited by plasma-enhanced chemical vapor deposition (PECVD) on various types of substrates including glass, polymer or metallic sheets with size than can reach several square meters. Silicon can be deposited with two different microstructures, hydrogenated amorphous silicon (a-Si:H) or hydrogenated microcrystalline silicon (μc-Si:H), sometimes also called hydrogenated nanocrystalline silicon (nc-Si:H). Amorphous silicon can be used in single junction *p-i-n* or *n-i-p* devices and due to its direct bandgap, an *i*-layer thickness of only about 200 nm is required to absorb efficiently the incoming light. Such devices can achieve a stable conversion efficiency up to 9.5 % for laboratory scale cells [1] and about 7 % for large area commercial products. However, the major issue with a-Si:H is the light induced degradation, known as the Staebler-Wronski effect [2], that may reduce the cell efficiency by up to 20 % after several thousands of hours under light exposure. Considering the light induced degradation, μc-Si:H is very interesting because of its stability. However, its indirect bandgap make its light absorption lower than a-Si:H and therefore efficient device can be reached only with sufficiently thick (2 μm) intrinsic absorbing layer. Amorphous silicon can be combined with microcrystalline silicon in a tandem junction with a top a-Si:H cell and a bottom μc-Si:H cell. This structure enhances the spectral response compared to single junction silicon cells because of the difference in bandgap between a-Si:H and μc-Si:H. Such Micromorph cells show stable conversion efficiencies up to 11.7 % for laboratory scale cells [3].

From the processing point of view, a-Si:H and μc-Si:H films are manufactured within the same large area PECVD equipment from silane (SiH_4) and hydrogen (H_2) gas mixture. Only the deposition parameters are varied to deposit either a-Si:H or μc-Si:H. Vetterl *et al* [4] have shown that to achieve high performance photovoltaic device, the μc-Si:H intrinsic layer has to be deposited just at the transition between the two microstructures. The usual way to vary the microstructure and to find the correct deposition parameters is to vary the input silane concentration in hydrogen from high concentration to low concentration to cross the transition from microcrystalline to amorphous silicon.

This work presents the study of the transition width from microcrystalline to amorphous silicon as a function of the input silane concentration. It is shown that the higher the silane concentration, the wider is the transition (Section 3). This result is interpreted on the basis of an analytical plasma chemistry model presented in Section 4.

2. EXPERIMENTAL ARRANGEMENT

Experiments were performed in a KAI-S reactor manufactured by Oerlikon-Solar AG. This large area plasma-enhanced chemical vapor deposition (PECVD) apparatus is based on the Plasma-Box concept with an RF (40.68 MHz) electrode suspended in a grounded aluminum box as shown in Fig. 1. The gases (SiH_4 and H_2) were introduced through the RF electrode by the use of a shower-head and were pumped out from one side. This configuration guarantees a uniform gas distribution and composition over the whole substrate area [5].
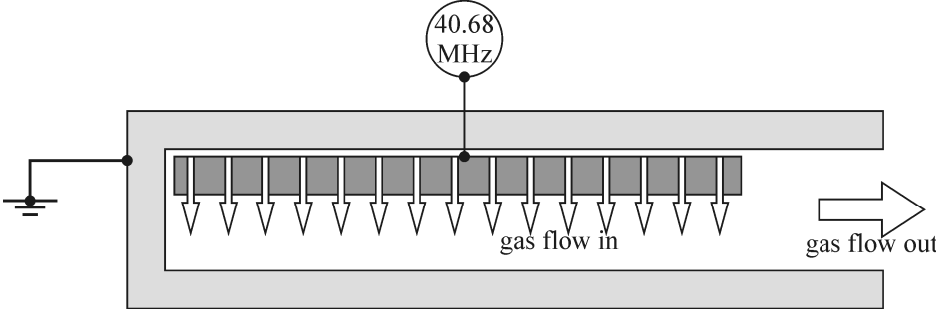
Figure 1: Side view of a Plasma-Box type reactor with RF gas-showerhead electrode and unilateral gas extraction.

Deposited films were characterized by micro-Raman spectroscopy to determine the film crystallinity defined by the ratio $(A_{510}+A_{520})/(A_{480}+A_{510}+A_{520})$, where A_{520}, A_{510} and A_{480} are the integrated area of the Raman peaks associated to crystalline (520 nm), defective crystalline (510 nm) and amorphous (480 nm) phase of silicon, respectively.
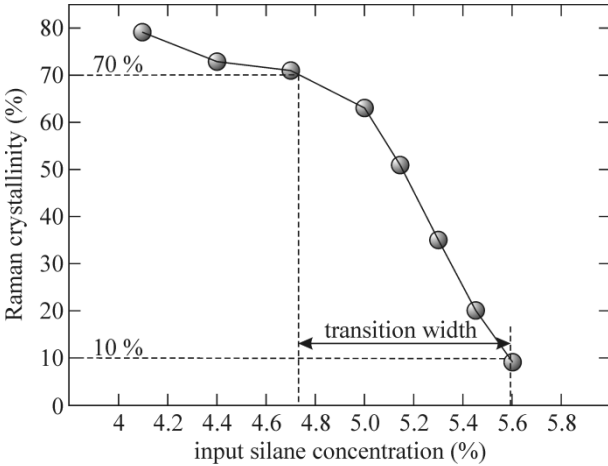
Figure 2: Transition width determination as a function of the silane concentration.

The input silane concentration, c, determined as the silane flow rate to the total flow rate, was varied to cross the amorphous to microcrystalline silicon deposition transition for 6 different sets of deposition parameters. The silane concentration was varied by changing the silane flow rate while keeping the total flow rate constant by adjusting the H_2 flow rate for every series. The deposition parameters are summarized in Table 1. The microstructure transition width in terms of silane concentration was determined by the difference in silane concentration used to deposit the films having a Raman crystallinity of 70 % and 10 % as shown in Fig. 2.

Concentration (%)	Total flow (sccm)	Pressure (mbar)
≈ 2.5	1600	3.5
≈ 4	1300	1.2
≈ 20	210	1.2
≈ 29	230	1.5
≈ 45	160	1.8
≈ 50	150	2.0

Tab. 1: Deposition parameters.

3. RESULTS

Figure 3 presents the microstructure transition width as a function of the input silane concentration for the 6 sets of deposition parameters. It shows that for low input silane concentration the transition is very narrow and as the input silane concentration increases, the transition width becomes wider until it reaches a plateau at 8 %. This means that a variation of only 1 % of the input silane concentration is sufficient to cross the microstructure transition if the film is deposited close to the transition with a silane concentration lower than 5 %. For input silane concentrations higher than 10 %, the microstructure of the films deposited close to the transition is less sensitive to input silane concentration fluctuations and a change as high as 8 % is needed to modify the microstructure of the film from microcrystalline to amorphous.
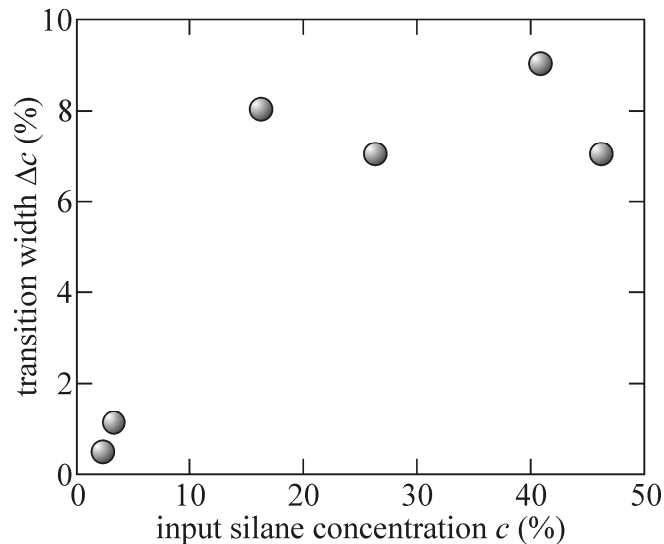

Figure 3: Microstructure transition width measured as a function of the input silane concentration.

4. DISCUSSION

The effect of the input silane concentration on the microstructure transition width presented in the previous section can be interpreted on the basis of the role of the plasma composition in determining the deposited film crystallinity. As shown recently [6], the silane concentration *in the plasma*, as opposed to the input silane concentration, is a major determining factor for the deposited film microstructure. Above about 1 % in silane concentration in the plasma, c_p, the deposited films are amorphous, and bellow this limit they are microcrystalline. The microstructure transition is not a sharp edge, but presents a certain width called the transition zone. The silane concentration in the plasma determines the film crystallinity because it is directly linked to the flow of radicals reaching the growing film [6]. The silane concentration in the plasma determines especially the flow ratio between atomic hydrogen and silane radicals which is of crucial importance for the growth of silicon films. According to all existing silicon growth models (selective etching, chemical annealing and surface diffusion [7]), this ratio has to be high enough to deposit microcrystalline silicon.

The silane concentration in the plasma can be decomposed and expressed as a function of the input silane concentration, c, and the silane depletion, D, which is defined as the loss in silane density in the plasma relative to the silane density in the gas before discharge break-down:

$$c_p = c(1 - D). \qquad\qquad (1)$$

Using relation (1), the transition zone between amorphous and microcrystalline silicon can be represented as a function of D and c (grey zone in Figure 4) and stands between two iso-c_p (c_p=0.5 % and c_p=1.2 %) curves determined empirically [6].
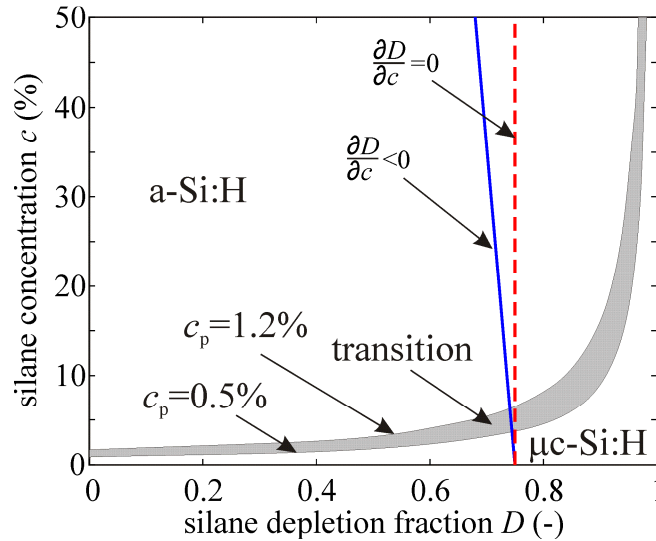

Figure 4: Silicon microstructure represented as a function of the silane depletion, D, and silane input concentration, c.

The experiments performed in this work can intuitively be represented by vertical lines (dashed line in Fig. 4) corresponding to variation of the silane concentration at constant silane depletion ($\partial D/\partial c$=0). The width of the microstructure transition zone can be then determined by the length of the vertical segment in the transition zone (grey zone in Fig. 4). The resulting transition width dependence on the input silane concentration is represented by the dashed line in Fig. 5. The calculated transition width depends linearly on the input silane concentration and the agreement with the experimental data is limited to input silane concentration lower than 20 %. The intuitive approach is therefore not sufficient to explain the plateau in transition width for silane concentrations greater than 20%.
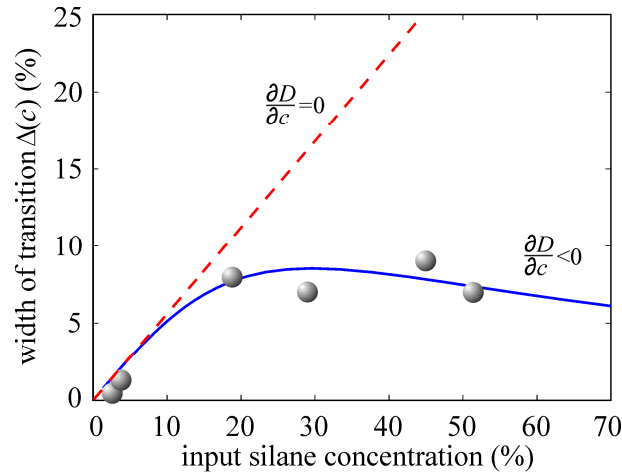
Figure 5: Experimental results and analytical models of the transition width dependence on the input silane concentration.

The intuitive approach used in the previous paragraph was based on the hypothesis that the silane depletion and the input silane concentration are independent. However, silane depletion measurements by Fourier transformed infrared absorption spectroscopy [6] presented in Fig. 6 show that the silane depletion varies as a function of the input silane concentration, while keeping all other deposition parameters constant. Therefore, the trajectories in the (D, c) plane corresponding to variations of the silane concentration are not vertical lines but linear curves with a negative slope ($\partial D/\partial c < 0$) as shown by the solid line in Fig. 4. The resulting microstructure transition width as a function of the input silane concentration is given by the solid line in Fig. 5. The agreement between the experimental data and the simulated transition width is almost perfect for the whole range of silane concentration from pure hydrogen to 50 % silane if the silane depletion dependence on c is taken into account.

This dependence of the transition width on the input silane concentration is of importance to choose appropriate deposition parameters to deposit uniform microcrystalline layers for photovoltaic application. As the microcrystalline cells present better performances when the intrinsic layer is deposited close to the microstructure transition, the uniformity of the layers over the large area substrates as well as the reproducibility between successive depositions is especially delicate to achieve and is a crucial issue for a successful transfer of this technology from laboratory to mass production scale. The results presented in Section 3 show that for high input silane concentrations, i.e. higher than 10 %, the crystallinity of the layer is less sensitive to the input silane concentration than conventional deposition regimes using very low silane concentration. Therefore, if for any reason, the gas distribution is not perfectly controlled over the whole substrate area and induces some variation in silane concentration, working with higher input silane concentration may be sufficient to deposit uniform microcrystalline layers. However, one has to carefully use high silane concentrations because of the risk of powder formation that may also induce non-uniformities. Moreover, if we have to deal with both non-uniform gas distribution and non-uniform electro-magnetic field distribution resulting from improper RF design, a trade-off has to be found because crystallinity is less sensitive to electro-magnetic imperfections when low input silane concentration is used [8].

5. CONCLUSIONS

In this work, the transition width from amorphous to microcrystalline silicon has been shown to depend on the input silane concentration. The higher the input silane concentration, the wider is the transition, until a plateau is reached for silane concentrations above 20 %. The dependence of the transition width on the input silane concentration has been simulated analytically using the relation between the silane concentration in the plasma and the resulting film crystallinity. An almost perfect agreement between model and experiments has been shown if the dependence of the silane depletion in the plasma on the input silane concentration is taken into account. The consequence of the wider transition while using high input silane concentration is that the film crystallinity is less sensitive to silane concentration fluctuation in that case than for very low silane concentration usually used to deposit microcrystalline silicon. Therefore,

to reduce non-uniformity of the crystallinity over large area substrate used nowadays in the photovoltaic industry or poor reproducibility that may rise from imperfect gas distribution in large area PECVD reactors, the input silane concentration should be higher than 10 %. However, one has to pay attention to other sources of non-uniformities such as the powder formation or improper RF design that have more influence at high silane concentration than in the conventional low silane concentration regime.
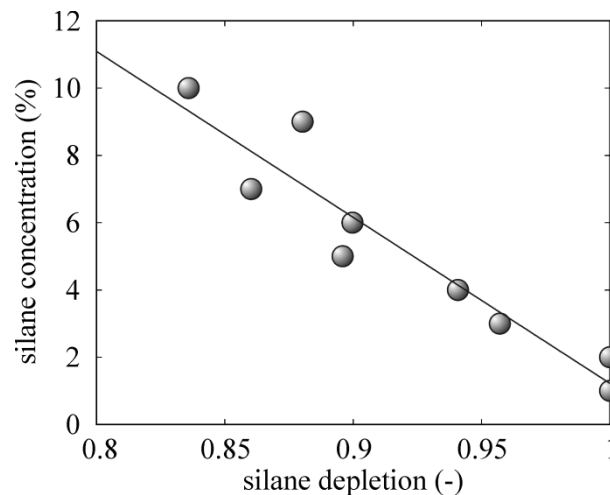

Figure 6: Silane depletion measured by Fourier transformed infrared absorption spectroscopy as a function of the input silane concentration. Data taken from Ref. [6].

References

[1]   Meier J., Spitznagel J., Kroll U., Bucher C., Fay S., Moriarty T. and Shah A., High Efficiency amorphous and Micromorph silicon solar cells, Proc. 3rd World conference PV-SEC, Osaka (Japan), 2001-2008, (2003).

[2]   Staebler D.L. and Wronski C.R., Reversible conductivity changes in discharge produced amorphous Si, Appl. Phys. Lett., 31(4), 292-294 (1977).

[3]   Yoshimi M., Sasaki T., Sawada T. *et al*, High efficiency thin film silicon hybrid solar cell module on 1 m2-class large area substrate, Proc. 3rd World conference PV-SEC, Osaka (Japan), 1566-1569, (2003).

[4]   Vetterl O., Finger F., Carius R., Hapke P., Houben L., Kluth O., Lambertz A., Mück A., Rech B. & Wagner H., Intrinsic microcrystalline silicon: A new material for photovoltaics, Solar Energy Mat. Solar Cells, 62, 97-108 (2000).

[5]   Sansonnens L., Howling A.A. & Hollenstein Ch., A gas flow uniformity study in large-area showerhead reactors for RF plasma deposition, Plasma Sources Sci. Technol., 9, 205 (2000).

[6]   Strahm B., Howling A.A., Sansonnens L. & Hollenstein Ch., Plasma silane concentration as a determining factor for microcrystalline to amorphous silicon transition in SiH_4/H_2 discharges, Plasma Sources Sci. Technol., 16, 80-89 (2007).

[7]   Matsuda A., Microcrystalline silicon: Growth and device application, J. Non-Cryst. Solids, 338-340, 1-12 (2004).

[8]   Strahm B., Hollenstein Ch. and Howling A.A., Uniformity of silicon microcrystallinity in large area RF capacitive reactors, Prog. Photovoltaics 16(8) 687-691 (2008).