

# Layer-by-layer deposition of thin silicon films from hydrogen diluted silane

Gijs van Elzaker<sup>1</sup>, Frans D. Tichelaar<sup>2</sup> and Miro Zeman<sup>1</sup>

<sup>1</sup>Delft University of Technology, DIMES-ECTM

P.O. Box 5053, 2600 GB Delft, The Netherlands

Phone +31 (0)15 2781651, Fax +31 (0)15 2622163

Email: [g.vanelzakker@dimes.tudelft.nl](mailto:g.vanelzakker@dimes.tudelft.nl)

<sup>2</sup>Delft University of Technology, National Centre for HREM

Lorentzweg 1, 2628 CJ Delft, The Netherlands

**Abstract**– Thin silicon films were deposited using rf-PECVD from silane diluted with hydrogen. Thin interlayers from pure silane were applied in an attempt to interrupt the formation of microcrystals which is characteristic for the growth using high hydrogen dilution. A structural investigation using Raman spectroscopy and transmission electron microscopy (TEM) has shown that 5, 10 and 15 nm thick interlayers do indeed suppress the crystallinity of the layers. Dual beam photoconductivity (DBP) measurements were used to obtain the absorption coefficient spectra of the films in the sub-bandgap region.

**Keywords**– a-Si:H,  $\mu$ c-Si:H, protocrystalline, Raman, TEM, phase transition, DBP, layer-by-layer

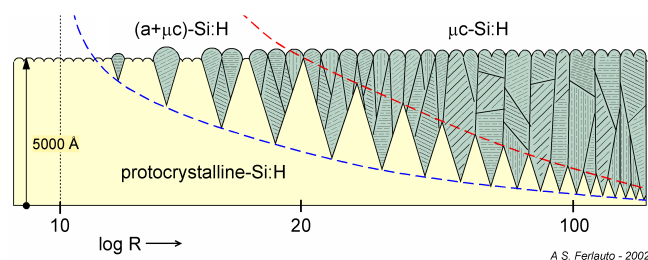
## I. INTRODUCTION

Amorphous hydrogenated silicon (a-Si:H) solar cells represent a promising solar cell technology of the second generation. Although the efficiency of a single a-Si:H solar cell is relatively low, multi-junction schemes can be applied to utilize a larger part of the solar spectrum and thereby increase the cell efficiency. Especially promising is the micromorph concept, in which an a-Si:H top cell is combined with a microcrystalline ( $\mu$ c-Si:H) bottom cell [1]. Initial efficiencies of up to 14.1% have been reported for this type of cell [2].

In addition to a relatively low initial efficiency a second drawback of a-Si:H is the light-induced degradation, called Staebler-Wronski effect [3]. The degradation causes a reduction of the cell efficiency until a stabilized value is reached which is much lower than the initial efficiency. The result of the Staebler-Wronski effect on the stabilized efficiency of the device is less pronounced in multi-junction cells, due to the higher electric field in the individual cells that causes an improved charge collection. However, the degradation

in multi-junction cells is still significant, and a further improvement of the cell stability will require optimization of the a-Si:H material.

The effort to fabricate more stable a-Si:H using the plasma enhanced chemical vapour deposition (PECVD) technique has resulted so far in demonstrating the beneficial effect of hydrogen dilution of the source gas on the quality of a-Si:H. Solar cells with a-Si:H absorbers prepared within a specific range of the hydrogen dilution ratio of silane showed a better performance after light exposure than their conventional undiluted counterparts [4],[5]. This range of growth conditions, characterized by a sufficiently high hydrogen dilution and a structural phase evolution during growth, is referred to as the protocrystalline growth regime.



**Figure 1** Schematic representation of the phase transitions in the protocrystalline growth regime as a function of the hydrogen dilution ratio (picture taken from [6].)

In this regime the growth of the film evolves through three phases: from amorphous to mixed phase and eventually microcrystalline. The ratio between the silane and hydrogen gas flows during deposition,  $R$ , strongly affects the phase evolution. For lower dilutions ( $R < 10$ ), films are invariably amorphous and no phase transition occurs. For increasingly high dilution ratio's ( $R > 10$ ) the phase transition will occur more abrupt and at smaller

thicknesses. This behavior is schematically represented in Figure 1. Protocrystalline silicon material, i.e. amorphous *a*-Si:H grown in the protocrystalline growth regime, reportedly shows an improved stability against light soaking when applied in solar cells compared to solar cells that utilize a conventional *a*-Si:H absorber layer deposited from pure silane.

The improved stability and quality of protocrystalline Si:H layers compared to conventional *a*-Si:H deposited from pure silane or using a low hydrogen dilution is attributed to an improved structural order. An enhanced medium-range order is determined by measuring the full width at half the maximum ( $\Delta 2\theta$ ) of the first X-ray diffraction (XRD) peak for *a*-Si:H, which is centered at a scattering angle of  $2\theta \sim 28.5^\circ$ . A typical value for *a*-Si:H is  $\Delta 2\theta \sim 6^\circ$ , which decreases for protocrystalline Si:H to  $\Delta 2\theta \sim 5^\circ$  [7].

In Figure 2 transmission electron microscopy (TEM) images of films grown with a hydrogen dilution of R=0 and R=30 to a thickness of approximately 1  $\mu\text{m}$  are shown. The undiluted R=0 sample is amorphous throughout the complete film, whereas the sample with R=30 has an amorphous incubation layer of approximately 100 nm after which the growth has evolved into the microcrystalline phase.

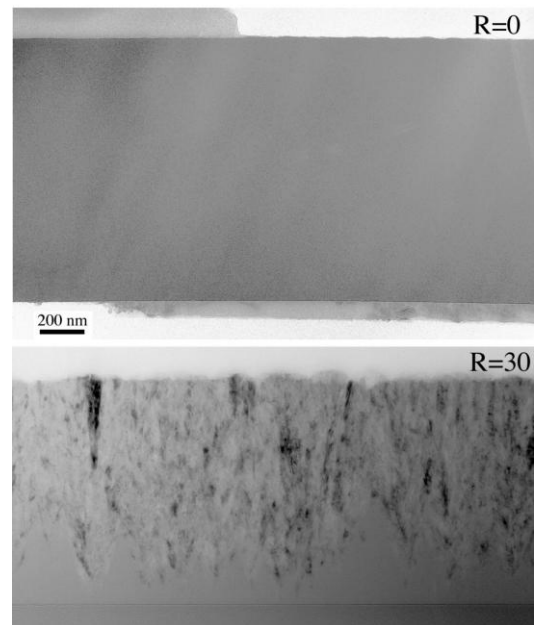
It has been suggested that the stability of the films increases with the hydrogen dilution. However, when the hydrogen dilution is increased the transition to the microcrystalline phase occurs quickly and the amorphous incubation phase is very thin. For example, the amorphous region in the sample with R=30, shown in Figure 2, has a thickness of only 100 nm. This is a problem since the thickness of the absorber layer of a solar cell should be in the order of 300 nm. The question is how one can grow a completely amorphous layer at high hydrogen dilutions which is thick enough for application in solar cells.

Several approaches have been used to circumvent the transition from the amorphous to the microcrystalline phase. One of the techniques is dilution profiling, in which the hydrogen dilution ratio is gradually decreased during growth to stay below the transition, growing so-called “edge” material [8]. However control of the growth is difficult without in-situ monitoring techniques.

Another approach is the layer-by-layer technique. This approach has so far mainly been applied on the microcrystalline side of the phase transition to avoid the amorphous incubation layer. Here the deposition of a thin amorphous layer and a hydrogen plasma treatment are applied alternately. The hydrogen plasma treatments

crystallize the amorphous layers and the process results in completely microcrystalline films [9].

The aim of the work presented in this article was to grow completely amorphous layers using high hydrogen dilution with sufficient thickness ( $> 300$  nm). In order to avoid phase transition a layer-by-layer approach was applied on the amorphous side of the phase transition.



**Figure 2 TEM bright field images of 1  $\mu\text{m}$  thick layers deposited with hydrogen dilution ratio R=0 and R=30**

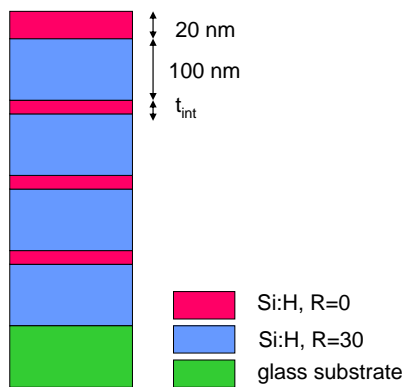
In the layer-by-layer technique the growth from hydrogen diluted silane is interrupted with thin interlayers from pure silane. The interlayer should result in new surface conditions for the growth of the consecutive layer grown with hydrogen dilution. In this way a stack of amorphous incubation layers should be obtained resulting in a film grown with high hydrogen dilution and a total thickness larger than the thickness of a single incubation layer. In the experiments that are presented in this article the thickness of the interlayers was chosen as a variable. Structural properties (using TEM and Raman spectroscopy) and electrical properties (using DPB) are investigated as a function of the interlayer thickness.

## II. EXPERIMENT

Si:H films were deposited with rf-PECVD on Corning C1737 glass following a layer-by-layer scheme. Layers grown with hydrogen dilution of the silane source gas are alternately interrupted with thin interlayers from pure silane. To increase the adhesion of the Si:H films to

the glass, the substrates are roughened using wet etching. After etching, the surface of the substrates is treated with hydrogen plasma for 5 minutes before the layer deposition.

Each sample consists of 4 layers deposited from silane diluted with hydrogen of 100 nm with 3 interlayers from pure silane in between. A thickness of 100 nm for the diluted layers was chosen based on the results on a film grown with fixed hydrogen dilution of  $R=30$ . In this case the first 100 nm of the sample was completely amorphous as shown in Figure 2. The thickness of the interlayers was varied; thicknesses of 5, 10 and 15 nm were used. The diluted layers and interlayers are deposited using different deposition conditions and the plasma is re-ignited before each consecutive layer. The diluted layers are deposited using a pressure of 2.0 mbar, rf power of 13.5 W, silane gas flow of 5 sccm and hydrogen gas flow of 150 sccm. The interlayers are deposited using a pressure of 0.7 mbar, rf power of 4.0 W and a silane flow of 40 sccm. The samples are covered with a 20 nm thick capping layer grown from pure silane, using conditions equivalent to those used for the interlayers. All layers are deposited at a temperature of 180°C. A schematic structure of the samples prepared by layer-by-layer technique is shown in Figure 3.



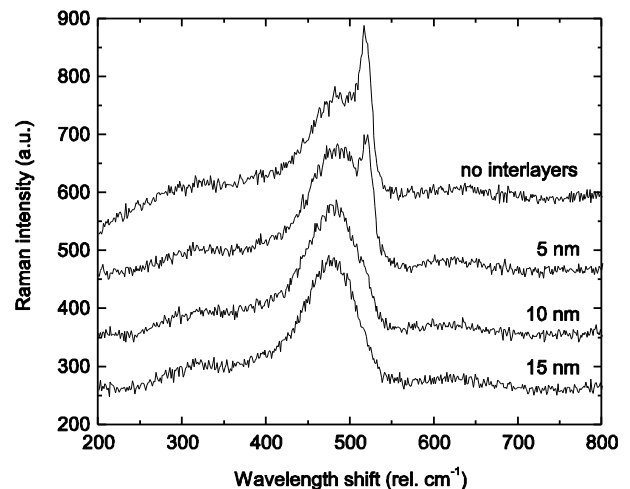
**Figure 3 Schematic drawing of the layer-by-layer structure. The interlayer thickness  $t_{\text{int}}$  is varied from sample to sample from 5 to 10 and 15 nm.**

Raman measurements were carried out using a home-built setup with a frequency doubled Nd:YVO4 laser wavelength of 532 nm. The spectra were measured in a 180° backscatter geometry. TEM bright field and dark field images were taken using a Philips CM30T and CM300UT-FEG TEM operating at 300 kV. Dual beam photoconductivity (DBP) combined with reflection and transmission (RT) measurements were used to determine the absorption spectra of the layers. For the DBP

measurement aluminum electrodes of 300 nm thick and a width of 4 mm are deposited on top of the layer. The electrode spacing is 0.5 mm over which a voltage of 100 V is applied during the measurement. More details about the Raman, TEM, DBP and RT measurement setups were published in earlier work [10].

### III. STRUCTURAL PROPERTIES

Raman spectroscopy was used for an initial investigation of the crystallinity of the deposited layer stacks. The crystalline fraction can be estimated by comparing the peak in the Raman spectrum at 520  $\text{cm}^{-1}$ , which is attributed to crystalline silicon, to the peak at 480  $\text{cm}^{-1}$ , which is attributed to amorphous silicon. The spectra that were obtained for the samples with interlayer thicknesses of 5, 10 and 15 nm are compared with the spectrum of a continuously grown film in Figure 4. The continuously grown film was deposited using a fixed hydrogen dilution ratio of  $R=30$ , has approximately the same thickness as the layer-by-layer stacks and is also covered with a 20 nm a-Si:H capping layer to make a fair comparison.

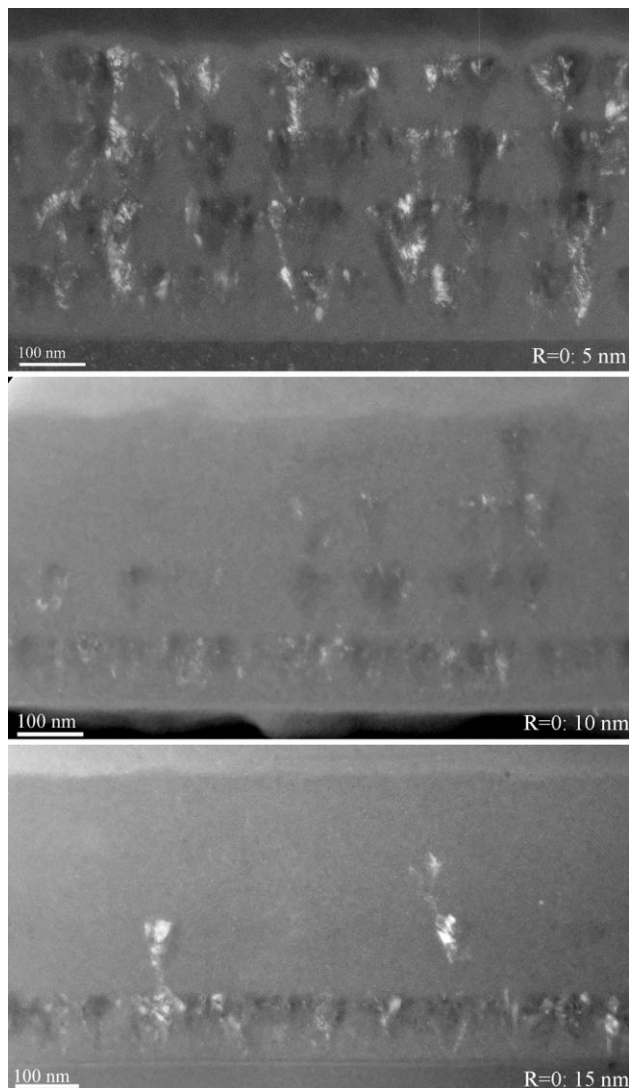


**Figure 4 Raman spectra of layer-by-layer samples with different interlayer thicknesses compared to a reference sample grown with continuous hydrogen dilution**

It is evident from the Raman spectra that the samples in which the growth using hydrogen dilution is interrupted with interlayers from pure silane have a decreased crystalline fraction. For interlayer thicknesses of 10 and 15 nm there is no crystalline peak visible at all. For interlayer thickness of 5 nm the crystalline growth was not completely suppressed, but the reduction in crystalline fraction is still significant. Due to the

absorption of the laser beam used for the Raman measurement, the Raman signal originates only from a region just below the surface of the sample (approximately 50 nm). To investigate the crystallinity in the bulk of the stacks TEM imaging was used.

Dark field TEM images of the layer-by-layer stacks are shown in Figure 5. The images show that the interlayers from pure silane have a large effect on the structural properties of the stacks. Application of 5 nm thick interlayers has resulted in a mixed phase structure throughout the complete film. The 10 and 15 nm thick interlayer samples show that the crystalline fraction strongly decreases with each interlayer. This results in the fact that the upper part of those samples is purely amorphous, in accordance with the Raman spectra presented in Figure 4.



**Figure 5** TEM dark field images of layer-by-layer samples on glass with interlayer thicknesses of 5, 10 and 15 nm.

It is concluded that interlayers from pure silane are an efficient means of interrupting the development of microcrystals which is characteristic to the growth using high hydrogen dilution. However, the aim of obtaining completely amorphous layers was not achieved. All samples show a heterogeneous mixed phase structure. The crystalline fraction in the initial layer of the stacks is much higher than was expected from results on the growth with a fixed hydrogen dilution as shown in Figure 2. It seems that the crystallization of the initial layer is somehow facilitated by the deposition of the consecutive layers. However, the cause of this effect is not known and more research is needed to investigate this phenomenon.

#### IV. ABSORPTION COEFFICIENT SPECTRA

Degradation of a-Si:H is related to the creation of extra defects which cause additional states in the bandgap. To study the stability of a-Si:H it would be useful to study the defect density in the material before and after light soaking. Absorption coefficient spectra obtained from RT measurements combined with DBP measurements have been investigated. The sub-band gap part of these spectra is interesting because they provide a measure for the density of defect states.

The absorption coefficient spectra of the layer-by-layer samples are shown in Figure 6. Reference curves for crystalline silicon and amorphous silicon have been included for comparison. The absorption coefficient spectra of the layer-by-layer samples lay in between the reference curves. This reflects the fact that the samples are neither amorphous nor microcrystalline, but rather of a heterogeneous mixed-phase structure.

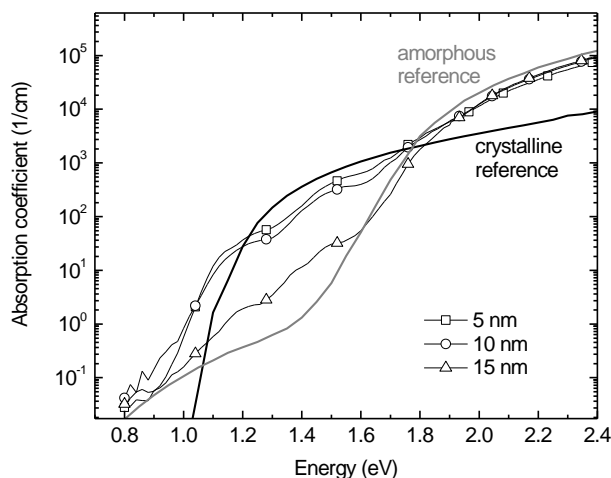
The sample with 15 nm thick interlayers shows the absorption coefficient spectrum which is the most amorphous-like. This corresponds to the observations from the Raman and TEM imaging measurements. Due to the heterogeneous nature of all samples it is impossible to assign the sub-bandgap absorption to defects in the material. A higher absorption coefficient in this region compared to the amorphous reference curve could also be caused by the microcrystalline phase rather than defects. However, once a completely amorphous sample is obtained the absorption coefficient spectra would be a suitable means for investigation of the defect density.

## V. SUMMARY

Thin silicon films were deposited using rf-PECVD in which the silane source gas was diluted with hydrogen. In order to interrupt the crystalline growth which is characteristic to these deposition conditions, thin interlayers from pure silane were applied. Stacks were made in which layers with and without hydrogen dilution are alternately deposited. The thickness of the interlayers deposited from pure silane was varied from 5 to 10 and 15 nm, whereas the thickness of the layers deposited from hydrogen diluted silane was kept at 100 nm for all depositions. Raman spectroscopy and TEM measurements show that the interlayers do indeed reduce the crystallinity of the film. Application of 15 nm interlayers has resulted in a completely amorphous top layer. The attempt to grow completely amorphous stacks was not successful, due to a crystalline fraction in the first layers which was higher than expected. The heterogeneous structure of the films is also reflected in their absorption coefficient spectra. The results demonstrate the complexity of the growth using hydrogen dilution, and more research is needed to be able to grow fully amorphous films with required quality using the layer-by-layer approach.

## REFERENCES

- [1] J. Meier, S. Dubail, R. Flückiger, D. Fischer, H. Keppner, A. Shah, Proc. 1st WCPEC, Hawaii, USA (1994) 409.
- [2] K. Yamamoto, M. Yoahimi, Y. Tawada, S. Fukuda, T. Sawada, T. Meguro, H. Takata, T. Suezaki, Y. Koi, K. Hayashi, T. Suzuki, M. Ichikawa, A. Nakajima, Sol. En. Mat. & Sol Cells, 74(2002) 449.
- [3] D.L. Staebler and C.R. Wronski, Appl. Phys. Lett., **31** (4) (1977) 292.  
D.L. Staebler, R.S. Crandall, and R. Williams, Appl. Phys. Lett., **39** (9) (1981) 733.
- [4] L. Yang and L.F. Chen, Mater. Res. Soc. Proc., 336 (1994) 669.
- [5] J. Yang, X. Xu, and S. Guha, Mater. Res. Soc. Proc., 336 (1994) 687.
- [6] R.W. Collins, A.S. Ferlauto, Curr. Opin. Solid-State Mater. Sci., 6 (2002) 425.
- [7] A.H. Mahan, R. Biswas, L.M. Gedvilas, D.L. Williamson, and B.C. Pan, *J. Appl. Phys.*, **96** (7) (2004) 3818-3826
- [8] J. Koh, Y. Lee, H. Fujiwara, C.R. Wronski and R.W. Collins, Appl. Phys. Lett., 73 (1998) 1526.
- [9] P. Roca I Cabarrocas, S. Hamma, A. Hadjadj, J. Bertomeu and J. Andreu, Appl. Phys. Lett., 69 (1996) 529.
- [10] G. van Elzakker, V. N. ádaždy, F.D. Tichelaar, J.W. M. etselaar, and M. Zeman, Thin Solid Films, 511-512 (2006) 252.



**Figure 6** Absorption coefficient spectra of the layer-by-layer samples compared to crystalline silicon and amorphous silicon reference curves.