

# From amorphous to microcrystalline silicon films prepared by hydrogen dilution using the VHF (70 MHz) GD technique

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## Abstract

The amorphous and microcrystalline silicon films have been prepared by hydrogen dilution from pure silane to silane concentrations  $\geq 1.25\%$ . At silane concentrations of less than 10%, a transition from the amorphous phase to the microcrystalline phase can be observed. X-ray diffraction spectroscopy indicates a preferential growth of the crystallites in the [220] direction. Additionally, the transition into the microcrystalline regime is accompanied by a shrinking of the optical gap, a reduction in hydrogen content and by a modified trend of the deposition rate. The observed changes in the infrared absorption modes indicate modifications in the hydrogen bonding and can be correlated with results known from monocrystalline silicon. Close to the transition zone, but still in the amorphous regime, the hydrogen content is increased, whereas the microstructure parameter reaches its smallest value. Precisely these films have a 0.06 eV higher optical gap and a reduced defect density by a factor of 4 as compared to a-Si:H layers prepared from pure silane.

*Keywords:* VHF-GD; Hydrogen dilution; Amorphous and microcrystalline silicon films; a-Si:H/ $\mu$ c-Si:H structural transition; Hydrogen bonding structure

## 1. Introduction

Recently, the dilution of silane by hydrogen has attracted special attention for the fabrication of more stable hydrogenated amorphous silicon (a-Si:H) solar cells [1,2]. Increasing dilution of the silane even further, leads to a known morphological transition [3,4] of the structure to hydrogenated microcrystalline silicon ( $\mu$ c-Si:H). This latter material has also recently acquired a considerable interest, as a new photovoltaically active material by itself [5] as well as in stacked tandem cells; the latter leads to the

so-called 'Micromorph Concept' [6]. Furthermore, the deposition in the very high frequency (VHF) range shows some important differences compared to the standard glow discharge (GD) at 13.56 MHz [7–9] and has beneficial effects on the  $\mu$ c-Si:H growth [10].

Hence, using the VHF-GD technique we were motivated to investigate the amorphous/microcrystalline silicon films prepared by hydrogen dilution. In a former study [11], the hydrogen incorporation together with the internal film stress in the whole dilution range passing over the amorphous/microcrystalline transition has already been investigated. In the present study, additional properties such as optical absorption, microstructure and crystalline

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phase in the microcrystalline regime will be presented.

## 2. Experimental details

The films were deposited in a capacitively-coupled parallel plate reactor using a plasma excitation frequency of 70 MHz. Using the VHF (70 MHz)-GD technique, an increased deposition rate as compared to 13.56 MHz is observed. Details are published elsewhere [7]. The silane concentration in the feed gas varied from 100% to 1.25% by adapting the ratios of the silane and hydrogen flows, while keeping the total feed gas constant at 50 sccm.

The depositions were performed at a pressure of 0.4 mbar, a HF-power input of 7 W and a substrate temperature of 225°C. Under these conditions, 1.5 to 2  $\mu\text{m}$  thick films were grown on glass (Corning 7059) and on double side-polished  $\langle 100 \rangle$  Si-wafers.

Infrared spectroscopy (IR) was used to measure the hydrogen content [11,12] and to determine the microstructure parameter,  $R$ , as defined in Ref. [13].

Photothermal deflection spectroscopy (PDS) was applied to investigate the optical gap and to determine the defect absorption (the latter being related directly to the defect density [14]). The absorption determined by PDS has been absolutely calibrated by optical transmission and reflection measurements. In the microcrystalline growth regime, the presence of crystallites has been determined by X-ray diffraction measurements.

## 3. Results

The dependence of the deposition rates over the full dilution range is shown in Fig. 1a. With decreasing silane concentration the deposition rate is reduced over a range from about 7 to 0.3  $\text{\AA}/\text{s}$ . However, the inflection in the deposition rate at a silane concentration of about 10% indicates two different growth regimes. Just around these silane concentrations the hydrogen content (Fig. 1b) is increased and reaches its maximum in the whole dilution range investigated here. In addition, as it has already been reported elsewhere [11] the internal stress of these films is also largest.

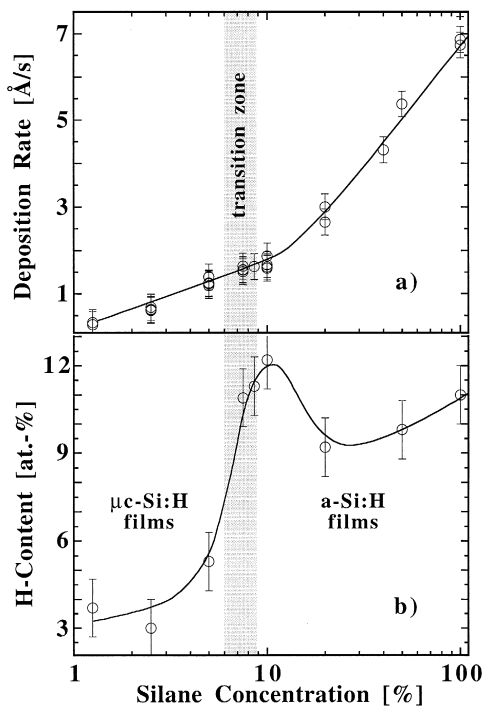


Fig. 1. Deposition rate (a) and hydrogen content of the films measured by IR-absorption (b) vs. the silane concentration. The lines are merely for guiding the eye.

Fig. 2 shows the IR-absorption spectra used for the determination of the hydrogen content in the films. The thin vertical lines in the graph indicate the positions of the absorption modes usually found in a-Si:H films [12,15]. The layers prepared from pure silane down to silane concentrations of around 7.5% retain the bands at 640, 840, 880, 2000 and 2090  $\text{cm}^{-1}$  pertaining to a bonding structure of typical a-Si:H layers. To investigate the H-bonding configuration in these a-Si:H layers, the microstructure parameter,  $R$  [13,16], is presented in Fig. 3. This parameter obtained by a deconvolution of the hydrogen-silicon bond stretching modes around 2000  $\text{cm}^{-1}$  is a rough measure for H-clusters and Si-H bonds on internal surfaces of voids and is therefore related to the void structure of the deposited material.

For silane concentrations less than 7.5%, narrower bands around 626, 900 and 2101  $\text{cm}^{-1}$  arise and, hence, differ from the modes associated with a-Si:H. This latter observation is an indication for

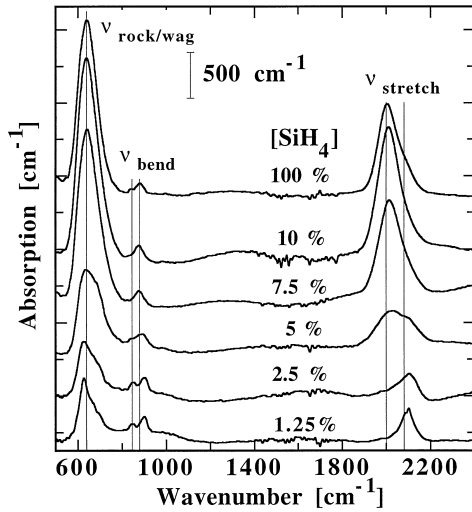


Fig. 2. IR-absorption spectra of layers prepared at different silane dilution levels as indicated in the figure; the spectra are shifted vertically for clarity. The positions of the absorption modes found in a-Si:H films are marked by thin vertical lines.

changes in the hydrogen bonding nature and in the bonding environment. By comparison with the results presented in Refs. [16–19] all these vibration modes (i.e., the rocking–wagging, bending and particularly the different stretching modes around  $2100\text{ cm}^{-1}$ ) can be assigned to mono and/or dihydride bonds on (100) and (111) surfaces of crystalline silicon. Therefore, for silane dilution  $< 7.5\%$  growth of microcrystallites occurs. In Fig. 4, the X-ray diffraction spectra are represented for samples where microcrystalline growth is suspected. Indeed for

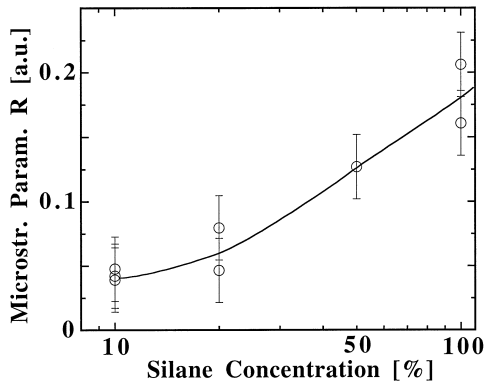


Fig. 3. Microstructure parameter  $R$  of the a-Si:H films vs. the silane concentration. The line is merely for guiding the eye.

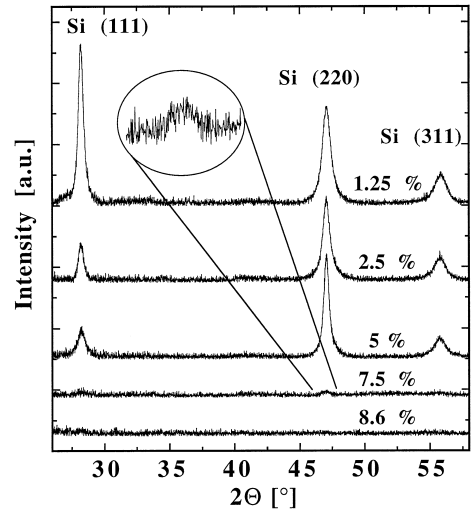


Fig. 4. Evolution of the X-ray diffraction patterns for films prepared at different dilution levels as indicated in the figure.

silane concentrations  $\leq 7.5\%$  crystallites are detectable and a comparison with silicon powder diffraction pattern indicates a preferential growth of the crystallites in the [220] direction in our films. It is interesting to note that this preferential growth is hampered at silane concentrations around  $1.25\%$ .

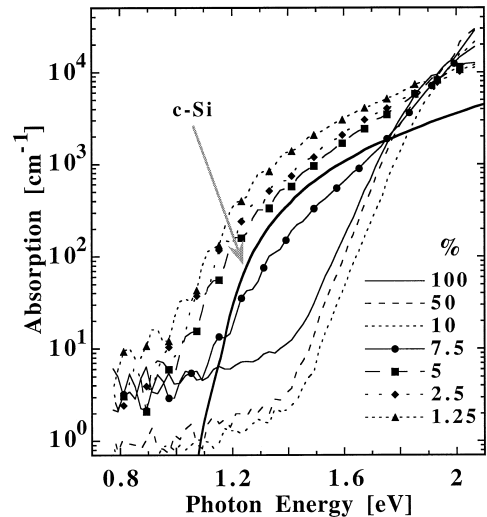


Fig. 5. Optical absorption of the amorphous and microcrystalline films prepared at different silane concentrations as indicated in the figure. For comparison, the absorption of monocrystalline silicon is added.

This can be concluded because the intensity ratio of the (111) and (220) peaks is close to the ratio found in silicon powder diffraction pattern.

Finally, Fig. 5 shows how the optical properties are affected by hydrogen dilution.

#### 4. Discussion

At similar silane concentrations also using VHF-GD at 70 MHz an amorphous/microcrystalline transition has been reported by Prasad [4], whereas using the standard frequency of 13.56 MHz Tsai [3] found, related with a comparable tendency for the hydrogen incorporation in the films, that the onset of the crystallinity appears at smaller silane concentrations of about 4%.

In the amorphous regime, medium silane dilution  $\geq 20\%$  decreases the hydrogen content in the films. At further dilution towards the transition zone, but still in the amorphous regime, there is a considerable increase of hydrogen incorporation. As long as the deposition stays in the amorphous regime, an increasing hydrogen concentration in the gas phase due to the dilution enhances the microstructure of the deposited films (Fig. 3). The a-Si:H material deposited close to the transition zone has smallest  $R$  although the hydrogen content attains here its maximum.

We suggest that applying hydrogen dilution a better hydrogen coverage of the growth zone enhances the diffusion lengths of the deposition precursors. In addition, the presence of more atomic hydrogen might enlarge the etching of weak bonds and weakly bonded atoms. Thus, the growth under these conditions is more relaxed and accompanied by a reconstruction of the amorphous network both resulting in a better microstructure.

Furthermore, first, still in the amorphous regime, increasing hydrogen dilution increases the optical gap and reduces the defect absorption and hence, the defect density Fig. 5. The a-Si:H layer prepared close to the transition zone has a defect density reduced by a factor of 4 as compared to samples prepared from pure silane. However, above a certain dilution level, the diffusion of deposition precursors, the rearrangement of the network and the etching of weakly bonded atoms at the growth zone are so

pronounced that a morphological phase transition from amorphous to microcrystalline structure occurs. As soon as the onset of the formation of microcrystallites starts, substantial changes of the optical absorption can be observed. The absorption of the sample prepared at a silane concentration of 7.5% is just in between the absorption curves for typical a-Si:H and  $\mu\text{c-Si:H}$ , suggesting an essentially amorphous material but with few crystallites embedded. At further dilution, the apparent optical absorption now similar to monocrystalline silicon is steadily enlarged even to values lying above the monocrystalline silicon. It has been suggested [20,21] that this astonishing fact is based on an enhanced optical scattering in  $\mu\text{c-Si:H}$  films.

#### 5. Summary and conclusions

Silicon layers have been deposited by the VHF-GD technique using silane dilution by hydrogen over the range from pure silane down to silane concentrations of 1.25%. Increasing dilution leads to a continuous reduction of the deposition rate from 7 Å/s down to 0.3 Å/s. Accompanied by a considerable reduction of the hydrogen content and lower optical gap at silane concentrations of less than 10%, a transition from the amorphous phase to the microcrystalline phase occurs. Moreover, the growth rate tendencies in the  $\mu\text{c-Si:H}$  and in the a-Si:H growth regime are clearly different. X-ray diffraction measurements indicate a preferential growth of the crystallites in the [220] direction. It is interesting to note that this preferential growth is hampered at low silane concentrations around 1.25%. The changes in the IR-absorption modes at increasing dilution levels suggest that hydrogen in  $\mu\text{c-Si:H}$  material is preferentially bonded at surfaces of the crystalline grains.

At dilution levels close to the transition, the hydrogen content of the a-Si:H films is considerably enhanced and reaches its highest value. In spite of the much higher hydrogen incorporation, the microstructure parameter reaches here its lowest value. This improved microstructure might be responsible for the generally observed lower light-induced degradation of H-diluted a-Si:H films [22,23] and cells [1,2]. Furthermore, precisely these films have a 0.06 eV higher optical gap and by a factor of 4 reduced

defect density as compared to a-Si:H layers prepared from pure silane. These findings might explain the higher open circuit voltage of cells containing such i-layers [1,2].

### Acknowledgements

We would like to thank S. Dubail for his technical assistance. The work was supported by the Swiss Federal Department of Energy BEW/OFEN, under grants 2757 and 19431.

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