

Influence of Deposition Pressure on Protocrystalline Silicon Films as Solar Cell Absorber Layer

G. van Elzaker, J. Melskens, M. Zeman

Abstract—A series of thin silicon films was deposited using rf plasma-enhanced chemical vapor deposition using hydrogen dilution of silane. The influence of the deposition pressure on the structural properties of the films was investigated using Raman and Fourier transform infrared spectroscopy. The defect density of the amorphous films is estimated using Fourier Transform Photocurrent Spectroscopy. These films were applied in single-junction thin-film silicon based solar cells as the absorber layer. The stability of the solar cells was investigated in a degradation experiment.

Index Terms — Hydrogenated amorphous silicon, Hydrogenated microcrystalline silicon, Plasma-enhanced chemical vapor deposition (PECVD), Fourier Transform Photocurrent Spectroscopy (FTPS)

I. INTRODUCTION

HYDROGENATED amorphous 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 silicon ($\mu\text{c-Si:H}$) bottom cell [1]. Initial efficiencies of up to 14.1% have been reported for this type of solar cell [2].

Another drawback of a-Si:H is the light-induced degradation of its structural and electronic properties, known as the Staebler-Wronski effect [3]. The result of this effect on the solar cell efficiency is less pronounced in multi-junction solar cells, due to the higher electric field across thinner absorber layers in the individual cells, that results in an improved charge collection. However, the degradation in multi-junction cells is still significant, and a further improvement of the cell stability requires optimization of the a-Si:H material.

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It has been found that dilution of the silane source gas with hydrogen during the rf plasma enhanced chemical vapor deposition (rf-PECVD) can result in thin hydrogenated silicon (Si:H) films with increased stability [4]. The amorphous silicon deposited under these conditions is referred to as protocrystalline silicon. The use of hydrogen dilution also results in a phase transition from the amorphous to the microcrystalline phase during the growth of Si:H. For increasing dilution ratios the amorphous incubation layer becomes increasingly thin [5].

In this study we investigate the influence of the deposition pressure on the structural phase and the defect density of protocrystalline films deposited using a hydrogen-to-silane dilution ratio of $R=[\text{H}_2]/[\text{SiH}_4]=20$. The structural properties are investigated using Raman and Fourier transform infrared (FTIR) spectroscopy. The defect density in the films is estimated from Fourier transform photocurrent spectroscopy (FTPS) measurements.

The same deposition conditions were used to deposit the absorber layers of a series of single-junction solar cell devices. The external parameters of the solar cells are investigated in the initial state and after a degradation experiment. Besides the investigation of the degradation of the solar cells with absorber layers deposited at different deposition pressure, a comparison is made with a reference cell having a conventional undiluted a-Si:H absorber layer.

II. EXPERIMENT

A. Deposition of films and solar cells

A series of films was deposited on Corning Eagle 2000 glass using rf-PECVD and a hydrogen dilution of $R=20$. The deposition pressure was varied from 1.35 to 2.6 mbar. The substrate temperature during deposition was 180 °C and a power of 4.0 W was applied to the rf electrodes. The thickness of all films is approximately 300 nm.

Solar cells were deposited on Asahi U-type substrates that include the above described individual films as the absorber layers. The solar cells consist of the following structure: p-type a-SiC:H layer / a-SiC:H buffer layer / intrinsic absorber layer (300 nm) / n-type a-Si:H layer. The back contact consists of 300 nm aluminum. A reference solar cell was deposited using a standard undiluted absorber layer ($R=0$).

B. Characterization of films and solar cells

Infrared absorption spectra were determined using a Thermo Electron Nicolet 5700 FTIR spectrometer. Since the

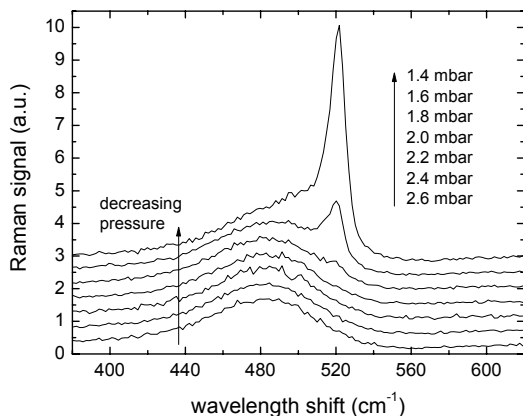


Fig. 1 Raman spectra of Si:H films deposited at different pressures. The broad peak around 480 cm^{-1} represents the contribution of amorphous silicon. The sharper 520 cm^{-1} peak originates from the TO mode of c-Si. The crystalline fraction increases with decreasing pressure.

films were deposited on glass, the ATR configuration was utilized using a ZnSe crystal. Simple transmission type measurements are not suitable due to the strong absorption in the glass substrate.

Raman measurements were carried out on the individual films using a Renishaw InVia type spectrometer with a laser wavelength of 514 nm .

FTPS was used to measure the photocurrent spectra of the individual films as well as the absorber layers of the solar cells [6]. The photocurrent spectra were scaled to the absorption data obtained from standard reflection and transmission (RT) measurements in the high-energy range ($E_{\text{ph}} > 1.8\text{ eV}$) to obtain the absorption coefficient spectra in a broad range from 0.7 eV to 2.4 eV .

The external parameters (efficiency η , fill factor FF, short-circuit current I_{SC} , open-circuit voltage V_{OC}) of the solar cells were determined using I - V measurements under standard illumination conditions with an Oriel Corporation solar simulator.

C. Light soaking

The solar cells were degraded under open-circuit conditions for a period of 10,000 minutes using metal halide lamps at a power density of 100 mW/cm^2 . All samples were kept at a constant temperature of $50\text{ }^\circ\text{C}$. The external parameters of the solar cells were monitored in time by means of repeated I - V measurements.

III. RESULTS

The results of the Raman measurements on the thin silicon films are shown in Fig. 1. The broad peak in the spectra at 480 cm^{-1} originates from the amorphous phase, whereas the sharp peak around 520 cm^{-1} is due to the crystalline phase. The films that were deposited with pressures of 2.0 mbar and higher do not show the 520 cm^{-1} peak and are completely amorphous. The films that are deposited at lower pressures show an increasing crystalline fraction with decreasing pressure.

The FTIR measurements were analyzed in order to obtain the microstructure factor R^* of the films. The microstructure

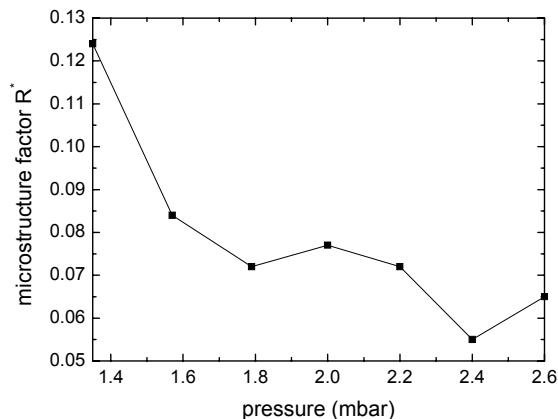


Fig. 2 Microstructure factor R^* as a function of the deposition pressure. The microstructure factor increases strongly for lower pressures.

factor is obtained by comparing the area under the $\sim 2000\text{ cm}^{-1}$ peak, which is due to the stretching mode of Si-H bonds in vacancies, to the area under the absorption peak at $\sim 2100\text{ cm}^{-1}$, which is mainly ascribed to Si-H bonds located at void surfaces. In general, a value of $R^* < 0.1$ is required for device quality material. In Fig. 2, the microstructure factor is plotted as a function of the deposition pressure of the films. The microstructure factor increases strongly for low deposition pressures. This corresponds to the strong development of the microcrystalline phase, as concluded from the Raman measurements. The increasing R^* values represent an increasing void fraction in the microcrystalline material.

Absorption coefficient spectra were determined using FTPS measurements. Fig. 3 shows the absorption coefficient spectra for the films deposited at different pressures. The spectra of the samples deposited at pressures of 2 mbar and higher show a typical shape corresponding to a-Si:H. On the other hand, the spectra of the films deposited at lower pressures show a shape corresponding to microcrystalline silicon.

For amorphous films the absorption coefficient at $E_{\text{ph}}=1.2\text{ eV}$ has been found to be approximately proportional to the defect density in the films [7]. However, this is not valid for the microcrystalline films, as the increased absorption coefficient at 1.2 eV is due to the crystalline phase in the material. In Fig. 4, the absorption coefficient at 1.2 eV is plotted as a function of the deposition pressure. The strong increase in the absorption coefficient for pressures below 2.0 mbar is due to the presence of the microcrystalline phase and is not related to an increase in defect density. For the amorphous films deposited at 2.0 mbar and higher, the defect density seems to decrease with increasing pressure.

FTPS can also be used to measure the absorption coefficient spectra of the absorber layer in the solar cell device. The measurement of the series of solar cells has yielded spectra indicating fully amorphous absorber layers. Apparently, the transition to the microcrystalline phase observed at low pressures in the individual films does not occur in the absorber layers. This is also clear from Fig. 4

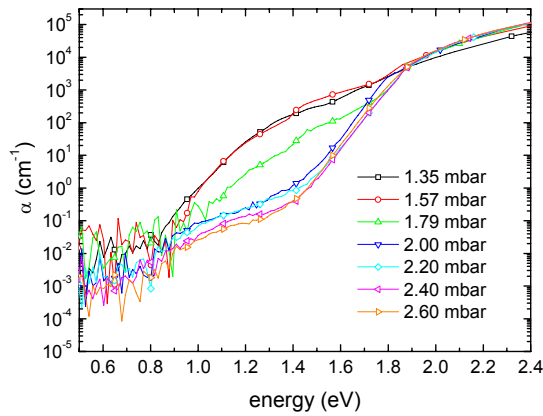


Fig. 3 Absorption coefficient spectra of films deposited at different pressures measured with FTPS. The high-energy part of the spectra was measured by RT measurements.

where the values of $\alpha_{1.2\text{eV}}$ obtained from the absorber layers are included. Further, the high V_{OC} values of the cells (> 0.8 V) confirm that all absorber layers deposited in the investigated pressure range are amorphous. The difference in structural phase between the solar cell absorber layers and the individual films is explained by the strong substrate dependence of the growth with hydrogen dilution.

Another difference with the $\alpha_{1.2\text{eV}}$ values from the individual films is that the values are also significantly lower in the amorphous regime (≥ 2.0 mbar). There are several possible explanations for this discrepancy. One possibility is the substrate dependence which might cause the (initial) growth to be less defective in case of the solar cell absorber layers, where the growth occurs on the amorphous buffer layer. The absence of the microcrystalline phase for the solar cell absorber layers deposited at low pressures already points to the strong substrate dependence. Furthermore, the p-i-n structure causes a pinning of the Fermi level in the solar cell device, which will change the defect distribution according to the defect pool model [8]. A further difference between the individual layers and the solar cells, which is not taken into account in the evaluation of the measurement data, is the infrared absorption of the TCO layer utilized in the solar cells. For these reasons, it is not possible to directly compare the absorption coefficient of the absorber layers with those of the individual films. Nevertheless, it is possible to make a mutual comparison between the different solar cells. This shows a slightly decreasing defect density, as was also observed for the individual amorphous films.

Fig. 5 shows the efficiency and fill factor of the series of solar cells as a function of the deposition pressure used for the absorber layer. A small increase in fill factor and efficiency is observed with increasing pressure. The fill factor increase seems to correspond to the decreasing defect density measured with FTPS.

Fig. 5 also includes the fill factor and efficiency after 80 and 10,000 minutes of light soaking. After 10,000 minutes of light soaking the fill factor of all R=20 solar cells had stabilized [9]. It was found that the amount of degradation does not depend significantly on the deposition pressure. In

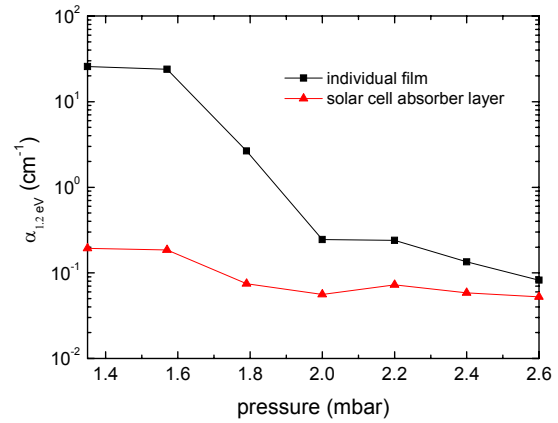


Fig. 4 Absorption coefficient $\alpha_{1.2\text{eV}}$ determined from the absorption coefficient spectra recorded with FTPS. The value of $\alpha_{1.2\text{eV}}$ is proportional to the defect density in amorphous silicon films.

the initial state the cells deposited at the highest pressure show the best fill factor and efficiency, and the same holds for the degraded state.

The horizontal lines in the figure mark the fill factor and the efficiency of the reference R=0 cell at the same stages of the degradation experiment. The fill factor and efficiency of the reference cell show a relatively much larger degradation. Furthermore, unlike the R=20 solar cell, the fill factor of the R=0 solar cell showed no sign of stabilization after 10,000 minutes of light soaking [9]. This clearly confirms that the cells with hydrogen diluted absorber layers are more stable than the undiluted reference cell.

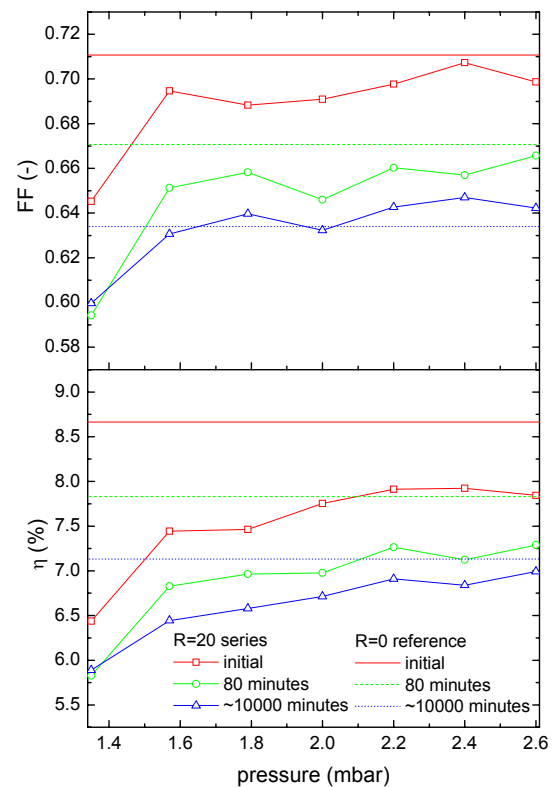


Fig. 5 Fill factor and efficiency of the solar cells as a function of the deposition pressure of the absorber layer at three different stages of the light soaking experiment. The horizontal lines represent the fill factor and efficiency of the reference cell with an undiluted absorber layer.

The fact that the R=0 reference cell has a higher efficiency than the R=20 pressure series is due to the increase of the material band gap with increasing hydrogen dilution. The increased band gap of the R=20 cells results in a lower short-circuit current in this comparison between cells with equal absorber layer thicknesses.

IV. CONCLUSIONS

The investigation of the structural phase of the individual films by Raman spectroscopy has revealed that lower deposition pressures result in increased crystallinity of the films. In this study, all films deposited at pressures of 2.0 mbar and above are completely amorphous. The development of a microcrystalline phase for lower pressures is also reflected in the increasing microstructure factor. The increasing R^* points to voids in the microcrystalline material. The absorption coefficient spectra of the films were successfully determined using FTPS. The absorption coefficient at 1.2 eV has been used to compare the density of defects between the amorphous films. For the films that are not completely amorphous $\alpha_{1.2\text{eV}}$ cannot be used to estimate the defect density.

The solar cell absorber layers that were deposited using equivalent deposition conditions as used for the individual films do not show a microcrystalline phase fraction for all deposition pressures investigated in this paper. This is concluded from the shape of the absorption coefficient spectra measured on the cells as well as the fact that the V_{OC} of all cells is > 0.8 V. The fact that the phase transition is only observed for the individual layers is explained by the strong substrate dependence which is characteristic of the growth with hydrogen dilution of the silane source gas. Whereas the individual films are directly deposited on Corning glass, the solar cell absorber layers are deposited on textured SnO_2 of the Asahi U-type substrate and an amorphous p-layer / buffer layer combination.

A degradation experiment reveals that the cells containing R=20 absorber layers are more resistant to light soaking than the R=0 reference cell. However, within the pressure series there are no significant differences regarding the stability of the cells. The conditions leading to the best initial performance are equal to the conditions leading to the best stabilized performance, both in terms of fill factor and efficiency.

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