DEPOSITION OF μc-Si:H BY MICROWAVE PECVD
– INFLUENCE OF PROCESS CONDITIONS ON LAYER PROPERTIES

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Microwave PECVD (MWPECVD) is a well applicable deposition technique for large area and high rate deposition. Therefore, it is a very promising method for industrial scale fabrication of microcrystalline (μc-Si:H) and amorphous (a-Si:H) silicon solar cells. We have investigated the addition of argon (Ar) in the MWPECVD process and developed a start-up procedure of the deposition, which both stabilize the microwave plasma on different time scale and, therefore, improve the reproducibility of the process. It is shown that the material properties of the silicon layers deteriorate if one partly substitutes H_2 by Ar during the deposition. In conclusion a MWPECVD process without Ar should be developed. The new start-up procedure leads to silicon layers of low defect density as the analysis of electrical (σ_{photo}, σ_{dark}) and optical (α @ 0.8 eV, FTPS) measurements indicates. It ensures a stabilized plasma when the deposition is started. Further experiments indicate the need of a substrate temperature of T = 200°C or lower for the deposition of μc-Si:H-, and a-Si:H-layers with improved optical and electrical properties.

Keywords: PECVD, μc-Si:H, manufacturing and processing

1 INTRODUCTION

The microwave PECVD (MWPECVD) method is a common technique for the fabrication of functional layers for electronic applications. As anti-reflection coating and passivation layer in crystalline silicon solar cells high quality SiN_x:H is deposited by MWPECVD with high deposition rate [1]. As a remote technique – the substrate is not an electrode of the plasma source – it is easy to apply in a roll-to-roll process. The linear geometry of the plasma source enables an easy upscaling, and thus MWPECVD is a relevant technology for the PV industry.

Inspired by the successful industrial implementation of the SiN_x:H layers, the aim of ECN is the development of a pilot production line for high efficiency solar cells based on amorphous (a-Si:H) and microcrystalline (μc-Si:H) silicon. The major difference with respect to fabrication of SiN_x:H layers is the focus on good electronic and morphological properties instead of the optical properties of the layers. Therefore, the deposition conditions must be optimized with respect to minimization of defects in the layers. Because the MW-PECVD is working in a totally different frequency regime in comparison to the commonly used plasma techniques for thin film silicon solar cell production (e.g. RF-PECVD [2]) one cannot directly transfer process conditions of these well established techniques to the MWPECVD process.

This work presents insights into the influence of the deposition conditions of the MWPECVD process on the electronic and optical quality of the a-Si:H- and μc-Si:H-layers. The influence of silane (SiH4) presence during plasma ignition on the layer properties is discussed. Recent observations of the effect of several process parameters such as substrate temperature and additional plasma stabilizing gases (e.g. Ar) on the defect density of the deposited silicon layer, are presented.

2 EXPERIMENTAL

2.1 Deposition Process

Intrinsic microcrystalline silicon films have been deposited simultaneously on crystalline silicon wafers and on aluminosilicate glass (Corning 1737) in a single chamber MWPECVD reactor, in which a substrate holder with a substrate area of 60x15 cm^2 moves underneath a linear microwave source [3]. A mixture of H_2 and, if needed, Ar is injected in the vicinity of the microwave source, while silane (SiH_4) diluted in H_2 is injected closer to the substrate [3].

For the investigation of the influence of Ar on layer properties the silane fraction, defined as SiH_4 flow divided by the total of SiH_4, H_2, and Ar flows ($\Phi_{SiH4}/(\Phi_{SiH4} + \Phi_{H2} + \Phi_{Ar})$), was kept constant at 2.3%. The total flow of diluting gases Ar+H_2 was kept at 350 sccm, and we varied the fraction of Ar in the diluting gases. The temperature of the substrates was 300 °C and the pressure during deposition was 0.3 mbar.

For the experiment in which the plasma was ignited under different conditions (ignition with / without presence of SiH_4) several samples were deposited. Here, the silane fraction was varied between Φ_{SiH4} = 8 sccm and Φ_{SiH4} = 13 sccm. The total flow of H_2 (Φ_{H2}) was kept at 300 sccm, Φ_{Ar} was reduced to 5 sccm. The temperature of the substrates was 250 °C, and the total pressure during deposition was 0.3 mbar.

In the last experiment, different combinations of total pressure and substrate temperature were investigated. Φ_{SiH4} was varied between 10 sccm < Φ_{SiH4} < 14 sccm; the substrate temperature was chosen between 200 °C and 250 °C. Before each deposition a 30 min long H_2-plasma treatment was carried out. The power density P of the microwave sources was varied between 0.1875 W/cm^2 < P < 0.225 W/cm^2. A minimum P was chosen at which plasma stability was guaranteed.

For all samples in the different experiments deposition times were chosen such that layer thicknesses of approximately 1 μm were obtained.

2.2 Characterisation

Optical emission spectroscopy (OES) in the wavelength range from 200 to 1000 nm has been performed during deposition and the characteristic lines for H_α, H_β and SiH^* in the plasma, at 656, 486 and 412 nm, respectively, have been analyzed.

From FTIR measurements between 400 cm^{-1} and 4000 cm^{-1}, performed with a Perkin Elmer BX II spectrometer, information on the hydrogen bonding as well as hydrogen concentration of the deposited films have been obtained. The layer thickness and the refractive index at 0.5 eV have been determined by fitting the interference fringes in the IR transmission spectra [3].

We used Raman spectroscopy (with an Ar laser at 514 nm) to determine the crystallinity of the silicon layers. The crystalline fraction was calculated as $(I_{520}+I_{505})/(I_{520}+I_{505}+I_{480})$, where I_m is the area of the peak in the Raman spectrum at m cm^{-1}.

The absorption of the silicon layers in the near-infrared has been investigated by Fourier transform photocurrent spectroscopy (FTPS) [4]. The determined absorption coefficient α at a photon energy of 0.8 eV strongly depends on the defect density in the layer and represents the "figure of merit" of good solar cell material [5]. To scale the absorption obtained by FTPS, we determined the absorption from 300-1200 nm by reflection and transmission measurements. A single-beam spectrophotometer equipped with an integrating sphere was applied, in order to exclude errors due to optical scattering of porous or rough layers.

The dark conductivity σ_{dark} has been measured in 2-point configuration with a source-measure unit (Keithley) after applying Al electrodes on the layers. The photoconductivity σ_{photon} has been measured under simulated AM 1.5 light.

3   RESULTS AND DISCUSSION

To develop an easy controllable and reproducible plasma enhanced deposition process of µc-Si:H- and a-Si:H-layers one of the basic requirements is a stable plasma. The stability can be proven by optical emission spectroscopy (OES) by which the optical emission spectrum of the optically active species inside the plasma is monitored.

A plasma consisting of H_2 and SiH_4 can become unstable at high H_2/SiH_4-ratios and at low power conditions. As observed by OES, sudden changes of the plasma conditions can take place. Especially under high silane dilution/low power conditions, the addition of Ar to the gas mixture can help to stabilize the plasma. For RF PECVD it was also found that in some cases the deposition rate could be enhanced by adding Ar [6]. Nevertheless, the usage of Ar dilution in film silicon deposition by PECVD has not become widespread, and this is merely due to negative effects of this type of dilutant: reduced layer quality due to Ar ion bombardment and enhanced formation of SiH_2 and SiH radicals in the plasma [6, 7]. For microwave PECVD the influence of Ar on the electrical and optical quality of the deposited Si-layer has not been discussed in literature intensively, till now.

When partially replacing H_2 by Ar in the deposition of microcrystalline silicon, OES reveals interesting phenomena occurring in the plasma. Due to this partial replacement one would expect a decrease of intensity of
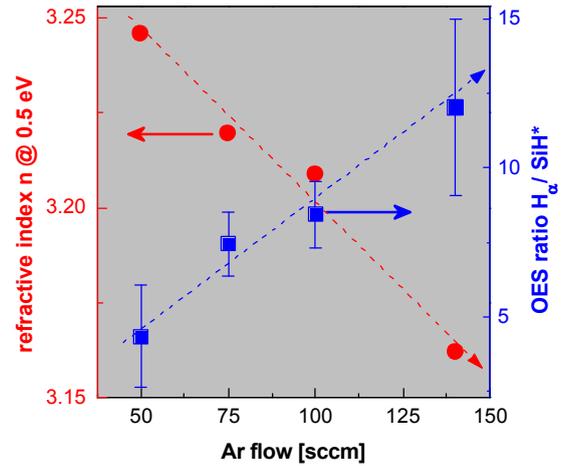

Figure 1: Influence of the Ar-content on OES ratio Hα/SiH* and on refractive index n. Later is determined by FTIR.

both, the H_α and H_β signal. However, it appears that the intensity of H_β drops more than the intensity of H_α, indicating that the average electron temperature T_e decreases if one replaces H_2 by Ar [8]. Further, we observe that the OES ratio of H_α divided by SiH* increases with increasing Ar-content (fig. 1, square). It is generally assumed that the ratio H_α/SiH^* in the plasma is an important factor determining the crystallinity of the layers, thus, one would expect larger crystalline fractions for larger Ar fractions. In addition, in previous experiments [9] we observed a decrease in refractive index n typically when the layers become more crystalline. Also here n @ 0.5 eV, which is determined by FTIR, decreases with increasing Ar-content (fig. 1, circle).

Both, the change in plasma chemistry and the drop in the quality of the deposited layer lead to the expectation of an increase in crystalline fraction with increasing Ar content. But the opposite is observed here (fig. 2), since the crystalline fraction, which is determined by Raman spectroscopy, is decreasing with increasing Ar-flow. The
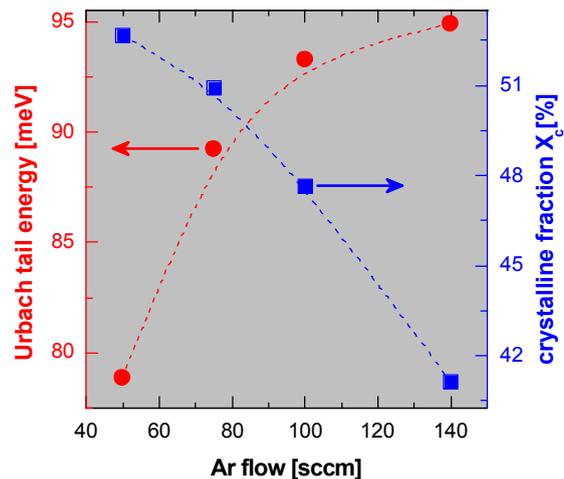
Figure 2: Behaviour of Urbach tail energy derived from FTPS data and crystalline fraction determined by Raman measurements with increasing Ar content during deposition

increase in Ar content leads to more amorphous Si-layers
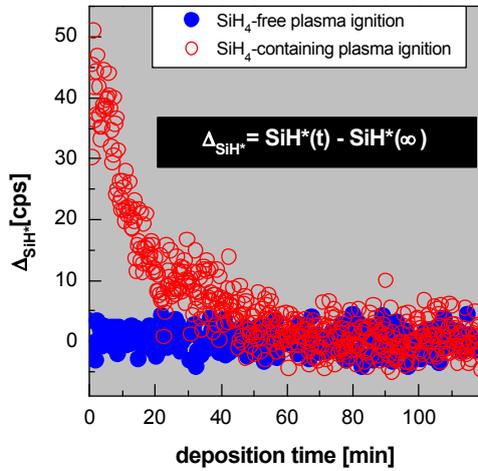
Figure 3: Deviation (ΔSiH*) of the OES SiH*-signal during the deposition as a criteria of plasma ~~stability~~

of worse optical quality. This loss in quality can also be seen in an increase in Urbach tail energy (fig. 2), which is determined by the analysis of the FTPS-spectra in the red-to-near infrared wavelength region. An increase in Urbach tail energy indicates an increase in defect density in the layers, and therefore a lower material quality.

As a consequence of the negative influence of Ar on the material quality we reduced Ar to a minimum with respect to stable plasma conditions for future process optimisation. For pressures larger than 0.1 mbar we found that Ar can be completely omitted under well-chosen process conditions without having sudden changes of the plasma conditions.

Additionally, an alternative start-up procedure of the deposition process had to be developed due to another type of plasma instability. In fig. 3 the time dependent behavior of the OES-signal intensity, which is assigned to the optically excited state SiH*, is shown. Here, ΔSiH* is the difference of this signal intensity at time t (SiH*(t)) to the signal intensity at the time, at which the plasma is stable (SiH*(∞)). As can be seen in the plot, the ignition of the plasma in a silane (SiH_4) containing atmosphere
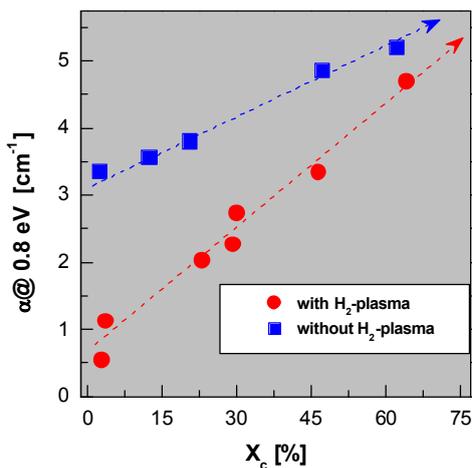
stabilization process silane is present and therefore, a deposition takes place. Such an uncontrollable process can be suppressed by using a shutter, or, like we do, the plasma is now ignited without the presence of silane. Then, after a minimal stabilization time of the plasma of t = 30 min, silane is injected, with the result, that the plasma keeps stable during the whole deposition (fig. 3, blue curve).

The result of such a silane-free ignition of the plasma, which we call H_2-plasma treatment, is a significant reduction of the defect density as measured by the absorption coefficient α at a photon energy of 0.8 eV. As shown in fig. 4 for all crystalline fractions X_c, α @ 0.8 eV is clearly lower, if the Si-layers are deposited after a H_2-plasma treatment (circles). For instance at a crystalline fraction of X_c= 47 % the absorption drops from α=4.9 cm^{-1} to α=3.3 cm^{-1} due to such a plasma treatment. This defect reduction leads to a significant improvement in photo/dark conductivity ratio ($\sigma_{photo}/\sigma_{dark}$): due to the H_2-plasma treatment the $\sigma_{photo}/\sigma_{dark}$ of the μc-Si:H-layer (X_c= 47 %) increases from 15 up to 56.

With the developed start-up procedure of a H_2-plasma treatment the process stability is significantly improved and this even by the use of low microwave power. For the fine-tuning of the process parameters the silane fraction was varied in a range at which the transition region from microcrystalline to amorphous Si-layers is expected, like previous investigations have shown [9]. In this region we hope to find μc-Si:H of photovoltaic quality. An intensive screening of different total pressure/microwave power/substrate temperature combinations revealed an optimum of total pressure (with respect to electrical and optical layer properties) of 0.3 mbar, so far. Therefore, this total pressure is used in the following experiment:

By decreasing the substrate temperature from T = 250°C (fig. 5, circle) to T = 200°C (fig. 5, square) for all crystalline fractions X_c a clear improvement of $\sigma_{photo}/\sigma_{dark}$ of the samples is observed. The higher

Figure 4: Decrease of the absorption coefficient α at a photon energy of 0.8 eV of Si-layers with varying crystallinity, due to a H_2-plasma treatment before the deposition.

Figure 5: Increase of $\sigma_{Photo}/\sigma_{Dark}$, if the deposition temperature is decreased from T = 250°C (circle) to T = 200°C (square).
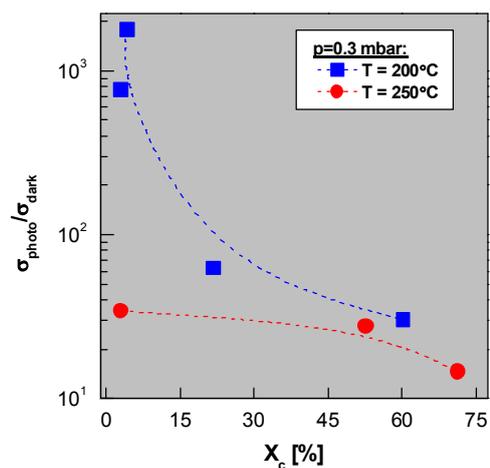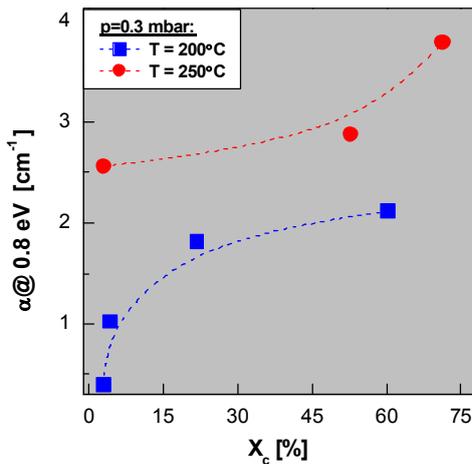
leads to an unstable plasma (fig.3, red curve); in general, it takes 30 min to 50 min time to stabilize the plasma, depending on the process conditions. During this

$\sigma_{photo}/\sigma_{dark}$ of samples which are deposited at low substrate temperature, is accompanied with a lower α @ 0.8 eV (fig. 6).

Figure 6: Decrease of α @ 0.8 eV due to a reduced defect density, if the deposition temperature is decreased from T = 250°C (circle) to T = 200°C (square).

This indicates a reduction of active defects in low temperature deposited Si-layers. Possible explanations for this improvement are a suppressed O donor formation [10] and an enhancement of H incorporation at lower growth temperature.

4 CONCLUSION

For a reproducible deposition of a-Si:H- and μc-Si:H-layers by MWPECVD it is essential to have stable plasma conditions. Two types of plasma instabilities and the possibilities to remedy these deficiencies were discussed:

The first occurs at inauspiciously chosen deposition conditions at low pressure and low microwave power without the use of argon. Argon is beneficial to avoid an instability of a microwave plasma on short time scale, if hydrogen is the main precursor gas. But it has detrimental effects on the electronic properties of the deposited silicon layers. By minimizing the Ar flow, a significant improvement of the optical and electronic properties of the μc-Si:H layers is observed.

The second one is an instability during start-up of the deposition. To guarantee stable plasma conditions from the beginning of the deposition one can use a shutter or, as presented here, one introduces a so-called H_2-plasma treatment before the deposition. It is shown that Si-layers with a significantly lower defect density, which is indicated by a strong reduction of α @ 0.8 eV and a clearly improved $\sigma_{photo}/\sigma_{dark}$-ratio, can be prepared this way.

The electrical and optical quality of μc-Si:H-films is clearly improved by decreasing the substrate temperature to T = 200°C or even lower.

5 ACKNOLEGDEMENTS

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