Presented at the 20th European Photovoltaic Solar Energy Conference and Exhibition,
Barcelona, Spain, 6-10 June 2005

OPTICAL AND STRUCTURAL PROPERTIES OF MICROCRYSTALLINE SILICON GROWN BY MICROWAVE PECVD

W.J. Soppe[1], H.J. Muffler[1], A.C. Biebericher[1], C. Devilee[1], A.R. Burgers [1], A. Poruba[2], L. Hodakova[2] and M. Vanecek[2]
[1] Energy research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands, email: soppe@ecn.nl
[2] Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 16253 Prague 6, Czech Republic, email: vanecek@fzu.cz

ABSTRACT:
We investigated the deposition of μc-Si by microwave PECVD. MWPECVD is an excellent tool for fast deposition of silicon at low temperatures; however, this fast growth is often accompanied by high porosity. In order to obtain dense Si layers we investigated a wide deposition parameter space, where we systematically varied substrate temperature T_s, pressure p, total flow Φ_{tot}, flow ratio Φ_{SiH4}/Φ_{H2} and microwave power P_{MW}. We identified a deposition regime for growth of dense μc-Si layers. Main characteristics of this regime are high substrate temperatures (300 ºC) and a reduced microwave power. Silicon layers grown in this regime have a refractive index above 3.0, showing that the porosity of the layers is low. Opto-electronic characterization shows that the layers already fulfill most requirements for absorber layers in thin film silicon solar cells.
Keywords: Micro Crystalline Si, PECVD, Optical Properties

1 INTRODUCTION

Application of μc-Si in thin film silicon solar cells offers a great perspective of achieving higher and more stable efficiencies of these devices than for a-Si devices, but will only be accomplished in a large-scale industrial production if the deposition rate of this material can meet industrial demands [1,2].

Microwave PECVD is a deposition method that can fulfill these industrial demands. In previous papers [3,4] we have shown that the method is capable of deposition rates for μc-Si higher than 1 nm/s in a stationary mode. Furthermore, by the linear character of the microwave source, the method is inherently suitable for continuous processing (e.g. roll-to-roll production) on large areas. In order to combine high deposition rates and high material quality we have to optimize the deposition conditions. In this paper we present the latest results of optical and structural properties of μc-Si obtained by microwave PECVD.

2 EXPERIMENTAL SETUP

2.1 Depositions by MWPECVD

The depositions were performed in a single chamber microwave PECVD reactor, in which a substrate holder with a substrate area of 60x15 cm² moves underneath a linear microwave plasma source (Figure 1). We systematically varied substrate temperature T_s, pressure p, total flow Φ_{tot}, flow ratio Φ_{SiH4}/Φ_{H2} and microwave power P_{MW}, keeping the silane concentration constant at a value of 5 %. In a second series we kept all deposition conditions constant but varied the silane concentration. The depositions took place simultaneously on glass substrates and on silicon wafers to allow various characterization techniques to be used on samples from the same batch.

Optical emission of the plasma (OES) was monitored by an Avantes spectrometer in the wavelength range from 200 - 1000 nm, with a resolution of 0.6 nm. Emitted light was collected through a sapphire view port in the reactor and was guided to the spectrometer through an optic fiber cable with high UV transmission. The view port is positioned slightly above the level of the substrates.

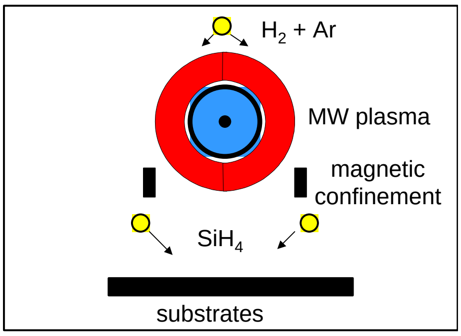

Figure 1: Cross section of linear microwave plasma source.

2.2 Characterization of the silicon layers

Fourier Transform Photocurrent Spectroscopy (FTPS) [5] was applied to obtain information on the defect density of the layers. Dark conductivity as a function of temperature was measured after evaporation of Al contacts on the layers, and an anneal time of 2 hrs under vacuum conditions at 120 ºC. The photo-conductivity was measured under illumination under AM1.5, applying a voltage of 10 V.

The crystallinity of the layers was investigated by Raman spectroscopy. Raman scattering spectra were obtained in backscattering mode, with incident laser light at a wavelength of 532 nm and with a resolution of 1 cm^{-1}. Reflection and transmission (R/T) spectra in the wavelength region between 330 and 1400 nm were obtained using an integrating sphere and a monochromator at a resolution of 5 nm. FTIR spectra in the range 400 - 4000 cm^{-1} were recorded by a Perkin-Elmer BX-II spectrometer, at a resolution of 8 cm^{-1}.

The optical constants were obtained by analysis of the R/T spectra and curve fitting of the interference fringes in the IR transmission spectra [4], similar to the approach of Swanepoel [6]. Microcrystalline silicon in general is less compact and more porous than c-Si and this porosity leads to lower refractive indices. FTIR measurements thus quickly provide information on the optical density and the porosity of the material.

3 EXPERIMENTAL RESULTS

3.1 Porosity of the layers

The most important deposition parameters that determine the density of the layers are the substrate temperature and the applied microwave power. Assuming that effect of surface roughness variation can be neglected, we can use the refractive index derived from the fringes in the FTIR spectra as a measure for the density of the layers. It appears that for a large part of the investigated parameter space, the layers are rather porous. In most of the cases the refractive index at 0.4 eV is well below 3.0 where the refractive index of bulk x-Si is about 3.4.

As shown in Figure 2, higher substrate temperatures lead to higher refractive indices, and thus to higher layer densities. We attribute this effect to higher surface mobilities of SiH_x species.

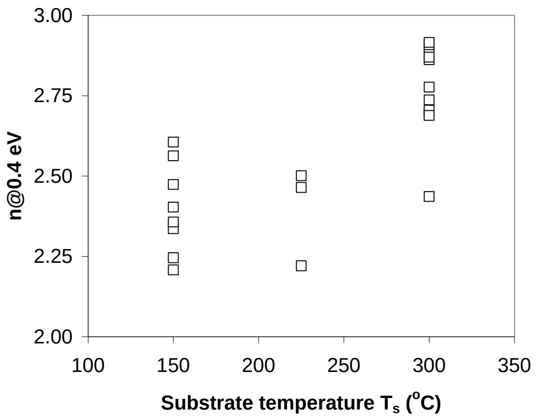

Figure 2: Refractive index of μc-Si as a function of substrate temperature T_s. Silane fraction was 5%. Scattering of the data is due to variation of the other deposition conditions.

The applied microwave power P_{MW} is another important factor determining the layer density. P_{MW} affects the electron energy in the plasma, and therewith the entire plasma chemistry. OES shows that with increasing P_{MW}, the dissociation of both H_2 and SiH_4 is increasing, but that the increase of H_2 dissociation is stronger probably because of its higher dissociation energy. In Figure 3 the ratio of optical emission of Hα and SiH is shown. This figure illustrates this difference in dissociation efficiency of H_2 and SiH_4, but also shows that the Hα/SiH ratio for all deposition conditions is well above 1.0, which is generally considered as a criterion for growth of μc-Si [7].

High microwave power leads to higher deposition rates, but a drawback of high P_{MW} is that it also leads to less dense layers. This is probably a result of enhanced formation of sticky Si* and SiH* radicals at the expense of SiH_3 radicals. This behavior is illustrated by Figure 4 in which the emission ratios of SiH and Si radicals are plotted against the applied microwave power.

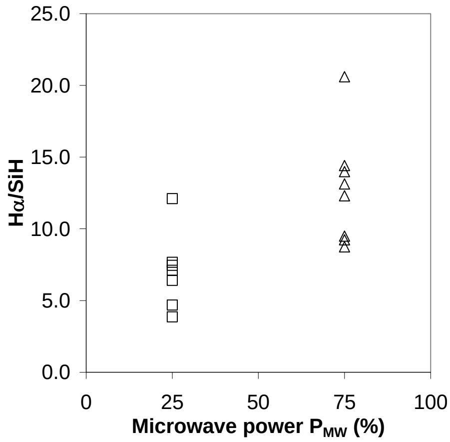

Figure 3: Ratio of Hα (emission at 656 nm) and SiH (emission at 414 nm) versus applied MW power. Silane fraction was 5%, other deposition conditions were varied.

The SiH/Si ratio decreases with increasing power and we may expect that the SiH_3/Si ratio will decrease analogously. The figure further shows that the decrease of the SiH/Si ratio is accompanied with a decrease of the refractive index, i.e. with a decrease of layer density.

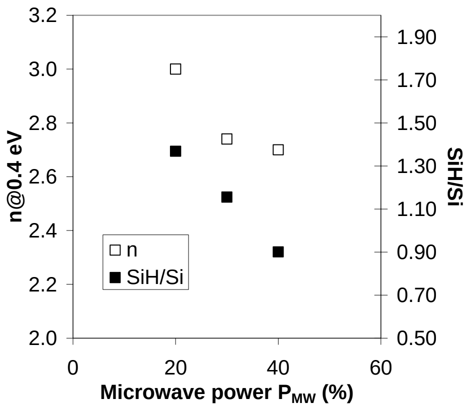

Figure 4: Refractive index determined by FTIR and emission intensities of SiH (414 nm) and Si (288 nm).

More generally, the porosity of the layers is strongly correlated with the efficiency by which available Si atoms are incorporated in the silicon layers. To study this effect we have performed a series of depositions in which we increased the SiH_4 flow rate and kept the other deposition parameters constant (using a high substrate temperature and a reduced microwave power).

Defining the SiH_4 utilization efficiency η_{SiH4} as the layer growth rate divided by the SiH_4 flow rate, we see that the refractive index decreases monotonously with increasing η_{SiH4}. This effect is illustrated in Figure 5. Interesting aspect of this graph is that η_{SiH4} is higher for growth of microcrystalline silicon than for amorphous silicon.

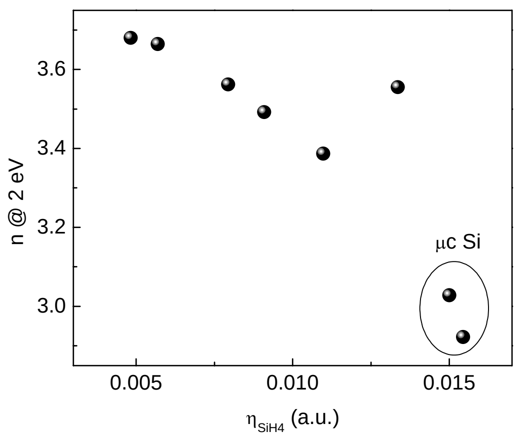

Figure 5: Refractive index of silicon layers versus the silane utilization efficiency η_{SiH4} defined as growth rate/SiH_4 flow. The two samples on the right are microcrystalline silicon; the others are largely amorphous.

For the same series of depositions we also determined the hydrogen content (by analysis of the 620-640 cm^{-1} band in the FTIR spectra) and the structure factor R* (by analysis of the 2000-2100 cm^{-1} bands). The results are plotted in Figure 6 together with the crystalline fraction X_c as determined by Raman spectroscopy. According to these measurements, the transition from μc-Si to a-Si takes place at a SiH_4 fraction between 4 and 5 %. The layers grown at a SiH_4 fraction of 4 % show a dual behavior: the crystalline fraction is significant (64 %), but the hydrogen content of 10 % and R* equal to 0.3 are typical for amorphous silicon.

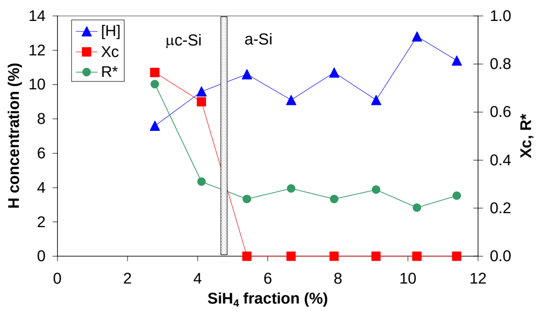

Figure 6: Hydrogen concentration and structure factor R* for silicon layers grown with various SiH_4 flows. Crystalline fractions X_c as determined by Raman spectroscopy have also been included.

3.2 Opto-electrical properties

To obtain the optical bandgap Eg for amorphous layers, we used reflection/transmission measurements but found that Tauc approach (extrapolation of $\sqrt{\alpha E}$) is not applicable for layers in the μc-Si/a-Si transition regime. A typical example of this behavior is shown in Figure 7.

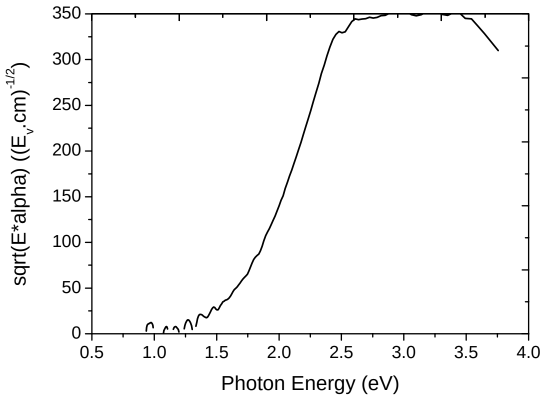

Figure 7: Typical example of $\sqrt{\alpha E}$ of a microcrystalline/amorphous Si layer , obtained with R/T measurements.

As an alternative E_{04}, the photon energy at which α equals 10^4 cm^{-1} could be used as a figure of merit for the optical absorption. The interpretation of E_{04} in general, however, is not unambiguous, since the value is simultaneously influenced by the hydrogen content and by the crystalline fraction. In Figure 8 we present values of E_{04} obtained for the same series of depositions with increasing SiH_4 fraction as discussed above. The series shows a decrease of E_{04} with increasing SiH_4 fraction, corresponding with a decrease of the crystalline fraction since the hydrogen content is more or less constant (see Figure 6).

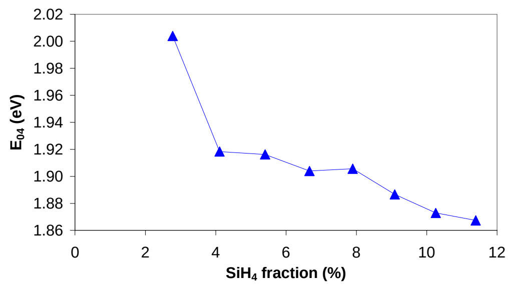

Figure 8: Bandgap E_{04} of layers grown with various SiH_4 flows.

Electrical conductivity measurements confirm the abrupt change of material properties in the μc-Si/a-Si transition regime. We obtain typical values for the activation energy for dark conductivity of μc-Si in the range 0.55-0.6 eV and 0.75-0.85 eV for a-Si layers. The dark conductivity at room temperature, and the ratio of photo and dark conductivity are plotted in Figure 9. For the μc-Si layers the dark conductivity is in the range of 10^{-7} to 10^{-6} S/cm, whereas for the a-Si layers σ_{dark} is more than two orders of magnitude smaller. The ratio of photo and dark conductivity is in the range 10-40 for the μc-Si layers and jumps to almost 500 upon trespassing the transition to a-Si layer growth.

For higher silane fractions a decrease of the photo to dark conductivity ratio is observed. For both the μc-Si and the a-Si layers deposited in this series the opto-electrical properties are slightly below the criteria for 'device quality material' [8].

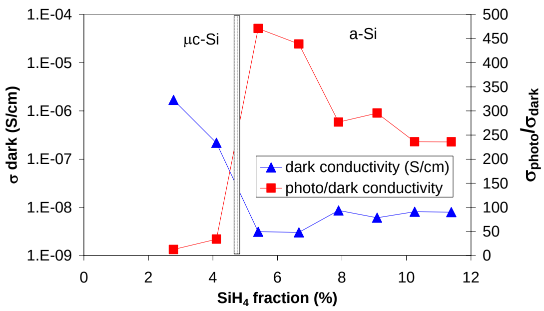

Figure 9: Dark and photoconductivity of a series of silicon layers grown with various SiH_4 fractions.

Optical absorption measurements by FTPS show for all investigated layers an enhanced absorption in the region from 1.3 – 1.8 eV. This indicates that the layers labeled as amorphous in the previous graphs, do contain a certain fraction of (nano)crystalline material although this phase is invisible in the Raman spectra.

Figure 10 gives an overview of the FTPS spectra of the series of layers grown with various SiH_4 fractions. Due to surface roughness of some samples the observed absorption is higher than the 'true' absorption, and correction for these scattering effects results in values for true absorption at 0.8 eV, which are below 1 cm^{-1}. This would imply a defect density of about 10^{17} cm^{-3}; a value that has to be improved for photovoltaic application.

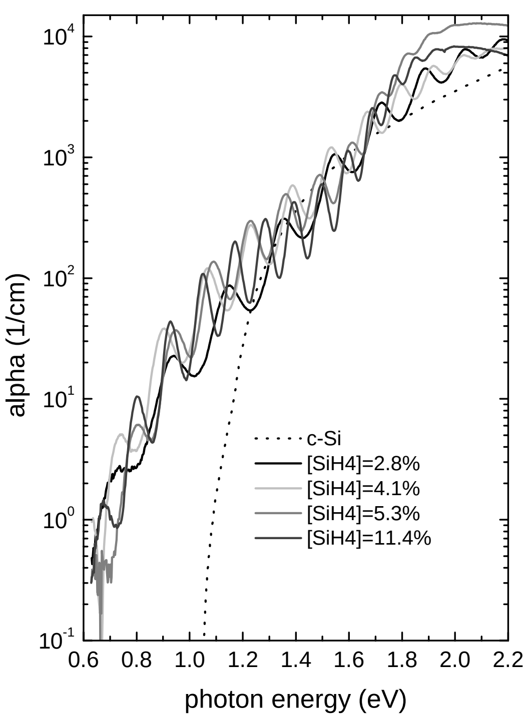

Figure 10: FTPS spectra of layers grown with various SiH_4 fractions

4 CONCLUSIONS

We identified a regime for deposition of dense μc-Si layers by microwave PECVD. This deposition regime is mainly determined by the substrate temperature and by the applied microwave power. Higher substrate temperatures lead to denser layers, probably because of enhanced surface mobility of growth species. Reduced microwave power leads to denser layers, probably because it favors the formation of SiH_3 species in the plasma, at the expense of the stickier Si and SiH species.

Silicon layers deposited in this regime at various SiH_4 fractions show opto-electrical properties which are typical for mixed phase μc-Si/a-Si material, and which approach the requirements for device quality film silicon.

ACKNOWLEDGEMENTS

This work has been financially supported by the Dutch Ministry of Economic Affairs (Projectno. TSIN3043) and by the European Commission under contract no. INCO-CT-2004-509178.

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