

DEPOSITION OF A-SI:H AND μ C-SI:H USING A NOVEL LINEAR RF SOURCE

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High-efficiency, high-throughput fabrication technology is paramount for further commercialisation of thin film Si solar cells. To support this development ECN and Roth and Rau AG have designed and built a pilot scale roll-to-roll coater for the production of Si solar cells on steel foil. High rate MW-PECVD will be used for intrinsic Si, and for doped Si a linear RF source has been developed. This novel RF source applies a very mild ion bombardment on the growing Si surface and is also very attractive for surface treatments, such as passivation of Si wafers by thin SiN_x or a-Si layers. In this contribution we will report on the development of deposition processes for intrinsic, both amorphous and microcrystalline, Si layers, deposited with the novel RF source. These results serve as starting points for the development of doped Si layers.

Keywords: RF PECVD, a-Si:H, μ c-Si:H

1 INTRODUCTION

Radio frequency PECVD is commonly used to deposit silicon layers at low temperatures for photovoltaic cells. In most industrial PECVD systems the plasma is generated in a capacitive mode. In a capacitive plasma, typically, the grounded substrate is part of the RF network and subject to bombardment by ions with energies in the range of 10-100 eV. This ion bombardment usually has a detrimental effect on the electronic quality of the silicon layers.

Here we present layers deposited with a novel RF source for PECVD. Details on the source characteristics are described in another paper at this conference [1]. In this set-up the substrate is electrically disconnected from the RF network. As a result, the ion bombardment is very mild, with ion energies limited to values typically less than 10 eV. 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 (μ c-Si:H) silicon thin films on steel foil coated with an insulating layer. For this purpose we have developed a pilot scale roll-to-roll PECVD system, the FLEXICOAT300, in collaboration with Roth & Rau AG.

In the FLEXICOAT300, the intrinsic layer will be deposited with microwave PECVD [2] as this combines good quality with high deposition rates. However, the linear microwave source employed by ECN is not suitable for deposition of doped layers. The quartz tube which shields the antenna will not transmit EM radiation when covered by a conducting doped silicon layer. The novel RF source has been introduced to circumvent this problem. Lower deposition rates for RF-PECVD with respect to MW-PECVD are of minor importance since the thickness of doped layers in thin film Si solar cells is small (≤ 20 nm) with respect to the required thickness of the intrinsic layer (≥ 1 μ m).

This work focuses on two aspects of our research programme. i) The suitability of the novel remote RF plasma source for large area, high throughput roll-to-roll production lines. ii) The relation between the deposition conditions of the RF-PECVD process and the optical, structural and electronic properties of a-Si:H and μ c-Si:H layers, in order to identify optimal conditions for device quality growth.

2 EXPERIMENTAL

2.1 Deposition process

The FLEXICOAT300 contains five vacuum chambers: a pay-off chamber, three PECVD chambers, for n-type, intrinsic and p-type Si deposition respectively, and a take-up chamber. The system is designed for continuous roll-to-roll deposition on moving foil substrates and can handle webs with a width of up to 30 cm. The intrinsic chamber can be equipped with four linear microwave sources [2] and has an effective deposition area of 120×30 cm². The p-type and n-type chambers are equipped with linear RF sources. The effective deposition area in the p-type and n-type chambers is 20×30 cm². All chambers are pumped with roots pumps allowing a base pressure in the range of 10^{-5} mbar. Plasma boxes shield the plasma and substrate, in order to reduce oxygen contamination due to water desorption from cold walls.

The RF source has been developed by Roth & Rau AG and consists of two aluminium rods (with a diameter of about 30 mm) which are symmetrically connected to the RF generator (13.56 MHz), with a maximum power of 600 W. This concept results in a significant voltage drop over the plasma sheath around the electrodes but only a small voltage drop over the plasma sheath around the substrate. The plasma generated by this source therefore enables deposition conditions with very small ion energies at the substrate surface of typically less than 10 eV. The substrate does not form part of the RF network and therefore does not need to be grounded.

The length of the rods (determining the width of the deposition area) is about 60 cm, but lengths over 1 m are possible without detrimental effects on the homogeneity of the plasma.

The pressure range in which this RF source can be operated is 0.01-1 mbar; if a magnetic field is applied the source can even be operated at pressures down to 0.001 mbar. For deposition of silicon layers we typically operate the source between 0.01 and 1 mbar and do not apply a magnetic field.

We have systematically varied deposition conditions, such as substrate temperature, RF power, pressure and SiH_4 fraction, defined as $\Phi_{\text{SiH}_4} / (\Phi_{\text{SiH}_4} + \Phi_{\text{H}_2})$, where Φ stands for the flows, to optimise the process for the growth of intrinsic a-Si:H and μ c-Si:H layers using the novel remote RF plasma source. These optimal processes

will be used in the further development of growth processes for doped Si layers.

2.2 Characterisation

For each set of deposition parameters, three 3×3 cm² samples have been deposited simultaneously, one on a double-sided polished CZ Si wafer and two on Corning 2000 glass. The typical layer thickness is about 300 nm. On one of the layers deposited on a glass substrate three 600 nm thick Al contacts (50 mm²) are evaporated with an E-beam PVD apparatus. The contacts are 0.5 and 0.2 mm apart and 10 mm wide. The quality of the layers was examined by a large range of techniques.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a Perkin Elmer BX II spectrometer between 400 cm⁻¹ and 4000 cm⁻¹. The spectra are fitted by varying the layer thickness, refractive index n and extinction coefficient k . The latter is transformed to the absorption coefficient α . The hydrogen content of the layer is determined from the area under the peak at ~ 630 cm⁻¹. The structure at 2000-2100 cm⁻¹ is used to calculate the microstructure factor R^* and yields information about the type of hydrogen bonding.

The temperature dependence (393-273 K) of the dark conductivity σ_d is measured after annealing at 393 K for 2 hours in a vacuum chamber to prevent oxidation and minimise the effect of water vapour. The activation energy is calculated from a linear fit to the Arrhenius plot.

An altered FTIR set-up is used to perform Fourier transform photocurrent spectroscopy (FTPS), see [3] for details. The FTPS data has been fitted to a model for the absorption of a-Si:H and μ c-Si:H [4, 5] to determine the Urbach energy E_{urb} . Reflectance and transmittance (R-T) are measured using an integrating sphere. R-T and FTPS data are combined to obtain absorption spectra in the range 0.6-2.5 eV.

Raman spectra have been measured on a Renishaw Raman spectrometer. The crystalline volume fraction ϕ_c is calculated from the ratio of the amorphous and crystalline contributions according to

$$\phi_c = \frac{I_{520} + I_{505}}{I_{520} + I_{505} + I_{480}} \quad (1)$$

where I_n is the intensity of the peak at n cm⁻¹.

3 RESULTS AND DISCUSSION

3.1 Novel linear RF source

H₂ plasmas generated with the RF source have been analysed to determine the uniformity of the current density and the energy distribution of the ion bombardment at the surface of the substrate. The current density, measured by Langmuir probes, is constant within 4% along the length of the RF antenna. The ion energy distribution has been measured using the retarding field analyse method [6, 7]. Whereas conventional RF sources yield a high energy tail in the ion energy distribution up to 60-100 eV [8], any sign of a high energy tail is absent for the novel symmetric source. Only a sharp peak at 4 eV, that rapidly falls off to zero at 10 eV is observed. This upper limit on the ion energy is well below the displacement energy for Si atoms.

The very mild energies of the ions arriving at the substrate will make this source very attractive for other applications where surface damage should be avoided, for instance during surface passivation of Si wafers by the deposition of SiN_x or a-Si layers.

3.2 Deposition of a-Si:H

Initial depositions in the RF chamber at relatively high pressure and high SiH₄ fraction resulted in amorphous layers. After some process optimisation steps, conductivity data, for instance a σ_{ph}/σ_d ratio of almost 10⁶ and an activation energy $E_{act} = 0.85$ eV, indicated that the layers were of high quality. FTIR data revealed a good dense layer with refractive index $n = 3.3$ at 0.5 eV and microstructure factor $R^* = 0.18$ for a layer of ~ 400 nm thickness. In table 1 the material properties of a-Si:H deposited with the novel RF source are compared to the device quality criteria as stated by Schropp and Zeman [9]. As can be seen, the present status is nearly of device quality. As these experiments are meant as preliminary investigations for the deposition of doped Si layers, we regard the present status as sufficient to start the development of deposition processes for doped a-Si:H.

Table I: Overview of properties of intrinsic a-Si:H thin films. For comparison data for device quality films are given [9].

Material parameter	present status	device quality
σ_{dark} [S/cm]	1.8×10^{-11}	$< 1.0 \times 10^{-10}$
σ_{photo} [S/cm]	1.7×10^{-5}	$> 1.0 \times 10^{-5}$
$\sigma_{photo}/\sigma_{dark}$	9×10^5	$> 10^5$
E_{act} [eV]	0.85	≈ 0.85
E_{gap} [eV]	1.7	≤ 1.8
E_{urb} [meV]	59	< 50
$n @ 0.5$ eV	3.3	≈ 3.5
R^*	0.18	< 0.10

The growth rate of these layers is about 0.3 Å/s. The proposed growth rate for the deposition of intrinsic Si with the MW source is > 1 nm/s. As the thickness ratio of intrinsic layer to doped layer is above 50:1, the growth rate observed for the RF source is fast enough to allow continuous roll-to-roll deposition of solar cells on steel foil in the FLEXICOAT300.

3.3 Deposition of μ c-Si:H

To find process parameters for the deposition of μ c-Si:H, the silane fraction in the reaction chamber is reduced. Raman data for these samples are plotted in Fig. 1. A clear transition from the growth of amorphous layers at higher silane fractions to the deposition of microcrystalline layers at lower silane fraction is observed. The corresponding R^* values, determined from the FTIR spectra are shown in the inset. Fitting of the peaks to the Raman spectra yields $\phi_c = 76\%$ for the 1% SiH₄ fraction sample, whereas for the 9% SiH₄ fraction sample only $\phi_c = 4\%$ is found.

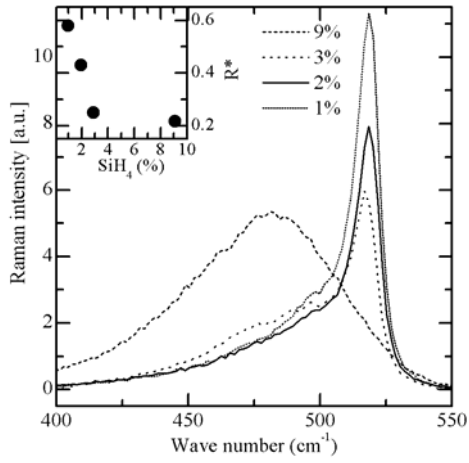


Fig. 1: The Raman spectra of thin film Si samples. The SiH_4 fraction during deposition is indicated in the legend. The left inset shows R^* as determined from the 2000-2100 cm^{-1} structure in the FTIR spectra.

The shift from a-Si:H to $\mu\text{c-Si:H}$ characteristics with decreasing SiH_4 fraction is also reflected in the hydrogen content, as determined by FTIR spectroscopy. Typical values for amorphous samples are 11-13%, whereas for microcrystalline material 4-5% is found. Furthermore, the transition is accompanied by an increase in refractive index (both at IR and VIS wavelengths), an increase in conductivity and a decrease in activation energy of the dark conductivity.

In Fig. 2 the conductivity parameters of a series of samples is shown. Within the series, the pressure during deposition is varied at a constant SiH_4 fraction. With decreasing pressure, we observe a decrease in the activation energy and an increase in the dark conductivity. There appears to be a sharp transition near 0.25 mbar.

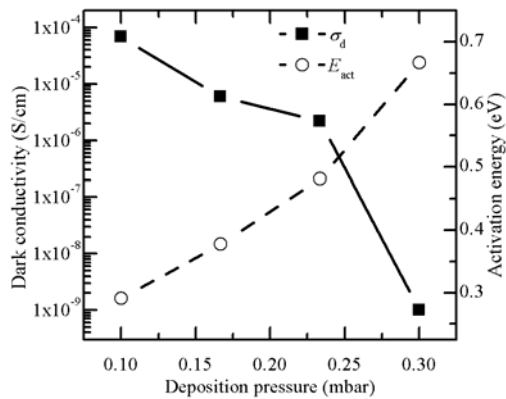


Fig. 2: Effect of deposition pressure on the electronic properties of thin film Si layers. The filled squares represent the dark conductivity σ_d at 300 K. The corresponding activation energy E_{act} is plotted as open circles.

Raman and FTIR spectroscopy confirm this transition, see Fig. 3. The sample grown at 0.3 mbar has a crystalline volume fraction of about 1%, where the other three samples are over 60%. Furthermore, similar to the silane concentration series, the hydrogen concentration in the amorphous sample is twice that of the microcrystalline samples.

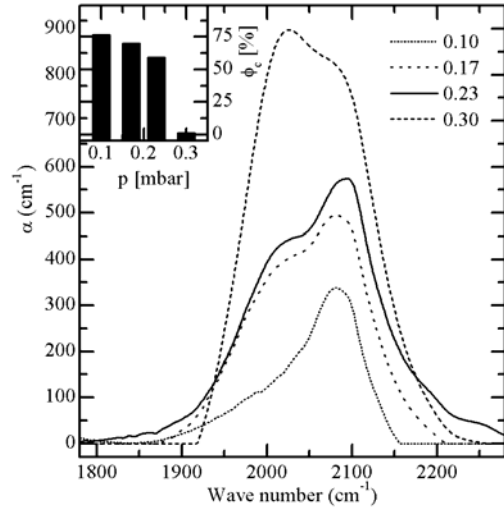


Fig. 3: Effect of deposition pressure on the structural properties of thin film Si layers. The FTIR spectra are shown in the main graph, the respective deposition pressures are indicated in the legend. The inset shows the crystalline fraction determined from Raman spectroscopy.

The data for the $\mu\text{c-Si:H}$ sample has been summarised in Table II. At the present state, the Urbach energy is too high for device quality intrinsic Si. Also, the refractive index is slightly too low. However, these samples are not intended to be the photo-active layer in solar cells, and we consider the results as good starting points for the deposition of doped $\mu\text{c-Si}$ samples with the novel RF source.

Table II: Overview of properties of intrinsic $\mu\text{c-Si:H}$ thin films. For comparison data for device quality films are given [9].

Material parameter	present status	device quality
σ_{dark} [S/cm]	1.5×10^{-7}	$< 1.5 \times 10^{-7}$
σ_{photo} [S/cm]	4.1×10^{-5}	$> 1.5 \times 10^{-5}$
$\sigma_{\text{photo}} / \sigma_{\text{dark}}$	267	≈ 100
E_{act} [eV]	0.567	0.53-0.57
E_{gap} [eV]	-	≤ 1.2
E_{urb} [meV]	96	< 50
n @ 0.5 eV	3.2	> 3.4
ϕ_c	75%	

As these layers satisfy our criteria, we have also investigated the dependence of the properties, in particular, the microcrystalline fraction, on the layer thickness. In Fig. 4, Raman spectra are plotted as a function of layer thickness. For the thinnest sample with

$d = 41$ nm, we find that $\phi_c = 21\%$. This is in agreement with the dark conductivity and other data, which also indicate a large amorphous fraction in this layer. We estimate that there is an incubation layer of around 10-30 nm present in these layers. Faster nucleation, i.e. thinner incubation layer, is expected to occur at higher H_2 dilution. This is presently not possible in the FLEXICOAT300, due to the limited range of the mass flow controllers.

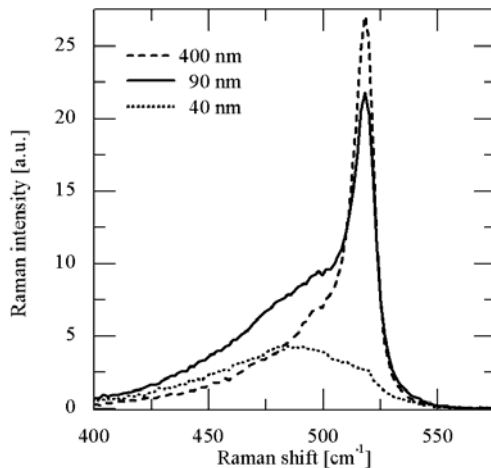


Fig. 4: Effect of layer thickness on the crystalline volume fraction. On the right hand side of the 40 nm curve a shoulder, indicating a small crystalline volume fraction, is discernable.

4 CONCLUSION

We have found deposition conditions for the novel linear RF source for intrinsic a-Si:H and μ c-Si:H layers of (near) device quality. For higher SiH_4 fractions good quality a-Si:H is deposited. At lower fraction and lower pressure μ c-Si:H layers are grown, but the quality is sensitive to other process parameters, such as RF power. The microcrystalline growth is retarded by an incubation layer of about 10-30 nm. We expect that at lower SiH_4 fractions this incubation layer can be made small enough for very thin (≤ 20 nm) doped microcrystalline layers of device quality. We are presently using these deposition conditions to develop processes for thin, n-type and p-type doped layers deposited with the novel linear RF source.

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