MW plasma enhanced CVD of intrinsic Si for thin film solar cells

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ABSTRACT

The aim of the thin film silicon PV research program at ECN is the development of high-throughput production technology for high efficiency, microcrystalline and amorphous thin film silicon photovoltaics (PV) on flexible substrates. For this purpose, a roll-to-roll system has been designed and constructed, consisting of three deposition chambers for the continuous deposition of n-type, intrinsic and p-type Si layer. In this paper, we will present optical and electrical characterisation of device quality intrinsic Si layers, deposited with Microwave (MW) plasma enhanced chemical vapour deposition (PECVD), with a special focus on UV-reflection spectroscopy (UVRS). UVRS can be used to determine the crystallinity in very thin silicon layer and is interesting as a possible inline tool for layer quality assessment and crystallinity control.

INTRODUCTION

Roll-to-roll (R2R) production of thin film Si solar cells combines the advantages of flexible substrates and high-throughput fabrication. Advantages include reduced handling costs, clean (closed) environment processing and the absence of pump-down cycles leading to potential significant cost reduction compared to batch-type processing using glass superstrates. However, in contrast to equipment adapted from display technology for the fabrication of thin Si layers on glass, equipment for roll-to-roll production is not commercially available. Therefore, ECN is developing high-throughput, roll-to-roll production technology for high efficiency thin film silicon solar cells. In our concept, steel foil, coated with an insulating barrier layer, is used as substrate. A sputtered back-contact and –reflector is applied, before the active Si layers are deposited by PECVD. On top of the Si layers, a transparent conductive oxide is sputtered. In order to achieve monolithical series connection, cells are defined and isolated by laser scribing followed by printing of insulating and conducting lines. In principle, the same concept can be used for plastic substrates. For the continuous deposition of amorphous and microcrystalline silicon n-i-p layers and thin film solar cells by PECVD, ECN and Roth&Rau AG developed a roll-to-roll system, the FLEXICOAT300.

In this contribution, we will report on intrinsic Si layers grown with MW-PECVD. We will pay particular attention to UVRS as characterization tool for determination of the crystalline fraction in thin silicon layers. The standard method for analysis of crystallinity of silicon layers is Raman spectroscopy, which, however, is less suitable for analysis of very thin layers (on top of other silicon layers), unless a UV laser is used for excitation. Further, Raman spectroscopy is rather difficult to implement as an inline monitoring tool in a PECVD system. UVRS is suited for measurement on very thin films and is easier to implement as inline monitoring tool. However, there is no standard evaluation method yet to determine the crystalline fraction in thin silicon layers from UVRS. We will present UVRS-analyses of crystalline fraction in

microcrystalline silicon, based on an approach developed by Harbeke and Jastrzebski [1], and show that this method is indeed a potentially well suited tool to determine crystalline fractions.

EXPERIMENT

The FLEXICOAT300 is designed for the continuous deposition of silicon on 300 mm wide (stainless steel) moving foil. The sources are all linear and the entire system including plasma sources can be scaled up to a width of 1500 mm. Plasma boxes shield both plasma and substrate from the water-cooled walls, in order to reduce oxygen contamination of the deposited layers due to water desorption. Gas locks are installed allowing to use different pressures in each of the deposition chambers and to prevent the contamination of the intrinsic chamber with dopant gases such as PH_3 and B_2H_6. All chambers are pumped with roots pumps allowing a base pressure in the range of 10^{-5} mbar
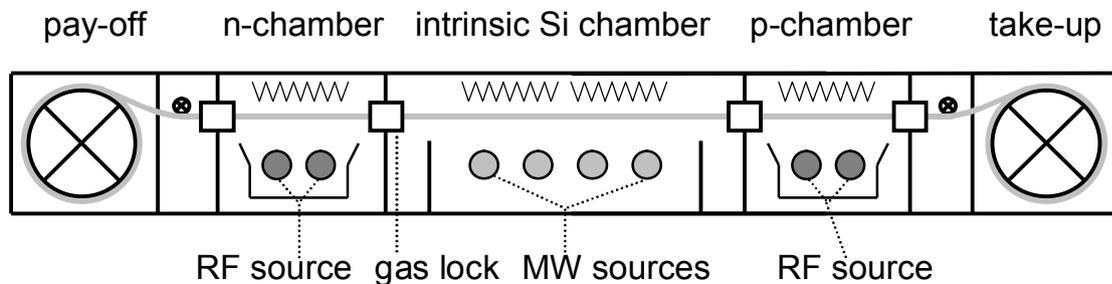

Figure 1. Cross-section through the FLEXICOAT300 roll-to-roll coater.

The intrinsic layer is deposited with MW-PECVD as this plasma method combines high deposition rates, uniform deposition on large areas and good layer quality [2]. High deposition rates, in the order of 1 nm/s, are needed for the deposition of the relatively thick intrinsic Si layers, ~300 nm for a-Si and 1-2 μm for μc-Si, in order to achieve high process throughput and thus low cost of ownership of the equipment. The linear microwave source consists of a linear antenna, which is placed inside a quartz tube to shield it from the plasma. Pulsed microwaves are fed in from MW power supplies on both ends of the antenna. Each MW source contains two linear arrays of magnets, along each side of the MW antenna. The magnet configuration influences the shape and extent of the plasma confinement around the source. This greatly affects the plasma physics and chemistry, and thus the layer quality and deposition rate.

While the MW sources are excellent for deposition of intrinsic silicon, they are not suitable for doped layer deposition, since parasitic deposition of conductive layers on the quartz tube will decrease the microwave power that can be coupled into the plasma. For that reason, we had to resort to another plasma source for the growth of n-type Si and p-type Si. The linear RF source that has been implemented in the Flexicoat300 has been developed by Roth&Rau AG and consists of two aluminium rods which are symmetrically connected to the 13.56 MHz RF generator, with a maximum power of 600 W [3]. In contrast to conventional asymmetric RF sources, here the substrate does not form part of the RF network and therefore does not need to be grounded. The absence of the need for grounded substrates is a significant advantage in roll-to-roll processing.

The ion energy distribution of the symmetric RF source leads to "soft" deposition conditions on the surface of the substrate. With this RF source, device quality n-type a-Si:P and μc-Si:P have been deposited at economically feasible deposition rates of 0.2-0.4 Å/s [4].

We use a wide range of characterization techniques to determine the optoelectronic quality of the deposited silicon layers, and most of them are extensively described in previous papers [4]. Raman spectra have been obtained with a Renishaw inVia Raman Microscope, using laser excitation wavelengths of 514 and 633 nm.

UV-reflection spectra are measured with a DH-2000 Deuterium Halogen light source from Top Sensor Systems, which provides a deuterium and a tungsten halogen light source in a single optical path with a stable wavelength range of 210 – 1700 nm. The light is guided through Oceanic Optics XSR optical fibers to a 30 mm Mikropack integrating sphere, which has a reflectivity of 98 % in the visible and infrared region and 95 % in the UV region. For detection of the reflected UV light an Avantes AvaSpec 2048 spectrometer, with a wavelength range of 200 – 1100 nm, is used. All measured spectra are scaled to a 99%-reflectance sample, however, the reflectivity of this sample in the UV-region is somewhat lower and less accurately known.

RESULTS and DISCUSSION

Si layers

Both a-Si and μc-Si layers have been deposited with MW-PECVD. Systematic variation of the MW pulse parameters, i.e., the pulse width, repetition rate and peak power, showed that shorter times between the MW pulses lead to dense, low defect a-Si layers. For instance, in continuous MW mode, a-Si layers with refractive index n ~ 3.35 and a microstructure factor R* ~ 0.12 could be grown. The properties of these layers are summarised in Table I. For reference, device quality criteria, as stated by Schropp and Zeman [5], are given as well. The layers deposited with MW-PECVD are, almost, of device quality, only the absorption coefficient at 600 nm, $\alpha(600)$, is somewhat too low.

Table I. MW-PECVD Si material parameters compared with device quality criteria [5].

	Amorphous silicon		Microcrystalline silicon	
	MW-PECVD	Device quality	MW-PECVD	Device quality
n (@0.5 eV)	3.35	-	3.0	~3.4
R*	0.12	<0.10	-	-
E_{urb} [meV]	57	<60	72	<60
$\alpha(600)$ [cm^{-1}]	1.8×10^4	$\geq3.5\times10^4$	-	-
σ_d [S/cm]	2.8×10^{-11}	$<10^{-10}$	4.2×10^{-8}	$<1.5\times10^{-7}$
E_{act} [eV]	0.88	~0.8	0.53	0.53-0.57
σ_{ph}/σ_d	1.5×10^6	$>10^5$	89	>100

Table I also gives the data for microcrystalline Si. Although the electrical properties are nearly of device quality, the optical parameters still need some improvement before these μc-Si layers can be incorporated in high efficiency μc-Si solar cells.

Figure 2 shows the absorption curve for a device quality intrinsic a-Si layer, by combining regular reflection/transmission measurements and FTPS experiments [6]. Note that the absorption values cover over 7 orders of magnitude. The defect density in the band tail states

is quantified by the Urbach tail energy E_{urb}. E_{urb} can be found by calculating the inverse slope below the band gap at ~1.80 eV as indicated in the graph.
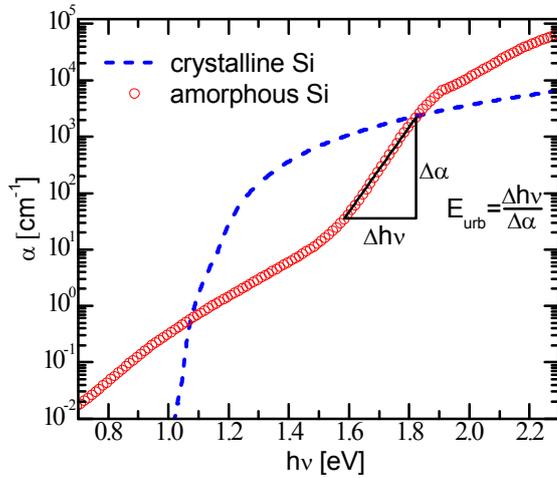

Figure 2. Absorption α as a function of the energy hν for a device quality thin film a-Si sample. For reference, the absorption coefficient for single crystalline Si with E_g = 1.12 eV is shown.

Raman and UV-reflection

Figure 3a shows typical UV-reflection spectra of a c-Si wafer, an intrinsic a-Si sample and a μc-Si sample. The c-Si spectrum shows, respectively at 281 nm and 365 nm, the X_4-X_1 and $\Gamma_{25'}$-Γ_{15} optical interband transitions [7]. The first of these transitions is also clearly visible in the microcrystalline sample (solid line in Figure 3b), but the second is very hard to identify. As expected, the a-Si spectrum (dashed line in Figure 3b) does not show these optical transitions.
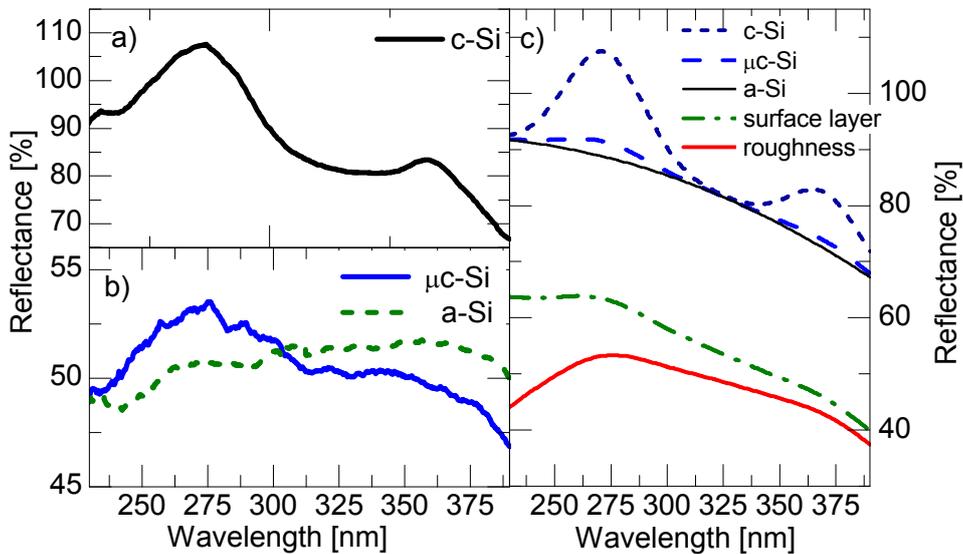
Figure 3. UV reflection data of different Si surfaces, scaled to the reflectance of a 99%-reflectance reference sample, with a lower reflectance in the UV. a) c-Si UV-reflectance spectrum. b) Smoothed UV-reflectance spectra for μc-Si (blue line) and a-Si (green dashes). c) Modelled effect of decreasing crystallinity, surface contamination and surface roughness on the UV-spectra. See text for an elaborate explanation of the model.

       The UV-reflection spectra of thin Si films are not only influenced by the crystalline fraction, but also by the surface roughness and the presence of contamination of the surface or a *foreign* surface layer, like SiO_x [1]. Roughness of the surface leads to a wavelength-dependent decrease of the reflection, whereas surface layer or contamination will decrease the reflection uniformly. A decrease in crystallinity is reflected by a reduction of the height of the two peaks. This is shown schematically in Figure 3b. The topmost curve is a numerical fit to the UV-reflection spectrum of c-Si. The next-lower curve takes the decrease in crystallinity into account for a typical μc-Si sample. For reference, the solid, black line shows the same curve for a completely amorphous sample. Next, the decrease as a result of a surface layer is added for the μc-Si curve. And finally, the Rayleigh-like scattering effect of surface roughness is included. Of course, using the reference c-Si sample and a measured UV-spectrum of a μc-Si or a-Si layer, we can calculate three parameters that quantify the three mentioned effects.

       Using the above described model by Harbeke and Jastrzebski [1], we extracted a UV crystallinity parameter for a range of a-Si and μc-Si layers, deposited with MW-PECVD as shown in Figure 4a. There is a clear linear relationship between the UV crystallinity parameter and the Raman crystalline volume fraction. UV-reflection spectroscopy can thus be used to monitor the crystallinity during continuous, roll-to-roll fabrication of Si layers.
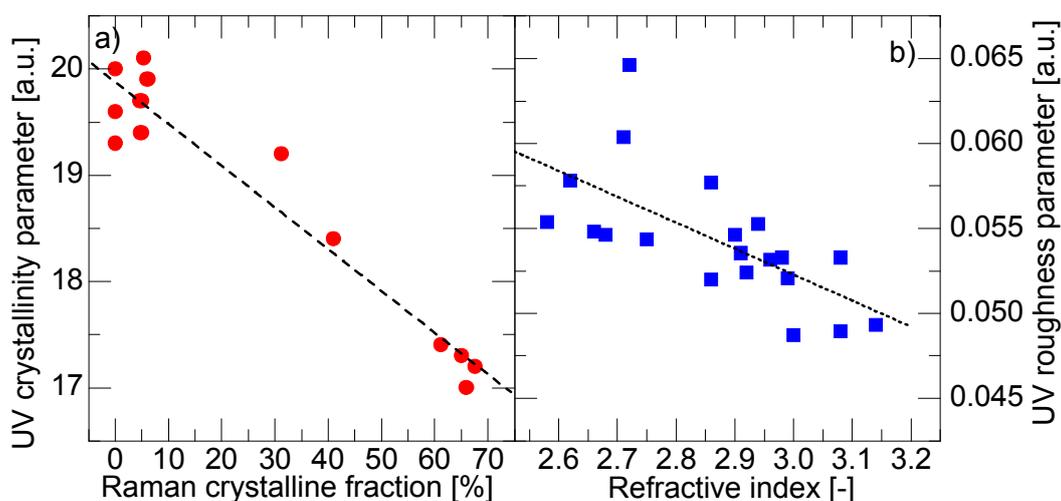
Figure 4. Fit parameters obtained from UV-reflection data. a) UV crystallinity parameter as a function of Raman crystalline volume fraction. b) UV roughness parameter as a function of the refractive index @ 0.5 eV for μc-Si samples with Raman crystal fraction of ~50-60%. Dotted and dashed lines are linear fits of the data, to guide the eye.

For a range of μc-Si samples with crystalline volume fractions of 50-60%, determined by Raman spectroscopy, the refractive index has been determined from FTIR spectra. Low refractive index is indicative of porous layer growth. We plotted the UV roughness parameter as a function of the refractive index. With decreasing refractive index, i.e. increasing porosity, the UV roughness parameter increases. This agrees with the expectation that porous, microcrystalline layers will also have rough surfaces.

CONCLUSIONS

To conclude: we developed, in collaboration with Roth&Rau AG, a roll-to-roll PECVD system, the FLEXICOAT300, for the continuous deposition of silicon n-i-p layers. Intrinsic layers with sufficient quality for solar cells can be grown with MW-PECVD. We will extend the research to the fabrication of nip and pin thin film Si solar cells on steel substrates by roll-to-roll processing. To facilitate continuous roll-to-roll production of Si layers, UV-reflection spectroscopy is an easy, fast and robust tool to control the crystallinity and quality of those layers.

ACKNOWLEDGMENTS

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