Hot Wire CVD for thin film triple junction cells and for ultrafast deposition of the SiN passivation layer on polycrystalline Si solar cells

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Abstract

We present recent progress on hot-wire deposited thin film solar cells and applications of silicon nitride. The cell efficiency reached for μc-Si:H n–i–p solar cells on textured Ag/ZnO presently is 8.5%, in line with the state-of-the-art level for μc-Si:H n–i–p's for *any* method of deposition. Such cells, used in triple junction cells together with hot-wire deposited proto-Si:H and plasma-deposited SiGe:H, have reached 10.5% efficiency. The single junction μc-Si:H n–i–p cell is entirely stable under prolonged light soaking. The triple junction cell, including protocrystalline i-layers, is within 3% stable, due to the limited thicknesses of the two top cells. The application of SiN_x:H at a deposition rate of 3 nm/s to polycrystalline Si wafer solar cells has led to cells with 15.7% efficiency. We have also achieved record high deposition rates of 7.3 nm/s for transparent and dense SiN_x:H. Hot-wire SiN_x:H is likely to be the first large commercial application of the Hot Wire CVD (Cat-CVD) technology.
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1. Introduction

The technology of Hot Wire Chemical Vapor Deposition or Catalytic CVD has made great progress during the last couple of years. Novel materials have been obtained with controlled properties and there is increasing evidence that large area continuous coating is feasible. This review discusses a number of examples of significant progress at our laboratory in the light of other achievements worldwide. Specifically, recent p–i–n and n–i–p solar cells are highlighted, as well as the application of silicon nitride (SiN_x:H) to polycrystalline solar cells.

The area of hot-wire deposited SiN_x:H has shown great progress and this material is likely to be the first to be commercially applied. Silicon nitride is used in many applications. The proceedings of this conference alone show the successful use of HW-SiN_x as encapsulation barrier against H_2O and O_2 (even on top of sensitive organic layers), as passivating dielectric in AlGaN/GaN high mobility FETs, as a mechanically strong material for microelectromechanical structures (MEMS), as a gate dielectric in TFTs, and as a passivating antireflective layer on polycrystalline solar cells.

2. Thin film a-Si:H p–i–n solar cells

Our 'standard' protocrystalline Si:H is deposited by HWCVD at a substrate temperature T_{sub} of 250 °C. We use Ta filaments at a temperature of 1850 °C, pure SiH_4 feed gas and a process pressure of 0.02 mbar, resulting in a deposition rate of 1 nm/s [1]. A fingerprint of the protocrystalline nature of this material is the narrow width of the first sharp peak in X-ray diffraction (XRD) [2]. For p–i–n type solar cells with a thickness of 300 nm, deposited on Asahi U-type SnO_2:F-coated glass, under AM1.5 light-soaking conditions a light-induced decrease in fill factor (FF) of less than 10% has been observed [3]. We incorporated 200-nm thick HW-deposited protocrystalline cells in top-cell limited micromorph tandem cells in order to study their stability against light-induced degradation. The results reflect the potential of top-cell limited multibandgap thin film silicon micromorph tandem cells, which is important for high-yield outdoor application (as expressed in kWh/kWp yr) [4]. In many

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Table 1
Performance of a 200 nm/1000 nm HWCVD proto-Si/HWCVD μc-Si:H superstrate p–i–n/p–i–n tandem cell on texture-etched ZnO (made at IPV Jülich) before and after light soaking

Thicknesses 200/1000 nm	V_{oc} (V)	J_{sc} (mA/cm2)	FF	η (%)
Initial	1.39	10.0	0.61	8.5
Stable (500 h)	1.39	10.1	0.60	8.5

Table 2
Present status of single junction HWCVD μc-Si:H n–i–p solar cells at various laboratories

Laboratory [ref]	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Utrecht [present work]	0.545	23.39	0.668	8.52
Jülich [8]	0.542	19.9	0.69	7.5
Kaiserslautern [9]	0.522	21.6	0.66	7.3
Ecole Polytechnique [10]	0.42	20.7	0.59	5.1
Gifu [11]	0.550	11.32	0.56	3.49
Unisolar [12] (non HWCVD)	0.568	23.59	0.671	8.99

regions of the world, a positive correlation between operation temperature and light intensity exists, which is advantageous for the daily and annual energy yield of the top cell, but adverse for that of the bottom cell. This is due to differences in the temperature coefficients for the performance of the top and bottom cell. Therefore, top cell limited micromorph tandem cells will provide more energy per annum than bottom cell limited tandem cells [5], but this imposes stringent stability requirements on the top cell. Table 1 shows the performance and stability of a top-cell limited p–i–n/p–i–n micromorph tandem cell on glass with texture-etched ZnO received from IPV Jülich. Both i-layers have been deposited by HWCVD. Between the short-circuit current densities generated by the two stacked cells a deliberate mismatch exists of 2.6 mA/cm^2. It is seen that this cell is perfectly stable even though the current-limiting amorphous Si cell dominates its fill factor (FF). The high stability is due to the protocrystalline nature of the active layer in the top cell.

By increasing the filament temperature, we investigated by how much the deposition rate r_d for a-Si:H could be further increased in order to take advantage of the high deposition rate capability of HWCVD. Special precautions were taken to protect the Asahi SnO$_2$:F coated substrates onto which the cells were deposited [1]. While the cells deposited at 1 nm/s reached an initial efficiency of 8.9% (0.88 V, 14.2 mA/cm^2, FF=0.71), we achieved 8.5% at an r_d of 1.6 nm/s, 8.1% efficiency at an r_d of 2.1 nm/s, and at an r_d of 3.2 nm/s still a high efficiency of 7.5% was obtained. The i-layer deposition time under the last conditions is only 3–4 min. Up to an r_d of 2.2 nm/s the cells
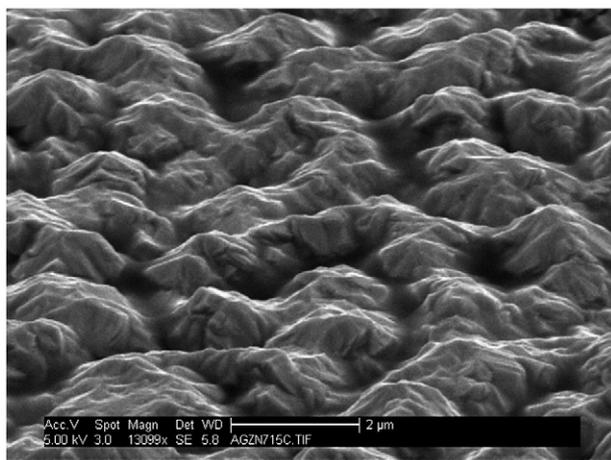
behave quite stable: for cells with i-layers thinner than 300 nm (as in tandem cells) the degradation in FF is less than 10%.

3. Thin film μc-Si:H n–i–p cells and triple cells

To enhance the efficiency in the n–i–p configuration, we developed textured Ag/ZnO back reflector layers on stainless steel substrates, using rf magnetron sputtering. An example of the surface morphology as observed with Scanning Electron Microscopy (SEM) is shown in Fig. 1. The μc-Si:H i-layer is deposited at 270 °C by HWCVD. We use Ta filaments at a temperature of 1850 °C, a SiH$_4$/H$_2$ gas mixture at a flow ratio of 5/100, and a pressure of 0.05 mbar, resulting in a deposition rate of 0.21 nm/s. The Raman ratio of crystallinity for this material is 40% and the crystallites have 10–20 nm sizes [6]. Further, we optimized the μc-Si:H n-type doped layer and the n/i interface, and in addition we used H$_2$/SiH$_4$ ratio profiling during i-layer deposition [7]. Table 2 shows the present results in comparison with other data obtained on single junction μc-Si:H n–i–p type cells on various substrates [8–12]. In our case, mainly due to the textured back reflector on stainless steel, the short-circuit current J_{sc} went up from the value of 15.2 mA/cm^2 obtained on plain stainless steel to 23.4 mA/cm^2 on textured Ag/ZnO. The spectral response curve is shown in Fig. 2. For comparison, Table 2 includes the latest best results obtained at United Solar Ovonic, LLC, for this type of cell as obtained using their 'modified VHF' technique. We believe that the obtained efficiency of 8.5% is a record value for hot-wire deposited μc-Si:H

Fig. 1. The SEM morphology of an rf magnetron sputtered Ag/ZnO textured back reflector.
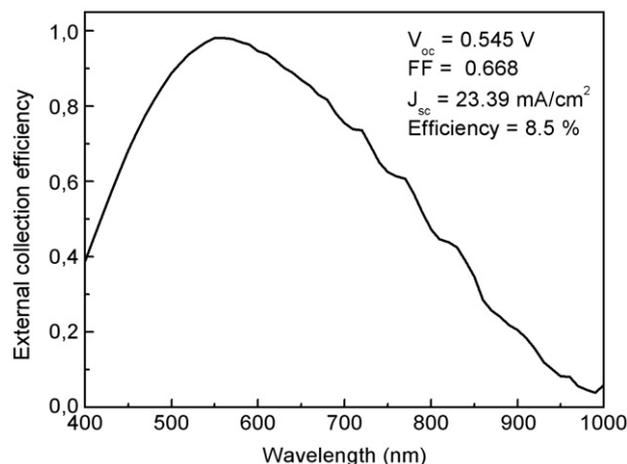

Fig. 2. Spectral response at 0 V of a 2-μm thick μc-Si:H nip solar cell on textured Ag/ZnO. The AM1.5 cell parameters of the cell are listed.

Table 3
Performance of HWCVD proto-Si/proto-SiGe/ HWCVD μc-Si:H triple n–i–p/ n–i–p/n–i–p cells on textured Ag/ZnO made in house and on substrates provided by Unisolar

Triple junction	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Utrecht substrate	2.030	7.84	0.657	10.45
Unisolar substrate	2.113	7.42	0.670	10.50

n–i–p cells. Moreover, when this cell is exposed to continuous illumination at 100 mW/cm^2 with near-AM1.5 spectrum at a temperature of 50 °C, the cell shows to be totally stable (relative efficiency loss $\Delta\eta < 0.6\%$ after 500 h of light soaking).

The results on single junction μc-Si:H cells have been utilized in triple junction n–i–p type cells. Previously, we have been optimizing triple junction cells of the type proto-Si/μc-Si:H/μc-Si:H, comprising active i-layers that were all deposited by HWCVD. In order to obtain sufficient current, however, this design leads to the use of very thick absorber layers, even when enhanced scattered back reflection is applied. For instance, if the top cell is 165 nm in order to generate ~8 mA/cm^2, the middle cell and the bottom cell have to be made as thick as ~2.4 μm and ~3.7 μm, respectively. The total thickness of over 6 μm of μc-Si:H material is very large compared to the micromorph tandem concept. If the μc-Si:H middle cell is replaced by a proto-SiGe:H cell, then not only the middle cell can be made an order of magnitude thinner, but also the bottom μc-Si:H cell can be made considerably thinner, since the SiGe:H middle cell does not absorb within exactly the same spectral region. A second important advantage is that a higher V_{oc} of the triple cell can be obtained, because SiGe:H has a higher band gap than μc-Si:H. Thirdly, in principle the achievable conversion efficiency is higher, because all three band gaps are different and less photon energy is lost as heat. For the moment however, we use PECVD for the deposition of the middle cell, since it was readily available in our lab. The SiGe:H middle cell can very well be made by HWCVD, as is demonstrated by the good single junction cell results obtained by NREL [13].

We obtained 10.45% efficiency for a proto-Si/ proto-SiGe/ μc-Si:H triple junction cell on a textured Ag/ZnO coated stainless steel substrate made in house. This compares very well with the 10.50% obtained on a United Solar Ovonic substrate in the same run. Table 3 shows the comparison between the cell results obtained on the two substrates. As can be seen from the J_{sc} versus FF trade off, the roughness of our homemade back reflectors is better optimized for J_{sc}. Fig. 3 gives the spectral response data of the cell made on our in-house Ag/ZnO coated substrate. It is worth noting that the three silicon cells stacked on top of each other are together less than 2.5 μm thick.

This cell appears stable. Preliminary light soaking tests show that the relative degradation under 100 mW/cm^2 near-AM1.5 illumination at 50 °C is less than 3%.

4. Passivating and antireflective HW-SiN$_x$:H

We studied HW-deposited SiN$_x$ as the top layer on cast polycrystalline silicon solar cells where it acts as antireflection coating (ARC) and simultaneously induces bulk and surface
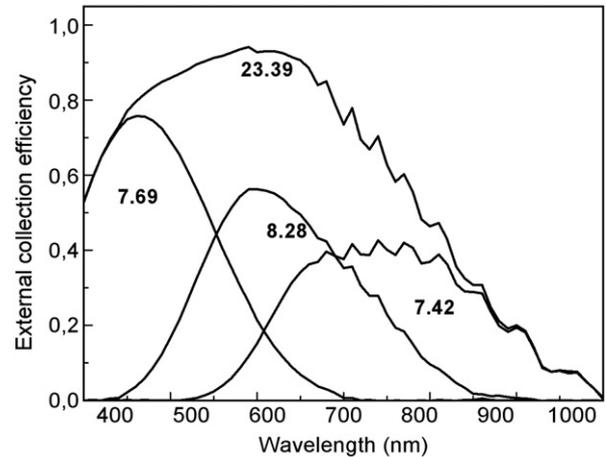

Fig. 3. Spectral response of a proto-Si:H/proto-SiGe:H/μc-Si:H triple junction solar cell on a textured Ag/ZnO back reflector.

passivation. The SiN$_x$:H coatings are able to act as good ARCs because of their high and tunable refractive index in combination with a low extinction coefficient [14]. During a short high-temperature anneal ('firing' at ~800 °C), hydrogen is released from the SiN$_x$:H layer and a part of it diffuses into the bulk of the polycrystalline Si wafer. Atomic H passivates the defects at grain boundaries enabling a significant enhancement of the cell performance.

Several series of cells with different HW-SiN$_x$ compositions were deposited on textured polycrystalline Si solar cells from ECN Solar Energy. The reference cells, made with microwave PECVD SiN$_x$, reached an average open circuit voltage V_{oc} of 606 mV. For the cells with HW-SiN$_x$, a maximum V_{oc} of 604 mV is reached for N/Si values between 1.25 and 1.31. The maximum J_{sc} is found at N/Si = 1.31. As a result the $V_{oc}*J_{sc}$ product, which is a good indicator of the cell quality, is optimal for the layers around a N/Si ratio of 1.31.

Apart from the obtained high V_{oc} values, the internal quantum efficiency (IQE) measurements also illustrate good passivation properties for the cells with HW-SiN$_x$. In Fig. 4, the
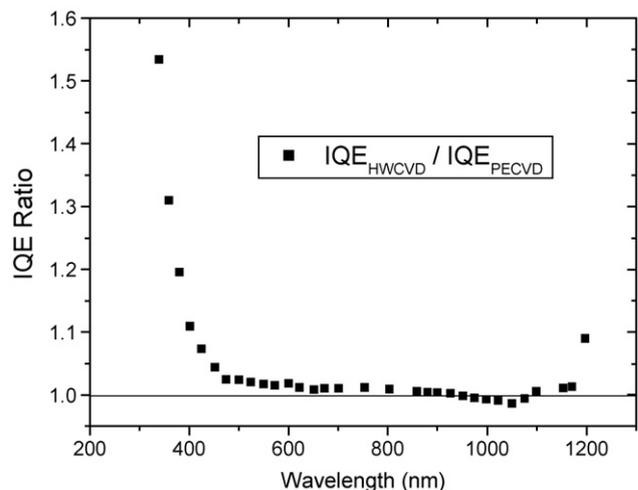

Fig. 4. The IQE ratio (HWCVD SiN$_x$/microwave PECVD SiN$_x$) for the experiments with the ECN cells.

IQE of the HW deposited SiN$_x$ is plotted relative to the IQE of reference cells. The IQE values are identical in the infrared region, proving good bulk passivation. Interestingly, at wavelengths smaller than 600 nm the IQE of cells with a HW coating appears to be better. The superior blue response may originate either from the absence of substrate damage as caused by ion bombardment during PECVD, resulting in better surface passivation by the HW-SiN$_x$ layers, or it may be due to the very low extinction coefficient of the latter layers in the blue region of the spectrum.

The best cell reached a high efficiency of 15.7% whereas the best reference cell was at 16.1% efficiency. The 15.7% efficiency is a major improvement with respect to the value of 14.3% reported by us two years ago [15] and even more so with respect to the earlier data reported by Holt et al. [16] who applied HW SiN$_x$ on String Ribbon substrates and achieved an efficiency of 12.4%. The difference with the reference cells is found mainly in the FF. There still is room for improvement, since HW deposited SiN$_x$ has a higher than usual mass density [17] (ρ=2.93 g/cm^3) and may therefore necessitate slightly different cell processing parameters, such as the firing conditions. Further, the homogeneity of the layers could play a role, since most cells are 6.5×6.5 cm^2, whereas the homogeneous zone in the presently available small HW reactor is only 5×5 cm^2. The design of specific equipment would thus improve the results. To our knowledge, never have hot-wire deposited SiN$_x$:H layers achieved such a high performance as passivating antireflective coating.

Application of this high density, high deposition rate SiN$_x$ as a dielectric layer is under study. For instance, Q. Wang et al. [18] have studied the HWCVD silicon nitride process because of the possible application of SiN$_x$ as barrier layers. The presently obtained density of 2.93 g/cm^3 is even higher than that of silicon nitride prepared by high-temperature CVD with dichlorosilane at 760 °C [19] and higher than any plasma method. The low stress of +50 MPa (tensile) in the layers made at 3 nm/s, much lower than most PECVD deposited SiN$_x$ samples, will be helpful, for instance, in plastic electronics. The electronic properties that we determined for this material are a fixed charge density $\sim 10^{16}$ cm^{-3}, an interface state density of $\sim 10^{10}$ cm^{-2}, as determined from the small hysteresis between the positive and negative sweep direction in the C–V measurement, a breakdown field of 2.5 MV/cm (thickness 300 nm) and the etch rate in a 16BFH etch solution of 5 parts of 40% NH$_4$F with 1 part 49.5% HF is 8 nm/min, much better than that for PECVD layers made at a significantly lower deposition rate [20]. The electrical breakdown field is expected to improve when more N-rich layers or thinner layers are used.

Next, we also investigated hot-wire deposition of SiN$_x$ at ultra high deposition rates of >7 nm/s. In order to increase the deposition rate while keeping a constant N/Si ratio in the film, it is necessary to improve the ammonia decomposition rate while increasing the silane flow. This is done by using a high filament temperature (2300 °C) and by increasing the deposition pressure. This leads to sufficiently high nitrogen incorporation.

Despite this high deposition rate, the SiN$_x$ layers still possess a relatively high mass density of 2.6 g/cm^3 and good thermal stability. This silicon nitride deposited at high deposition rate shows good potential for application as the dielectric layer in various applications.

Acknowledgments

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