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# Ultrafast deposition of silicon nitride and semiconductor silicon thin films by Hot Wire Chemical Vapor Deposition

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## ABSTRACT

The technology of Hot Wire Chemical Vapor Deposition (HWCVD) or Catalytic Chemical Vapor Deposition (Cat-CVD) has made great progress during the last couple of years. This review discusses examples of significant progress. Specifically, silicon nitride deposition by HWCVD (HW-SiN<sub>x</sub>) is highlighted, as well as thin film silicon single junction and multijunction junction solar cells. The application of HW-SiN<sub>x</sub> at a deposition rate of 3 nm/s to polycrystalline Si wafer solar cells has led to cells with 15.7% efficiency and preliminary tests of our transparent and dense material obtained at record high deposition rates of 7.3 nm/s yielded 14.9% efficiency. We also present recent progress on Hot-Wire deposited thin film solar cells. The cell efficiency reached for (nanocrystalline) nc-Si:H n-i-p solar cells on textured Ag/ZnO presently is 8.6%. Such cells, used in triple junction cells together with Hot-Wire deposited proto-Si:H and plasma-deposited SiGe:H, have reached 10.9% efficiency. Further, in our research on utilizing the HWCVD technology for roll-to-roll production of flexible thin film solar cells we recently achieved experimental laboratory scale tandem modules with HWCVD active layers with initial efficiencies of 7.4% at an aperture area of 25 cm<sup>2</sup>.

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## 1. Introduction

High deposition rates are required to reduce production costs of large area applications (e.g., displays and solar cells) in mass fabrication. The common approach in the development of plasma sources is to aim for high ionization rates and high gas utilization. Fundamentally, high electron energy is required to fragment molecules while the probability of occurrence is low, since point collisions are required in a 3D space. Hot Wire Chemical Vapor Deposition (HWCVD) is fundamentally different since molecules are cracked on a 2D catalyst material. Because source gases are catalytically decomposed, the method is often referred to as Thermo-Catalytic Chemical Vapor Deposition or Catalytic Chemical Vapor Deposition (Cat-CVD). A schematic view of a HWCVD reactor is given in Fig. 1. The technology of HWCVD has made great progress during the last couple of years. The quality of thin film materials can be accurately controlled and there is an increasing number of examples showing that large area continuous coating is feasible.

Thin film silicon nitride is a Hot-Wire deposited material that is likely to be commercially applied. Many applications are possible: Hot-Wire deposited silicon nitride (HW-SiN<sub>x</sub>) has been demonstrated as encapsulation barrier against H<sub>2</sub>O and O<sub>2</sub> (even on top of sensitive organic layers), as passivating dielectric in AlGaIn/GaN high mobility field effect transistors, as a mechanically strong material for micro-electromechanical structures (MEMS), as the gate dielectric in thin

film transistors (TFTs), and as a passivating antireflective layer on polycrystalline solar cells.

In this paper we show recent progress on the application of SiN<sub>x</sub>:H on multicrystalline solar cells, the results on Hot-Wire deposited thin film n-i-p type solar cells on stainless steel substrates, and results of our research on utilizing the HWCVD technology for the roll-to-roll production of flexible thin film solar cells.

## 2. Applications

### 2.1. Silicon nitride by Hot Wire CVD

Hot Wire CVD has some important advantages over techniques that utilize a plasma for decomposition of the source gasses, such as Plasma Enhanced Chemical Vapor Deposition (PECVD). The first requirement for obtaining high deposition rate is to obtain a high decomposition rate for the source gasses. The common approach in the development of plasma sources is to aim for high ionization rates and high gas utilization. Fundamentally, high electron energy is required to fragment molecules while the probability of occurrence is low, since point collisions are required in a 3D space. Hot Wire CVD is fundamentally different since molecules are cracked on a 2D catalyst material, which makes it far more probable for each source gas molecule to be decomposed.

Taking into account the thermal velocity of the gases and a rather low value for the operational pressure of 0.01 mbar, it can be calculated that the collision rate at a fixed surface per unit area is  $2\text{--}3 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ . A typical heated filament has a total surface of 50 cm<sup>2</sup>, so the number of

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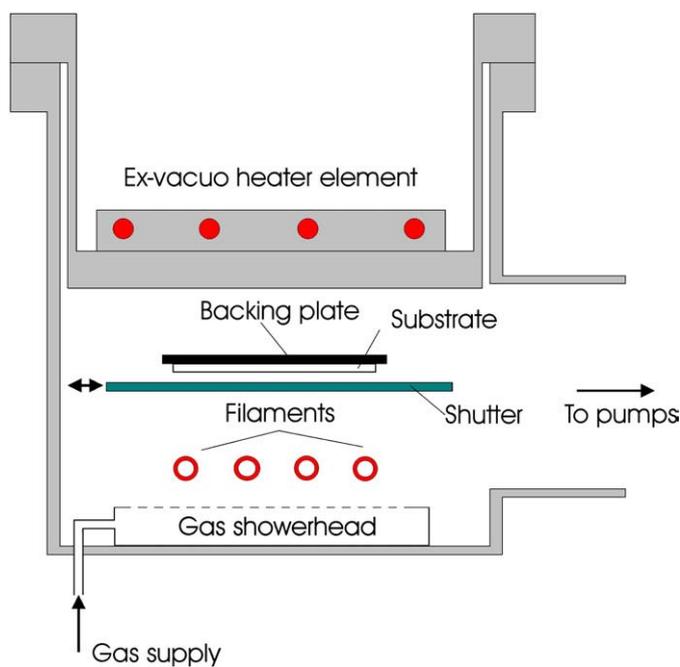


Fig. 1. Schematic drawing of the experimental HWCVD reactor.

collisions on the filament is  $>10^{20} \text{ s}^{-1}$ . Taking into account a residence time of the gas of  $\sim 1 \text{ s}$ , which means that  $10^{19}$  molecules are replaced per second, the result is that each molecule hits the filament at least 10 times. The decomposition probability for  $\text{SiH}_4$  in a collision with the filament is 40% [1] and therefore the overall decomposition probability of all  $\text{SiH}_4$  molecules is  $>1-(0.6)^{10}$  which is nearly unity. In practice, taking into account that also the reaction products can be pumped out, the total gas utilization efficiency for a-Si:H deposition from  $\text{SiH}_4$  is  $\sim 80\%$  [2], which is  $\sim 5$  times larger than in PECVD.

For a  $\text{SiH}_4/\text{NH}_3$  mixture at relatively low total flow rate, utilization rates of 98% and 52% for  $\text{SiH}_4$  and  $\text{NH}_3$  are obtained, respectively [3]. At a high deposition rate (3.0 nm/s) we have obtained a  $\text{SiH}_4$  utilization rate of  $>70\%$ . Good gas utilization and high deposition rate are highly desirable from a cost perspective point of view. The efficient catalytic decomposition of feedstock gases has led to ultrahigh deposition rates of up to 7.3 nm/s for device quality, transparent films [4]. The application of HW-SiN<sub>x</sub> at a deposition rate of 3 nm/s to polycrystalline Si wafer solar cells has led to cells with 15.7% efficiency in collaboration with the Energy research Center of the Netherlands (ECN) [5]. Table 1 lists the solar cell results. The 7.3 nm/s material has recently been tested as passivating layer on polycrystalline silicon cells in collaboration with Centrotherm Photovoltaics Technology GmbH, Germany. Table 2 lists these cells results. It should be noted that the cell results from Tables 1 and 2 cannot be directly compared because in each table widely different fabrication processes have been used for cell manufacturing. A possible reason for the difference in performance of cells using HW-SiN<sub>x</sub> versus that of cells using PECVD-SiN<sub>x</sub> is the fact that the firing process was not specifically optimized for the HW-SiN<sub>x</sub> (having higher mass density). An optimized time-temperature profile may lead to better performance of cells using HW-SiN<sub>x</sub>. Another possible reason is that the HW-SiN<sub>x</sub> layers were deposited in a small laboratory reactor due to which the homogeneity was not optimal. A third possible reason for the slightly lower performance with HW-SiN<sub>x</sub> layers might be that the finished solar

Table 1  
Solar cell parameters for ECN polycrystalline Si cells with high-rate HWCVD SiN<sub>x</sub>:H

Method for SiN <sub>x</sub> :H deposition	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Eff. (%)
HWCVD 3 nm/s (Utrecht University)	604	34.6	0.750	15.7
Microwave PECVD (ECN)	606	34.3	0.774	16.1

Table 2  
Solar cell parameters for Centrotherm polycrystalline Si cells with ultra-high rate HWCVD SiN<sub>x</sub>:H

Method for SiN <sub>x</sub> :H deposition	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Eff. (%)
HWCVD 7.3 nm/s (Utrecht University)	610	33.25	0.735	14.9
PECVD (Centrotherm)	608	33.74	0.765	15.7

cells had to be transported with the emitter exposed before they received the HW-SiN<sub>x</sub> layer and that they had to be transported back to receive the grid contact. Especially during the first transport (by mail) the surface might have picked up some contamination. Given these circumstances, it is remarkable that the high rate HW-SiN<sub>x</sub> layers performed so well.

Second, the technique is free of dust formation, is free from ion-bombardment issues and can easily be scaled up to offer large area capability [6]. The low H concentration of 9 at.%, specifically the low density of Si-H bonds [7], is an advantage for the use as sidewall and liner material in ultra large scale integration p-type metal-oxide-semiconductor transistors. We have applied HW-SiN<sub>x</sub> as the gate dielectric in TFTs [8].

Third, a-SiN<sub>x</sub> films deposited with conventional methods like PECVD tend to have high stress values in the range of 100–1000 MPa [9]. Passivating layers for organic light emitting diodes for example, require very low stress in the order of 10 MPa [10,11], in addition to low deposition temperatures. Low stress in thin films is also important in MEMS applications and plastic electronics.

## 2.2. Active solar cell layers by Hot Wire CVD

During the last few decades, the deposition parameter regime in plasmas has been explored intensively in order to improve materials and increase the deposition rate, specifically for nanocrystalline silicon (nc-Si:H), because this material is the bottleneck for high-throughput tandem and triple cell fabrication due to its low deposition rate. The favored formation of nanocrystallites occurs under plasma conditions close to the transition regime [12]. In this regime, which is characterized by high pressure, high power, and low substrate temperature, secondary reactions are promoted. Unfortunately, this regime is close to that where unwanted powder formation occurs.

The HWCVD technique has been shown to be a viable method for the deposition of silicon-based thin films and solar cells [13–15]. It can be considered to be a remote technique, as the substrate itself has no active role in generating the active precursors, unlike the case of PECVD where it usually has at least a role as the grounded electrode. The absence of the requirement to achieve an equipotential plane at the substrate makes it easier to transport either rigid or foil type substrates during deposition and to scale up to large areas. Needless to say, the morphology and the atomic structure of the substrate surface still influence the film formation. Also the substrate temperature is still of importance. Therefore, when scaling up the substrate size and/or transporting the substrate during deposition, the substrate temperature should be kept homogeneous and at the desired value.

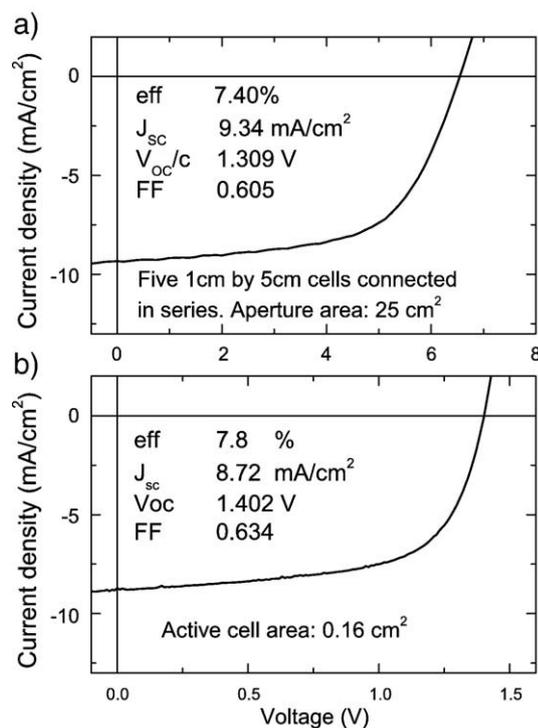
We have developed HWCVD intrinsic protocrystalline silicon (proto-Si:H), which is characterized by an enhanced medium range structural order and a higher stability against light-soaking [16] compared to amorphous silicon, and nanocrystalline silicon (nc-Si:H), which is characterized by a low density of states [17] at a Raman crystalline ratio of  $\sim 40\%$ . These materials were applied in high efficiency thin film solar cells on stainless steel [18,19]. The cell efficiency reached for (nanocrystalline) nc-Si:H n-i-p solar cells on textured Ag/ZnO presently is 8.6%, in line with the state-of-the-art level for such cells 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 10.9% efficiency. The single junction nc-Si:H n-i-p cell is entirely stable under prolonged light soaking. The triple junction cell, including protocrystalline i-layers, is

within  $\Delta\eta/\eta=3.5\%$  stable. It is worth noting that the three silicon cells stacked on top of each other are together only approximately  $2.5\ \mu\text{m}$  thick, which is of economical importance.

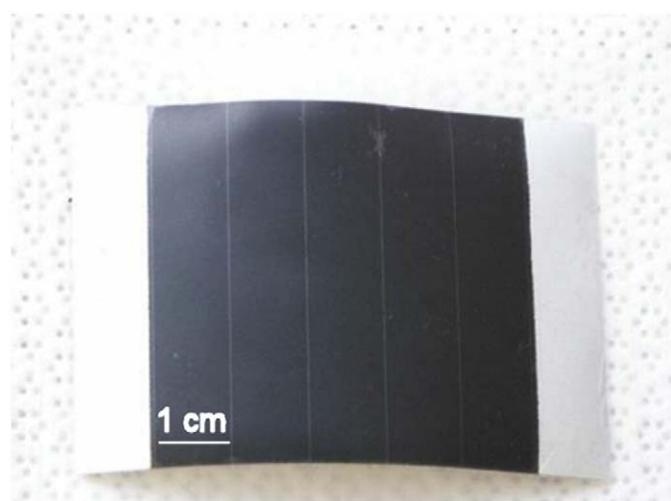
### 2.3. Hot Wire CVD for flexible solar cells

In co-operation with Nuon/Helianthos b.v., we are currently developing thin film silicon based solar cells with hot-wire deposited absorber layers using the Helianthos cell transfer process [20]. The unique feature of this process is that the solar cell is fabricated via the so-called temporary superstrate approach, in which aluminum foil is used as a temporary carrier. This allows the use of optimal processing temperatures during the atmospheric pressure chemical vapor deposition process of  $\text{SnO}_2:\text{F}$  and the CVD process for thin film – amorphous and nanocrystalline – silicon layers. The temporary superstrate is removed in a later stage of the process, and its carrier function is taken over by a commodity plastic foil. In this keynote paper we report the results of a series-connected a-Si:H/nc-Si:H tandem solar cell mini-module ( $\eta=7.40\%$ , aperture area  $25.0\ \text{cm}^2$ ) developed on plastic foil where both intrinsic layers are made with HWCVD.

The solar cells have an a-Si:H/nc-Si:H tandem p-i-n structure, namely, temporary Al substrate/ $\text{SnO}_2:\text{F}/\text{a-Si:H}$  p-i-n top cell/nc-Si:H p-i-n bottom cell/back contact. In the cell transfer process [20], the silicon stacks are transferred to a plastic foil substrate, resulting in a structure allowing light to enter through the p-type side of the top cell. All the Si layers were deposited in an ultrahigh vacuum multi-chamber system at the Utrecht Solar Energy Laboratory. Doped layers, p-type nc-Si:H and n-type a-Si:H, were deposited by conventional  $13.56\ \text{MHz}$  radio frequency PECVD; intrinsic a-Si:H (proto-Si:H [18]) and nc-Si:H layers [21] by Hot-Wire CVD. Two tantalum wires were used for the hot-wire reactions; a constant current of  $10.5\ \text{A}$  was used, yielding a filament temperature of  $\sim 1850\ ^\circ\text{C}$  in vacuum, as determined by a pyrometer. The aperture area of the solar cells was determined by the outer perimeter of the series-connected array of cells and amounts



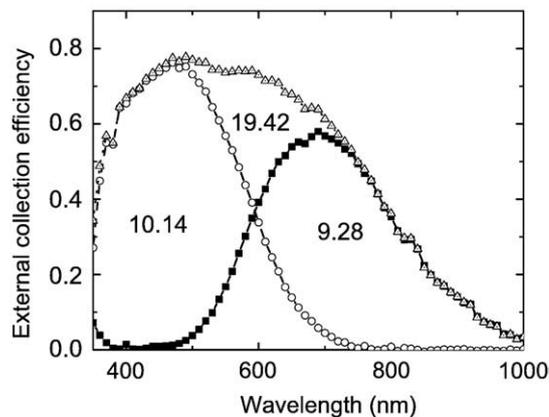
**Fig. 2.** a/b: The AM1.5 J-V characteristics of: (a) a  $25\ \text{cm}^2$  solar module (five  $1\ \text{cm}$  by  $5\ \text{cm}$  cells connected in series) fabricated with the Helianthos procedure on a plastic substrate,  $V_{oc}/c$  means  $V_{oc}/\text{cell}$  and was calculated from the module  $V_{oc}$  divided by the cell number (5); (b) a reference cell deposited identically to the cell shown in (a) using an Asahi-U TCO glass substrate.



**Fig. 3.** A picture of the minimodule of a HWCVD tandem cell. The dimensions of the aperture area is  $5\ \text{cm} \times 5\ \text{cm}$  (five  $1\ \text{cm}$  by  $5\ \text{cm}$  cells connected in series).

to  $25.0 (\pm 0.5\%) \text{ cm}^2$ . For each solar cell deposition, a reference cell was made using Asahi U-type transparent conductive oxide (TCO) coated glass substrates [22]. AM1.5 J-V characteristics were obtained using a dual beam solar simulator ( $100\ \text{mW}/\text{cm}^2$ ) while the cells were kept at a constant temperature of  $\sim 25\ ^\circ\text{C}$ . The external collection efficiency (ECE) of the reference solar cells was determined by a spectral response setup with the possibility of applying bias light and bias voltage.

The AM1.5 J-V characteristics of one of the a-Si:H/nc-Si:H tandem mini-modules are shown in Fig. 2a. The data were obtained after lamination of the cell with plastic foil. A picture of this sample is shown in Fig. 3. Fig. 2b shows the J-V curve of a reference cell using Asahi U-type TCO-glass substrate deposited under identical conditions. Since the reference cell is deposited on glass, it is not laminated. From Fig. 2 one can see that although the cell area of the flexible mini-module is much larger than that of the reference cell, their efficiencies are quite similar. Needless to say, in tandem cells the efficiency is greatly dependent on the degree of current matching, which is different for the cells on foil and on glass. The reference cell shows a high open circuit voltage ( $V_{oc}$ ) for an a-Si:H/nc-Si:H tandem ( $V_{oc}=1.40\ \text{V}$ ). Probably due to the strong mismatch that is present, the fill factor (FF) of the reference cell (FF=0.634) is rather low, hence, there is room for further optimization. The lower FF and  $V_{oc}$  of the flexible mini-module are typically observed for cells with larger area. One interesting observation in Fig. 2 is that the flexible mini-module shows a slightly higher  $J_{sc}$  than the reference cell. This can be attributed to: i) better current matching on the Helianthos TCO foil



**Fig. 4.** External collection efficiency (ECE) of a mini-module.

compared to that on the Asahi glass substrate, ii) the different scattering ability of the TCO layers, combined with a modified scattering effect of incident light due to the lamination material of the flexible mini-module, iii) a possible difference in the structure of the silicon layers grown on these two substrates, which also contributes to (some of) the difference in  $V_{oc}$ . Fig. 4 shows the ECE of the 25 cm<sup>2</sup> mini-module. One can see that the cell is bottom-cell limited, which is a result of a rather thin bottom cell i-layer, estimated to have a thickness of around 1.5  $\mu\text{m}$ .

To be able to implement Hot-Wire CVD into a complete roll to roll process, research is in progress on several issues, such as deposition rate, controllability, repeatability, and filament life. Regarding the latter issue, for 0.5-mm thin Ta wires, as used for silicon depositions, a lifetime of many months has been reported for applications in a laboratory environment [23]. A lifetime of thousands of hours of intensive use can be reached by a proper design of the filament mounting system, gas distribution system and a well-defined deposition/treatment process. In a production process, the filament replacement task can be combined with routine cleaning steps. The filament life time can be well predicted thanks to the clearly defined and constant deposition conditions normally used for mass production.

### 3. Conclusion

In conclusion, we have been able to show that hot-wire deposition of high density SiN<sub>x</sub>:H is possible at very high deposition rates in excess of >7 nm/s and that these nitrides are highly effective as the passivating layer for multicrystalline (polycrystalline) Si solar cells. The cell efficiency reached for Hot-Wire deposited (nanocrystalline) nc-Si:H n-i-p solar cells on textured Ag/ZnO presently is 8.6%. Such cells, used in triple junction cells together with Hot-Wire deposited proto-Si:H and plasma-deposited SiGe:H, have reached 10.9% efficiency. An a-Si:H/nc-Si:H p-i-n tandem solar cell mini-module containing absorber layers made with HWCVD using the Helianthos transfer process has resulted in an AM1.5 initial aperture area efficiency of 7.4%, very similar to that of reference cells deposited on Asahi U-type TCO-coated glass substrates ( $\eta=7.8\%$ ). Not earlier has a monolithically series-connected minimodule been reported that comprises a tandem cell that is hot-wire deposited. The identical deposition parameter settings used for producing these samples further confirm the independency of the HWCVD process on the

substrate electromagnetic properties and its suitability for application in the photovoltaic industry.

### Acknowledgments

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### References

- [1] N. Honda, A. Masuda, H. Matsumura, *J. Non-Cryst. Solids* 266–269 (2000) 100.
- [2] B.P. Nelson, Y. Xu, A.H. Mahan, D.L. Williamson, R.S. Crandall, *Mater. Res. Soc. Symp. Proc.* 609 (2000) A22.8.1.
- [3] S.G. Ansari, H. Umemoto, T. Morimoto, K. Yoneyama, A. Izumi, A. Masuda, H. Matsumura, *Thin Solid Films* 501 (2006) 31.
- [4] V. Verlaan, Z.S. Houweling, C.H.M. van der Werf, H.D. Goldbach, R.E.I. Schropp, *MRS Proc.* 910 (2006) A3.3.
- [5] V. Verlaan, C.H.M. van der Werf, Z.S. Houweling, H.F.W. Dekkers, I.G. Romijn, A.W. Weeber, H.D. Goldbach, R.E.I. Schropp, *Prog. Photovolt.: Res. Appl.* 15 (2007) 563.
- [6] R.E.I. Schropp, *Jpn. J. Appl. Phys.* 45 (2006) 4309.
- [7] V. Verlaan, C.H.M. van der Werf, W.M. Arnoldbik, H.D. Goldbach, R.E.I. Schropp, *Phys. Rev. B* 73 (2006) 195333.
- [8] R.E.I. Schropp, S. Nishizaki, Z.S. Houweling, V. Verlaan, C.H.M. van der Werf, H. Matsumura, *Solid State Electron.* 52 (2008) 427.
- [9] W.A.P. Claassen, W.G.J.M. Valkenburg, W.M. v.d. Wijgert, M.F.C. Willemsen, *Thin Solid Films* 129 (1985) 239.
- [10] A. Masuda, M. Totsuka, T. Oku, R. Hattori, H. Matsumura, *Vacuum* 74 (2004) 525.
- [11] M. Takano, T. Niki, A. Heya, T. Osono, Y. Yonezawa, T. Minamikawa, S. Muroi, S. Minami, A. Masuda, H. Umemoto, H. Matsumura, *Jpn. J. Appl. Phys.* 44 (6A) (2005) 4098.
- [12] O. Vetterl, F. Finger, R. Carius, P. Hapke, L. Houben, O. Kluth, A. Lambertz, A. Mück, B. Rech, H. Wagner, *Sol. Energy Mater. Sol. Cells* 62 (2000) 97.
- [13] H. Matsumura, *J. Appl. Phys.* 65 (1989) 4396.
- [14] A.H. Mahan, J. Carapella, B.P. Nelson, R.S. Crandall, I. Balberg, *J. Appl. Phys.* 69 (1991) 6728.
- [15] K.F. Feenstra, R.E.I. Schropp, W.F. van der Weg, *J. Appl. Phys.* 85 (1999) 6843.
- [16] R.E.I. Schropp, M.K. van Veen, C.H.M. van der Werf, D.L. Williamson, A.H. Mahan, *Proc. 19th European Photovoltaic Solar Energy Conf., Paris (France), 2004*, p. 1526.
- [17] J.J.H. Strengers, F.A. Rubinelli, J.K. Rath, R.E.I. Schropp, *Thin Solid Films* 501 (2006) 291.
- [18] M.K. van Veen, R.E.I. Schropp, *Appl. Phys. Lett.* 82 (2003) 287.
- [19] R.L. Stolk, H. Li, R.H. Franken, J.J.H. Strengers, C.H.M. van der Werf, J.K. Rath, R.E.I. Schropp, *J. Non-Cryst. Solids* 352 (2006) 1933.
- [20] E.A.G. Hamers, M.N. van den Donker, B. Stannowski, R. Schlattmann, G.J. Jongerden, *Plasma Process. Polym.* 4 (2007) 275.
- [21] R.L. Stolk, H. Li, C.H.M. van der Werf, R.E.I. Schropp, *Thin Solid Films* 501 (2006) 256.
- [22] R.H. Franken, H. Yu, Y. Liu, R.L. Stolk, C.H.M. van der Werf, J.K. Rath, R.E.I. Schropp, *Proc. 20th European Photovoltaic Solar Energy Conf., Barcelona (Spain), 2005*, p. 1588.
- [23] D. Knoesen, C. Arendse, S. Halindintwali, T. Muller, *Thin Solid Films* 516 (2008) 822.