

# Growth mechanism of nanocrystalline silicon at the phase transition and its application in thin film solar cells

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## ABSTRACT

Nanocrystalline (or microcrystalline) silicon (nc-Si:H or  $\mu\text{c-Si:H}$ ) is an absorber material that is crucial for obtaining thin film silicon tandem solar cells with high efficiency. This material is conventionally produced by direct plasma-enhanced chemical vapor deposition (PECVD), which is based on the dissociation of silane ( $\text{SiH}_4$ ) and hydrogen ( $\text{H}_2$ ) in a radiofrequency (rf) plasma. During the last few decades, the plasma deposition parameter regime has been explored intensively, in particular to improve the quality of nc-Si:H and to increase its deposition rate. The desired formation of nanocrystallites occurs under growth conditions close to the transition regime.

A technique that is not plasma based is hot-wire CVD (HWCVD), which is based on catalytic decomposition of  $\text{SiH}_4$  and dissociation of  $\text{H}_2$  gases on a hot filament. Because source gases are catalytically decomposed, the method is often referred to as catalytic CVD (Cat-CVD). The HWCVD technique has been shown to be a viable method for the deposition of silicon-based thin films and solar cells. We discuss the progress at our laboratory. Specifically, recent single junction and multijunction n-i-p-type solar cells are highlighted. Improvements have been achieved by addressing, among others, the morphology of the light-scattering rough surfaces, to avoid cavities and shunting paths, and by studying the structural evolution of the nanocrystalline phase during growth. The obtained solar cells are highly stable against light soaking.

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## 1. Introduction

In order to stabilize the  $\text{CO}_2$  emission at a reasonable level, estimates are that we need to install at least a 14 TW renewable energy generation capacity by the year 2050 [1]. It has been argued that among the various renewable energy options, only solar energy offers sufficient resources to cover this demand [2]. Given the large scale needed, the solar cell technologies that need to be developed should use earth-abundant and preferably non-toxic materials. Among the various options available, wafer-based silicon solar cells are presently dominating the market. Even though Si is the second most abundant material in the Earth's upper continental crust, high purification that is needed and the indirect optical absorption of these wafer-based solar cells make it an expensive source material. Therefore, further price reduction has to come from the use of thin films as well as from the implementation of nanostructured surfaces and materials.

We have investigated multibandgap proto-Si/proto-SiGe/nc-Si:H triple junction n-i-p solar cells, in which the first two cells

contain thin film silicon-based absorber layers with enhanced medium range order and a band gap of 1.8 and 1.5 eV, respectively, and the bottom cell contains nanocrystalline silicon (or microcrystalline) silicon (nc-Si:H or  $\mu\text{c-Si:H}$ ) with a band gap of 1.1 eV. The latter material contains 10–20-nm-sized nanocrystals, together taking up ~40–50% of the volume.

Nanocrystalline silicon is an absorber material that is crucial for obtaining thin film silicon tandem solar cells with a higher efficiency. This material is conventionally produced by direct plasma-enhanced chemical vapor deposition (PECVD), which is based on the dissociation of silane ( $\text{SiH}_4$ ) and hydrogen ( $\text{H}_2$ ) in a radiofrequency (rf) plasma. During the last few decades, the plasma deposition parameter regime has been explored intensively [3] in particular to improve the quality of nc-Si:H and to increase its deposition rate. The desired formation of nanocrystallites occurs under growth conditions close to the transition regime. The high growth rate parameter space of this regime, which is characterized by high pressure, high rf power, and low substrate temperature, promotes secondary gas phase reactions. Unfortunately, this regime is close to that where unwanted powder formation occurs.

In this paper, we present the use of hot-wire CVD (HWCVD) to fabricate the absorber layers in the top and bottom cell. HWCVD

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has been proven to be able to prepare high-quality intrinsic hydrogenated amorphous silicon (a-Si:H) [4–6], proto-crystalline silicon (proto-Si:H) [7], nanocrystalline silicon (nc-Si:H) (also called microcrystalline silicon  $\mu$ c-Si:H) [8,9], polycrystalline silicon (poly-Si:H) [10] (also called high-crystallinity  $\mu$ c-Si:H), and amorphous silicon germanium (a-SiGe:H) [11] materials that are suitable for use as the active layers in silicon-based thin film solar cells. Compared to conventional PECVD, the process of HWCVD is independent of electromagnetic properties of the substrate. The technique has the potential of high deposition rate; there is less dust formation and scaling up for mass production is straightforward.

At Utrecht University, we have been concentrating on developing thin film silicon-based multijunction solar cells employing active layers made with HWCVD [8,12,13]. The entire cell is deposited on a rough surface of a ZnO/Ag double layer that is deposited on a stainless-steel carrier foil. The effect of the morphology of the internal Si/ZnO/Ag interfaces on the structural integrity of the n-i-p solar cell has been studied. It is found that it is important to achieve control of this morphology, especially when the first-deposited cell is a nanocrystalline cell. Moreover, we stress the requirement of maintaining a constant crystalline volume fraction during the growth evolution of the nc-Si layer.

## 2. Experimental details

All the solar cells discussed in this paper have an n-i-p structure. The structure of the triple junction solar cell is substrate (stainless steel)/rough Ag/ZnO/nc-Si:H n-i-p bottom cell/proto-SiGe:H n-i-p middle cell/proto-Si:H n-i-p top cell/ITO/Au grid. The silicon layers were deposited in a multi-chamber ultra-high vacuum system called PASTA [14]. Doped layers (boron- and phosphorus-doped nc-Si:H) and intrinsic proto-SiGe:H [15] were prepared using 13.56 MHz PECVD, whereas HWCVD was applied to fabricate intrinsic proto-Si:H [7] and nc-Si:H [8,12,13,16]. Two straight Ta filaments were used for the hot-wire deposition, through which a current of 10.5 A was passed, yielding a wire temperature of approximately 1850 °C in vacuum as measured by a pyrometer. Stainless-steel foils coated with texture-grown highly reflecting Ag layers were used as the substrate. A single Ag target was used in an argon/oxygen ambient during sputtering. The ZnO and ITO layers were deposited by magnetron sputtering at room temperature, using ZnO:Al (1%) and  $\text{In}_2\text{O}_3/\text{Sn}_2\text{O}_3$  (10%) as the target material, respectively, with a typical thickness of  $\sim 100$  nm for the ZnO:Al and  $\sim 80$  nm for the ITO. Detailed deposition conditions for the Ag/ZnO back reflectors can be found in one of our earlier publications [17]. All the AM1.5  $J$ - $V$  data were obtained with an illumination mask in order to have a precise definition of the cell area. The illumination mask is the same as that used for the deposition of ITO top contact. Due to the finite thickness of the mask and the accompanying shadowing effect, the measured  $J_{sc}$  values may be slightly underestimated.

## 3. Results and discussion

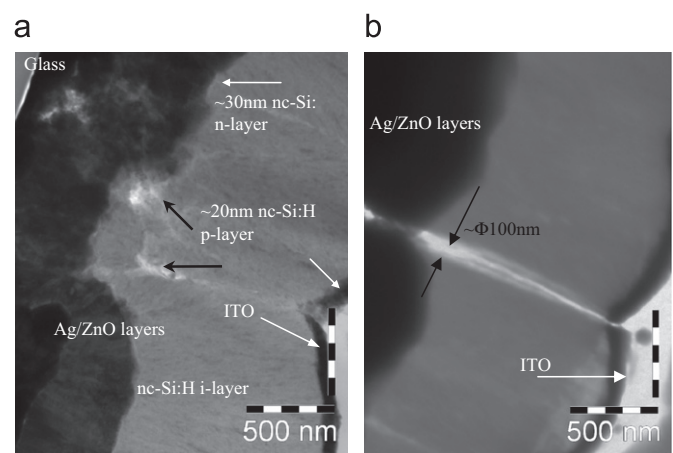
### 3.1. Low-bandgap nc-Si:H as bottom cells in multijunction solar cells

The roughness and the morphology at the back electrode/silicon interface are of importance for efficient light trapping in n-i-p-type thin film silicon solar cells. The texture of the Ag surface is obtained by magnetron sputtering at elevated substrate temperatures. Larger crystals are obtained—and thus increasing roughness—as the substrate temperature during sputtering is increased.

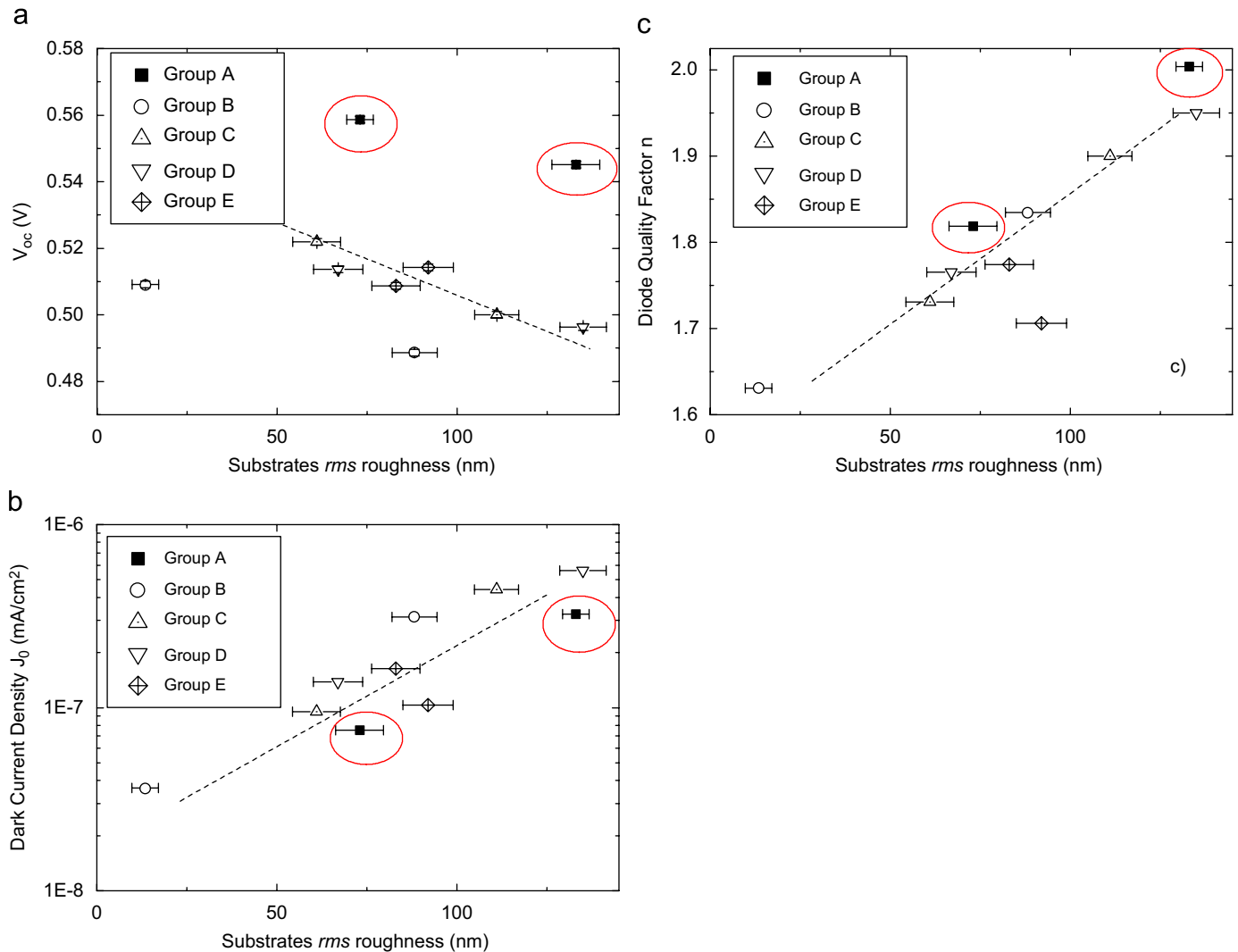
We deposited nc-Si:H n-i-p cells on surfaces with different surface morphologies and different degrees of roughness. The surface rms roughness varied from 13 to 135 nm, as determined from  $10\mu\text{m} \times 10\mu\text{m}$  atomic force micrographs. The silicon structure becomes more defective when deposited on the more rough substrates. Fig. 1 shows the typical structural defects observed from the cross-sectional TEM images of a nc-Si:H n-i-p solar cell deposited on one of the roughest Ag/ZnO surfaces. It can clearly be seen that structural defects are formed in the silicon layers near the edges of micro-valleys of the substrate surface. Structural defects of this kind may create shunting paths that largely deteriorate the cell performance [18]. In addition, electronic defects may be created in the bulk of the i-layers, reducing the solar cell fill factor and  $V_{oc}$ .

At higher substrate temperatures during Ag sputtering, the surface shows large crystal facets with steep angles, leading to canyon-like valleys and sharp V-shaped valleys. The sputtering conditions for the  $\sim 100$  nm thick ZnO cover layer on top of Ag were kept constant and it was shown that the ZnO layer with this relatively small thickness did not introduce significant alteration of the Ag surface morphology [19]. As the nanocrystalline Si growth evolves anisotropically (almost perpendicular to the local surfaces), the shadowing effect of the large grains leads to cavities during growth of the nc-Si:H, while in the V-shaped valleys long void-rich regions are formed that are large enough to form short-circuiting pinholes or cracks. For optimum yield, while still taking benefit from the internal light trapping effect, we use as an empirical guideline that the opening angles at the textured surface should be larger than  $110^\circ$  [20].

Fig. 2a shows the dependence of the AM1.5 open circuit voltage ( $V_{oc}$ ) on the substrate rms roughness. While the n-i-p layers of these samples (except group A) were made under identical conditions, a clearly decreasing  $V_{oc}$  is observed with increasing rms (group B through D are different morphology types). The encircled data points in this figure indicate samples of group A, having a clearly enhanced value for  $V_{oc}$ . These samples were made with a profiled n-layer using a two-step deposition process: the first part consists of standard n-type a-Si:H with a thickness of about 5 nm, and the second part is an n-type nc-Si:H layer, about 27 nm thick. Fig. 2b and c give the values of the reverse saturation current density  $J_0$  and the diode quality factor  $n$  deduced from the dark  $J$ - $V$  curves. Both parameters are clearly increasing as a function of the rms roughness, while samples in group A show somewhat lower  $J_0$  and higher  $n$  values than the other samples at



**Fig. 1.** Cross-sectional TEM pictures of a nc-Si:H n-i-p solar cell deposited on a rough Ag/ZnO coating. A Corning glass substrate is used instead of stainless steel to facilitate preparation of the cross section of the sample for TEM. The dark arrows point to the cavities, which appear not to be completely filled with silicon.

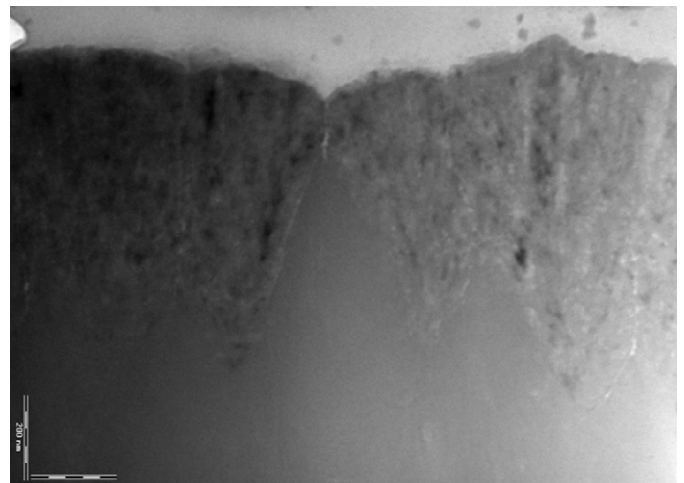


**Fig. 2.** Correlations of the open circuit voltage  $V_{oc}$ , the dark saturation current  $J_0$ , and the diode quality factor  $n$  with the substrate surface roughness rms value for cells deposited on textured back contacts with various roughness. The encircled symbols are for cells made with a double n-layer. The lines are guides to the eyes.

a similar substrate rms roughness. The reason for this might be that an extra series resistance is built in due to the double n-layer. This increases the  $V_{oc}$  and improves the  $J_0$ , but it also usually increases the diode quality factor, in this case by approximately 0.05.

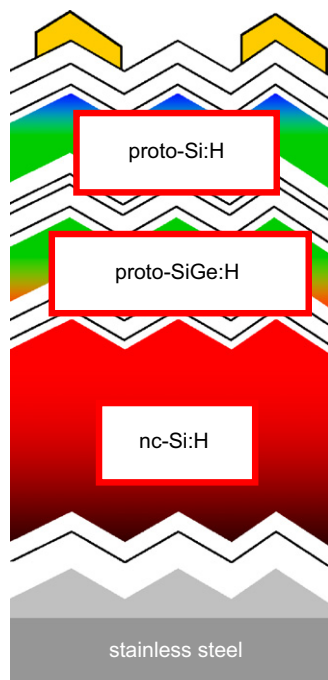
### 3.2. Reverse $H_2$ profiling in nc-Si:H bottom cells

One of the key factors in obtaining high-efficiency nc-Si:H cells is to achieve tight control of the crystallinity of the i-layer. It has been shown that the maximum cell efficiency is normally achieved when the intrinsic nc-Si:H is made near the phase transition between amorphous and microcrystalline structure [21], possibly due to the better passivation of grain boundary defects in such materials. Unlike the cells with nc-Si:H absorber layers made with PECVD (rf or VHF), for n-i-p cells with a nc-Si:H i-layer made with HWCVD, we showed that the crystallinity can decrease with increasing layer thickness, especially when depositing on a n-layer that is nanocrystalline while keeping the filament current constant during i-layer deposition [12,16].



**Fig. 3.** Transmission electron micrograph (TEM) of nanocrystalline growth on a 'non-seeding' amorphous silicon layer on Corning 1737 glass. The scale bar shown in the picture is 200 nm.

There are several possible reasons for the loss of crystallinity as the film thickens. One possible explanation is that there are gradual changes in the catalytic filament conditions during prolonged usage, which changes the reactivity of the decomposition reaction of the source gases. This effect, also called the ageing effect, can be caused by alloying of the filament with Si. This has also been observed by Stoke et al. [22]. Another explanation is that the initial nano-epitaxy that takes place on the first-deposited nc-Si:H n-type layer breaks down into the amorphous phase. This is a more likely origin of the loss of crystallinity. The opposite structural development, also strongly dependent on the substrate surface, is also seen when silicon films are deposited under nanocrystalline processing conditions on a ‘non-seeding’ amorphous silicon layer on a Corning 1737 glass substrate (Fig. 3). Due to the low density of nucleation centres in this case, the crystalline phase can grow in the growth direction as well as sideways, due to which nanocrystalline cones develop that eventually collide relatively far from the substrate.



**Fig. 4.** Schematic cross section of a triple junction thin film solar cell deposited onto a stainless-steel substrate with a textured back reflector. The different subcell absorber materials are nc-Si:H, proto-SiGe, and proto-Si (from bottom to top). On top of the silicon layers is an indium tin oxide/gold contact. The layers that remain unfilled (white) are doped layers, buffer layers, ITO, and ZnO layers.

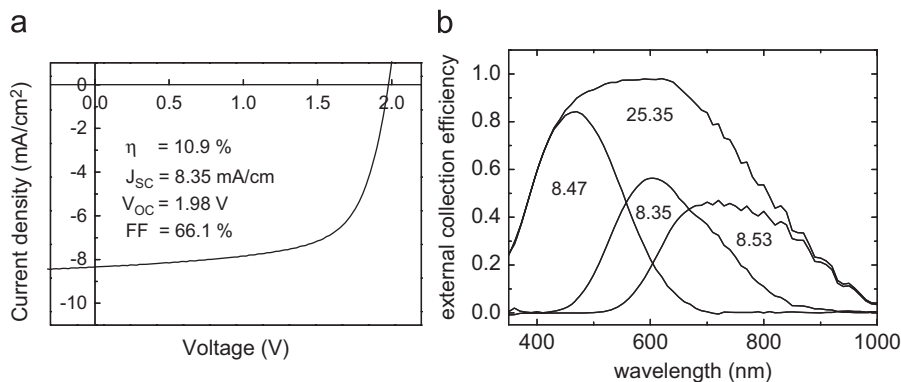
Although the dominating reason for this reverse development of nc-Si:H growth is not yet clear, the remedy is a technique in which the hydrogen dilution ratio is *increased* as the film thickens. The results for cells made on stainless-steel foil have shown an AM1.5 efficiency of 8.6%, which is close to the reported cell efficiency (9.0%) with the same cell structure and on the same type of substrate (SS/Ag/ZnO) but with the absorber layer made with (VHF) PECVD [23]. Since the cell structure and the substrate roughness for our samples are not optimal yet, we expect an increase of the efficiency after further optimization.

### 3.3. Multijunction n-i-p cells

The knowledge acquired in developing high-quality nc-Si:H single junction cells has also been used to develop thin triple junction solar cells ( $<2.5\ \mu\text{m}$ ) with a structure described in the introduction and shown in Fig. 4. The *J*-*V* and spectral response of the best cell obtained so far is shown in Fig. 5. Long-term continuous light soaking of these cells shows that these cells are very stable [24], with a relative efficiency degradation of only 3%. Compared to that published for cells with a similar structure but made with PECVD techniques [23], there is however still room for improvement of the efficiency. Higher initial efficiency could of course be obtained by using thicker active layers for all three cells. However, this is at the risk of reduced stability of the performance. One of the improvements is expected to come from optimization of the middle cell (which is still made with PECVD). At present the middle cell is a limiting factor for the triple cell performance [15].

## 4. Conclusion

We reviewed the main scientific challenges and achievements while developing triple junction solar cells on flexible stainless-steel substrates with amorphous Si and nanocrystalline Si active layers made with hot-wire-CVD. The result of our single junction nc-Si:H cells is very similar to the cells with the same structure on the same type of substrate but with the absorber layer made with (VHF) PECVD. We also developed very thin triple cells with 10.9% efficiency and stability within 3% relative. Both results are at present the best reported for cells with similar structure but with hot-wire-CVD-deposited silicon active layers. We conclude that hot-wire-deposited materials are very suitable for solar cells, and a significant step has been taken in developing this technique for utilization in industrial production.



**Fig. 5.** *J*-*V* (a) and external collection efficiency (b) of the best triple cell with hot-wire-deposited silicon active layers. The values shown in the ECE graph (b) are in  $\text{mA}/\text{cm}^2$ .

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