

Improvement of $\mu\text{c-Si:H}$ n–i–p cell efficiency with an i-layer made by hot-wire CVD by reverse H_2 -profiling

H. Li, R.H. Franken, R.L. Stolk, C.H.M. van der Werf, J.K. Rath, R.E.I. Schropp*

Utrecht University, Faculty of Science, SID-Physics of Devices, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

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Abstract

The technique of maintaining a proper crystalline ratio in microcrystalline silicon ($\mu\text{c-Si:H}$) layers along the thickness direction by decreasing the H_2 dilution ratio during deposition (H_2 profiling) was introduced by several laboratories while optimizing either n–i–p or p–i–n $\mu\text{c-Si:H}$ cells made by PECVD. With this technique a great increase in the energy conversion efficiency was obtained. Compared to the PECVD technique, the unique characteristics of HWCVD, such as the catalytic reactions, the absence of ion bombardment, the substrate heating by the filaments and filament aging effects, necessitate a different strategy for device optimization. We report in this paper the result of our method of using a *reverse* H_2 profiling technique, i.e. *increasing* the H_2 dilution ratio instead of decreasing it, to improve the performance of $\mu\text{c-Si:H}$ n–i–p cells with an i-layer made by HWCVD. The principle behind this technique is thought to be a compensation effect for the influence of progressing silicidation of the filaments during the growth of $\mu\text{c-Si:H}$, if the filament current is held constant during growth. The dependence of the material crystallinity on thickness with and without H_2 profiling is discussed and solar cell J – V parameters are presented. Thus far, the best efficiency of $\mu\text{c-Si:H}$ n–i–p cells made on a stainless steel substrate with an Ag/ZnO textured back reflector made in house has been improved to 8.5%, which is the highest known efficiency obtained for n–i–p cells with a hot-wire $\mu\text{c-Si:H}$ i-layer.

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1. Introduction

The application of solar cells with intrinsic hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) as the absorber layer (i-layer) has shown promise for further extending the spectral range of thin film silicon based solar cells. Compared to the conventional plasma enhanced chemical vapour deposition (PECVD) technique [1], hot-wire CVD (HWCVD) can produce device quality $\mu\text{c-Si:H}$ at a high rate without dust formation in the gas phase, therefore reducing the need of an extensive chamber cleaning process. At Utrecht University, we develop solar cells with an intrinsic $\mu\text{c-Si:H}$ i-layer made by HWCVD on stainless steel substrates with a n–i–p structure, aiming to use them as the bottom cell of a triple junction solar cell [2]. Previous cells deposited on plain stainless steel at a high substrate temperature (>400 °C) yielded a V_{oc} of only 0.41 V and a J_{sc} of 16.1 mA/cm^2 because of the very high crystallinity and the absence of a back reflector [3]. To quickly utilize our newly developed Ag/ZnO rough back reflector [4], the

decision was made to first optimize the bottom cell with a $\mu\text{c-Si:H}$ i-layer deposited at a reduced substrate temperature. In doing this, a careful review of the silicon growth mechanism was performed. Special techniques for the material optimization, such as the use of seed layers and defect density control by hydrogen profiling [5,6], were employed. This paper presents the result of $\mu\text{c-Si:H}$ n–i–p cells with an i-layer deposited with HWCVD by employing a *reverse* H_2 profiling technique.

2. Experimental details

All silicon layers were deposited in the multi-chamber UHV PASTA system [7]. The intrinsic layers were deposited by means of HWCVD, whereas for the doped layers in the cell PECVD at 13.56 MHz was used. The cell structure was: SS/rough Ag/ZnO/n-type $\mu\text{c-Si:H}$ /intrinsic $\mu\text{c-Si:H}$ /buffer/p-type $\mu\text{c-Si:H}$ /ITO/Au (gridlines), with an active cell area of 0.13 cm^2 . HWCVD was performed using two straight tantalum wires (0.5 mm in diameter) that were about 4 cm from the substrate, through which a constant current of 10.5 A was passed, yielding a wire temperature around 1850 °C as measured with a pyrometer in vacuum without source

* Corresponding author.

E-mail address: schropp@phys.uu.nl (R.E.I. Schropp).

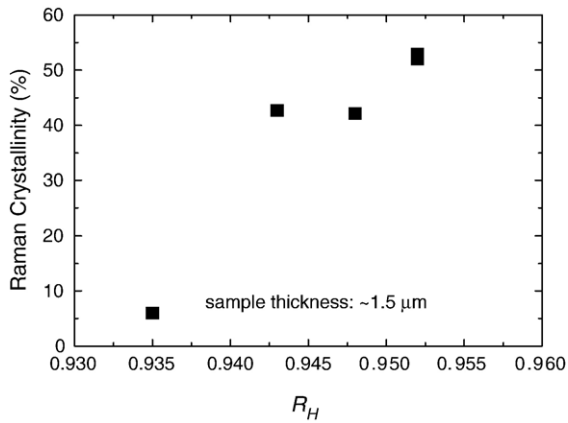


Fig. 1. Raman crystallinity of samples deposited on substrates with a textured back reflector (Asahi/Ag/ZnO/ $\mu\text{c-Si:H}$ n-layer) at different hydrogen dilution ratios R_H .

gas. No extra substrate heating was used, which results in a substrate temperature around 270 °C when the system is in an equilibrium condition. Raman spectroscopy at a laser wavelength of 514.5 nm was employed to measure the crystalline ratio of absorber layers and complete solar cells. The sample thickness for each silicon deposition was measured on accompanying glass substrates using a surface step profiler (Dektak). Average deposition rate for intrinsic $\mu\text{c-Si:H}$ layers was calculated accordingly and was typically around 2 Å/s. The current density–voltage (J – V) characteristics of the solar cells were measured at 25 °C under AM1.5 100 mW/cm² white light generated by a dual beam solar simulator (WACOM). A 0.3 mm thick SS mask used for depositing the ITO top contact was also used during the measurement to have a precise definition of the cell area.

3. Results

Various $\mu\text{c-Si:H}$ material samples have been made. Part of the data has been published earlier [8], from which a substrate dependence of sample crystallinity could clearly be seen. Based on these results, a series of material samples with different i-layer thickness and with a range of constant hydrogen dilution ratios ($R_H=0.935, 0.943, 0.948$, and 0.952 , where R_H is defined as the hydrogen fraction of the total gas flow, $\text{H}_2/(\text{H}_2 + \text{SiH}_4)$) were deposited on Asahi U-type TCO glass coated with Ag/ZnO and a thin n-layer, in order to simulate the situation of the surface when the i-layer is grown in a cell. Except for the difference in R_H , all other deposition conditions were kept the same. Raman spectroscopy showed that, except

Table 1
Raman crystallinity of $\mu\text{c-Si:H}$ samples made on top of Asahi/Ag/ZnO/n-type a-Si:H with different R_H

| Sample label | R_H | Total thickness (nm) | X_c (%) |
|--------------|--|----------------------|-----------|
| A | 0.952 | 500~1500 | 55±5 |
| B | 0.943 | 1420±50 | 43±5 |
| C | First 1 μm at 0.952 and then 0.5 μm at 0.943 | 1420±50 | 29±5 |

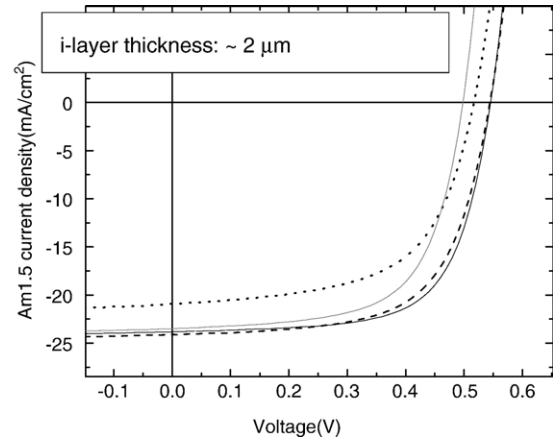


Fig. 2. AM1.5 J – V characteristics of $\mu\text{c-Si:H}$ n–i–p cells on SS with a Ag/ZnO TBR. (1) Grey line: constant H_2 dilution at $R_H=0.953$; (2) dotted line: constant H_2 dilution at $R_H=0.948$; (3) dashed line: two-step profiling, 1st half at $R_H=0.948$, 2nd half at $R_H=0.952$; (4) solid black line: with the same H_2 profile as (3), but with a cold start.

for samples deposited at $R_H=0.935$, all samples were microcrystalline (Fig. 1). The crystalline ratio X_c (defined as the integrated area ratio between the crystalline Si TO peak and the a-Si:H TO peak $(I_{520} + I_{510})/(I_{520} + I_{510} + I_{480})$) showed no sign of an increase with thickness for all the $\mu\text{c-Si:H}$ samples between thicknesses of 500 and 1500 nm. Some layers even showed a decrease in X_c . This was against our expectation, since it is widely observed that the crystallinity of $\mu\text{c-Si:H}$ material increases with thickness [9].

Moreover, we found, as shown in Table 1, for a 1500-nm thick sample grown with two hydrogen dilution steps (sample C), the first 1 μm at $R_H=0.952$ and the next 0.5 μm at $R_H=0.943$, that X_c showed much lower values than the samples grown with a constant $R_H=0.943$ (sample set B). These observations indicate that some other parameters influence the i-layer growth. Since the filaments used for growing sample C had been used longer before starting the deposition, we believe an aged filament state is responsible for the observed lower X_c for this sample. A good measure of the filament condition is the filament resistance. As reported earlier by Van Veen et al. [8] and by D. Grunsky et al. [10], the resistance of the filament increases after each deposition, for every filament used. This is attributed mainly to silicidation of the filament during the catalytic reaction. Its catalytic ability therefore decreases with time. This led us to design experiments in which the hydrogen

Table 2
AM1.5 output parameters of the $\mu\text{c-Si:H}$ n–i–p cells shown in Fig. 2

| Sample no. | Remarks | Efficiency [%] | J_{sc} [mA/cm ²] | V_{oc} [V] | FF |
|------------|---|----------------|--------------------------------|--------------|-------|
| 1 | Without H_2 profiling ($R_H=0.953$) | 7.5 | 23.5 | 0.498 | 0.641 |
| 2 | Without H_2 profiling ($R_H=0.948$) | 6.5 | 21.2 | 0.517 | 0.594 |
| 3 | With two-step H_2 profiling ($R_{H,1}=0.948, R_{H,2}=0.952$) | 8.4 | 24.2 | 0.544 | 0.636 |
| 4 | Two-step H_2 profiling+ cold start | 8.5 | 23.4 | 0.545 | 0.668 |

dilution ratio during i-layer deposition is *increased* instead of decreased, so it is changed in the *reverse* direction of that normally used by other groups when developing $\mu\text{c-Si:H}$ cells using the PECVD technique [5]. Fig. 2 shows the AM1.5 J - V characteristics of several $\mu\text{c-Si:H}$ n-i-p cells; the cell output parameters are listed in Table 2. “Cold start” means that the i-layer deposition was started somewhat before the point where the chamber reaches a thermal equilibrium condition. All cell parameters have improved dramatically by applying this ‘reverse profiling’. The cell efficiency has reached 8.5%, which is the highest value reported so far for a $\mu\text{c-Si:H}$ n-i-p cell with an HWCVD i-layer, and one that is in line with the best results reported for similar cells with VHF plasma-enhanced CVD i-layers [11].

4. Discussion

The decrease of X_c with the increase of layer thickness for $\mu\text{c-Si:H}$ materials deposited close to the phase transition from the amorphous to the microcrystalline regime was already observed in an earlier study by Van Veen et al. [12]. The difference between the present and the previous work is that we now used a slightly higher H_2 dilution ratio, i.e. the deposition starts at $R_{\text{H}}=0.948$ instead of 0.935 [12]. Our results are in disagreement with the widely accepted phase diagram concept of Collins et al. based on studies on samples prepared by PECVD [9], clearly indicating the uniqueness of the HWCVD technique in depositing $\mu\text{c-Si:H}$ material. Clear explanations for this phenomenon are not yet available, though filament aging is likely to play a key role. Further understanding requires a detailed knowledge of the reactions at the filament surface, as well as in the gas phase and on the growing sample surface.

Our results show that n-i-p cells with an i-layer made with $R_{\text{H}}=0.952$ and a thickness of about $\sim 2 \mu\text{m}$ do not suffer from a structure deviation (sample set A in Table 1) and, therefore, show a higher J_{sc} and a good FF (sample #1 in Fig. 2 and Table 2). The lower V_{oc} , $<0.5 \text{ V}$, is obviously related to the rather high X_c in the i-layer. A slight decrease in R_{H} (sample #2, $R_{\text{H}}=0.948$) promotes V_{oc} a bit, but at the cost of the FF due to the already started structural evolution in the i-layer. More seriously, carrier collection in the i-layer is negatively affected, which, together with the lower (infra)red absorption due to the lower X_c , results in a more than 2 mA/cm^2 decrease in J_{sc} . By using a two-step H_2 profiling (sample #3), the i-layer quality is maintained, and all cell parameters increase: the FF is back to ~ 0.64 , the V_{oc} jumps to 0.544 V , and the J_{sc} increases to more than 24 mA/cm^2 . The increase in V_{oc} can be attributed to the slight decrease in crystallinity compared to the cell with higher R_{H} and the increase in J_{sc} is because of the better collection for the photogenerated carriers. By using a cold start the cell efficiency further increases, mainly because of the increase in FF (sample #4).

The use of the “cold start” is based on the idea that properly lowering of the substrate temperature will increase the H residence time at the growing film surface, therefore resulting in a better defect passivation. The positive feedback from the experimental results hints that the defect density in the i-layer

might be further reduced if we use a reduced substrate temperature (T_{sub}) during the entire layer deposition. The T_{sub} used for this study, $\sim 270 \text{ }^\circ\text{C}$ in the equilibrium state, is quite high compared to that used by other groups [13]. This is due to the relatively small filament-to-substrate distance of $\sim 4 \text{ cm}$ we use. As a benefit, the i-layer deposition rate is nearly 2 times higher than that obtained by the Jülich group for their reported best $\mu\text{c-Si:H}$ cell with an HWCVD i-layer [13]. An increase in the filament-to-substrate distance will reduce the substrate temperature, but will also decrease the deposition rate. Other techniques, such as substrate cooling or use of moving substrates, are more favourable. The latter has a great advantage for mass production, especially in roll-to-roll technology. Here we note that the absence of strong electromagnetic fields in the hot-wire CVD technique makes the design of a vacuum chamber with a moving substrate much easier compared to that of a conventional PECVD chamber.

5. Conclusion

In this article, we presented our results on using a *reverse* H_2 profiling technique to improve the i-layer quality in single junction $\mu\text{c-Si:H}$ thin film solar cells with an i-layer made by hot-wire CVD. This design is based on our study of the structural evolution of HWCVD deposited $\mu\text{c-Si:H}$ in the phase transition region between a-Si:H and $\mu\text{c-Si:H}$. Cells with an i-layer grown with this technique showed a record efficiency of 8.5% for single junction n-i-p cells with an HWCVD $\mu\text{c-Si:H}$ i-layer. This new method allows the development of $\mu\text{c-Si:H}$ cells with higher efficiency at higher deposition rate.

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