HYDROGEN PASSIVATION OF POLYCRYSTALLINE SI THIN FILMS
BY PLASMA TREATMENT

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ABSTRACT: Hydrogen passivation can drastically improve the device performance of polycrystalline Si (poly-Si) thin film solar cells on glass. Due to limited process temperatures and the nature of poly-Si, the existence of grain boundaries and intra-grain defects still limits the device properties. To overcome this, a hydrogen plasma has been applied in order to passivate the defects and improve the thin-film solar cell performance. Large-grained poly-Si solar cells on glass have been prepared using electron beam (e-beam) evaporation. The effect of hydrogenation and temperature on solar cell performance has been investigated in the range of 400-620°C by exposing the samples to a hydrogen plasma. The open circuit voltage was improved significantly by hydrogen passivation and increased steadily with higher temperatures. As a promising result, the best cell had an open circuit voltage of 396 mV even without rapid thermal annealing and light trapping.
Keywords: Polycrystalline, Si-Films, Hydrogen Passivation

1 INTRODUCTION

Thin-film Si solar cells on foreign substrates are a candidate to reach high efficiencies at low costs [1]. Polycrystalline Si (poly-Si) hereby could combine high material quality with the advantages of thin-film technologies [2]. A promising approach is based on the seed layer concept [3, 4]. Thin poly-Si seed layers on glass are prepared by the Aluminium-Induced Layer Exchange (ALILE) process, that is based on aluminum-induced crystallization (AIC) of amorphous Si [5]. Large-grained poly-Si absorbers are realized with a subsequent low temperature epitaxy by electron-beam (e-beam) evaporation of Si at a temperature of 600°C [6, 7].

Due to the deposition by e-beam evaporation almost no hydrogen is incorporated in the absorber films. Still a lot of grain boundaries and intra-grain defects have been observed in the films[6]. An efficient passivation of defects cannot be achieved in-situ as in PE-CVD grown a-Si:H or μc-Si:H solar cells by the incorporation of hydrogen [8, 9]. Different post-deposition treatments must be carried out in order to improve the quality of the films. Common treatments involve rapid thermal annealing (RTA) at high temperatures [10], firing of a hydrogenated silicon-nitride [11] or the exposure of the sample to atomic hydrogen generated in a plasma [12].

Exposing poly-Si to atomic hydrogen can improve the electrical property of the material. Hydrogen diffuses in silicon and can passivate dangling bonds and grain boundaries [13]. Still the mechanism of hydrogen diffusion and passivation in poly-Si is quite complicated, depending on many parameters [14]. Hydrogenation leads not only to the passivation of defects but can also cause the formation of complexes and defects itself and passivate or compensate the doping of the film [15-18]. Therefore the hydrogenation process needs to be optimized in terms of process parameters like temperature, time, cooling phase and plasma parameters.

For commercially available poly-Si solar cells (CSG Solar) hydrogenation at around 610°C demonstrated its high potential by improving the efficiency by a factor of 4.6 to 8.1% [12]. Hydrogenation at high temperatures will be the object of investigation in this paper. An advantage is the higher hydrogen diffusion making short process times feasible for industrial applications.

2 EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

In addition to the large-grained poly-Si films, also fine-crystalline (fc-Si) samples have been prepared for comparison. Fig. 1 shows the sequence how the i) poly-Si and ii) fine-crystalline approaches were processed, respectively. In both cases Borofloat®33 glass serves as a substrate. For the poly-Si samples about 200 nm thin p^+-type poly-Si seed layers were prepared by the ALILE process [5]. The average grain size was around 7 μm [19]. With subsequent low temperature Si epitaxy by e-beam evaporation at 600°C, p-type absorbers were grown [7]. The thickness of the absorber was about 2 μm. For the fc-Si films the seed layer formation is omitted and the films (150 nm (p^+)/1650 nm (p)) were directly deposited at the same conditions onto the glass substrate. As was observed with scanning electron microscopy, this resulted in fine-crystalline lateral growth with a grain size of around 100 nm. The boron doping of the layers was 2×10^{19} cm^{-3} for (p^+) and $5\ldots10\times10^{16}$ cm^{-3} for (p), respectively. Defect passivation was realized by exposing the samples to a hydrogen plasma prior to the deposition of a 10 nm thick n^+-type a-Si:H heteroemitter [20] with transparent conduction oxide (TCO) (~80nm ZnO) on top. Hydrogen passivation needs to be applied before the deposition of the a-Si:H emitter to prevent recrystallization. To see an influence of the
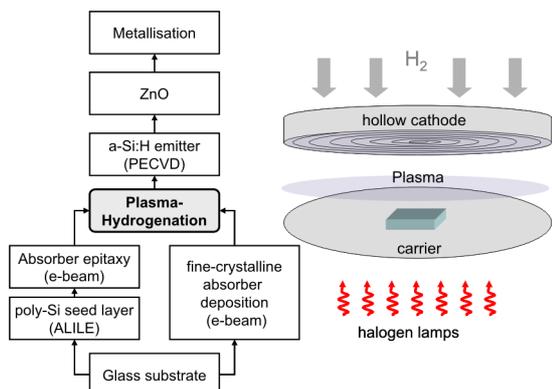
Figure 1: Process sequence of the solar cells and schematic design of the plasma tool.

hydrogenation only, RTA was not carried out and is investigated separately [10]. For contacting (Al) an interdigitated scheme was applied by photolithography. The cell area is 4×4mm² with an emitter area of 8.6 mm² (active 7.4 mm²). The sample size is 25×25 mm².

2.2 Hydrogen Passivation

An especially designed hydrogen plasma passivation tool was used to expose the samples to atomic hydrogen. It features a hollow-cathode RF high density plasma source (13.56 MHz) that was used in a simple diode configuration (see also scheme in Fig. 1). The partial H_2 pressure can be controlled from $0.1 - 1.3$ mbar with a maximum flux of 500 sccm. The samples are hold by an 8'' Si carrier. The distance between the carrier and the cathode can be varied in the range of 2…200 mm. Another special feature is the remote lamp radiation heater that allows controlled rapid heating and cooling phases with rates of up to 200°C/min and high temperatures of up to 650°C. For the experiments presented here an electrode distance of 20 mm was used together with a partial H_2 pressure of 1 mbar at 100 sccm and a plasma power density of 0.1 W/cm². The carrier was grounded, while the glass samples were on floating potential.

A typical temperature profile is shown in Fig. 2. The ramps are adapted to the Borofloat glass, heating up the samples slowly when passing the transformation point of 525°C. The plasma is ignited (represented by the blue background) when the sample reaches the desired plateau temperature (here: 620°C). After a certain passivation time the samples are cooled down rapidly within 3 min to 350°C meanwhile the plasma remains ignited to prevent any out-diffusion of the hydrogen. The influence of the temperature was investigated in the range of 400-620°C.

Before loading the native oxide of the samples was removed with 2% HF for 60 sec.

2.3 Characterization

Current-voltage measurements of the solar cell test structures were carried out under standard test conditions (AM1.5 illumination, 100 mW/cm², 25 °C). If not stated otherwise the emitter area was taken for the calculations and an underlying black absorber was used during the measurements to discard any reflections.
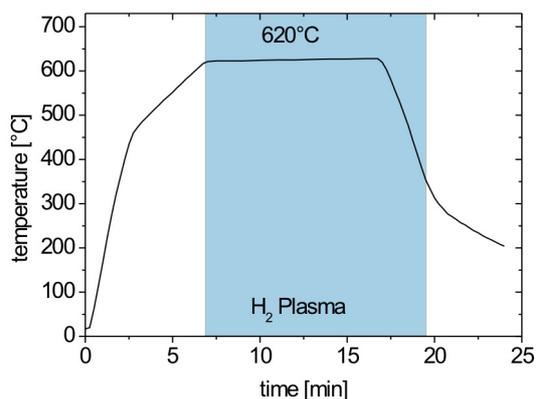
Figure 2: Profile of the substrate temperature during passivation

3 RESULTS

3.1 Impact of hydrogenation

Fig. 4 shows the I-V curves of the two different solar cell types poly-Si and fc-Si before (as-grown, dashed line) and after hydrogen passivation (solid line) under illumination. The blue curves in Fig. 4 refer to fc-Si and the red ones to poly-Si based cells. Table 1 gives the equivalent I-V parameters of the cells. The poly-Si sample was passivated at 520°C for 10 min whereas the fc-Si sample was exposed to the plasma for 30 min at 400°C. These parameters were taken as a first try to see an effect of hydrogenation in comparison to the untreated samples.

For the as-grown case the poly-Si sample shows a clearly better cell performance than the fc-Si sample. After hydrogenation the V_{OC} increases strongly for the poly-Si sample from 223 mV (as-grown) to 351 mV. It seems that mostly the V_{OC} is affected by the passivation. The short circuit current J_{SC} and the fill factor (FF) are improved by a factor of 1.2 so that the overall efficiency is more than doubled after hydrogenation.

The improvement of the fc-Si sample after hydrogenation is even larger. V_{OC} is increased by a factor of 4.3 from 70 mV (as-grown) to 319 mV. Also J_{SC} and FF are improved significantly, so that the overall efficiency reaches 1.2 %.

3.2 Influence of the plateau temperature

To investigate the influence of the plateau temperature four samples of ALILE based solar cells were prepared simultaneously. Different temperatures (400, 500, 550 and 620°C) were applied during hydrogenation for 10 min.
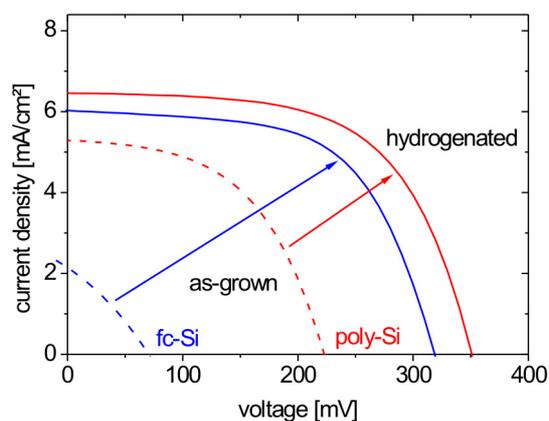
Figure 4: Current density versus voltage characteristics of as-grown (dashed line) and hydrogenated (solid line) solar cells. The blue curves refer to fc-Si and the red ones to poly-Si based cells.

Table 1: Comparison of solar cell parameters w/o (as-grown) and with hydrogen passivation

	V_{OC} mV	J_{SC} mA/cm²	FF %	η %
as-grown (poly-Si)	223	5.3	52	0.6
hydrogenated (poly-Si)	351	6.5	60	1.4
ratio	1.6	1.2	1.2	2.3
as-grown (fc-Si)	70	2.2	30	0.05
hydrogenated (fc-Si)	319	6.0	60	1.2
ratio	4.5	2.7	2.0	24
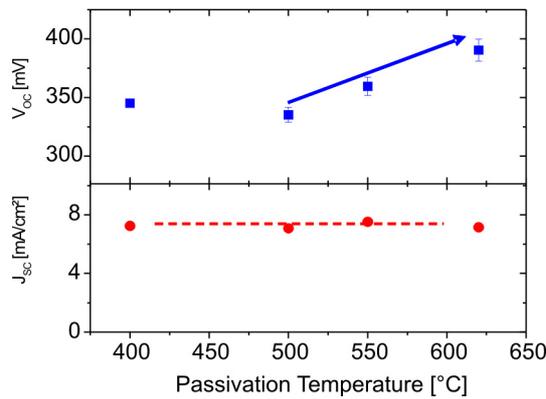
Figure 5: Dependence of the average open circuit voltage (blue squares) and the short circuit current density (red circles) on the substrate temperature during hydrogenation.

V_{OC} and J_{SC} were averaged for comparison over three cells from the same sample and the dependencies on the hydrogenation temperature are displayed in Fig. 5.

The open circuit voltages are shown in the upper part of Fig. 5 (blue squares). No influence of the passivation temperature is found between 400 and 500°C. Above 500°C the V_{OC} increases notably with the temperature. The highest average value of 385 mV is achieved for hydrogenation at 620°C. The short circuit current densities (red circles in Fig. 5) were not influenced significantly by different temperatures.

The best cell regarding efficiency was also obtained after a hydrogenation at 620°C. After contact annealing at 200°C for 30 min and with a white reflector at the rear the cell shows an active area efficiency of 2.7 %, a V_{OC} of 396 mV, a J_{SC} of 10.3 mA/cm² and a fill factor of 66%. The error bars in Fig. 5 can hardly be seen due to the symbol size. The divergence in V_{OC} and J_{SC} is small meaning that the samples are very homogeneous. This is also underlined by a 10×10 mm² cell that was processed on the same sample. It exhibits the same V_{OC} and J_{SC} as the best 4x4 mm² cell, presented before. Due to the cell design and a higher series resistance, the fill factor and the efficiency (2.3%) are slightly lower.

The corresponding dark I-V curve of the best sample (black line) is shown in Fig. 6 together with the as-grown (red) and the equivalent hydrogenated poly-Si sample (blue) from Fig 4. In forward bias they can be analyzed with the two-diode model:

$$J = J_{01}\left[\exp\left(\frac{eV}{k_BT}\right)-1\right] + J_{02}\left[\exp\left(\frac{eV}{2k_BT}\right)-1\right] + \frac{V}{R_{shunt}}$$

J_{01}(n=1) and J_{02}(n=2) are the saturation currents for band-band recombination (n=1) and recombination in the space-charge region (n=2). Here n is the ideality factor. The as-grown sample is primarily dominated by a high n=2 recombination. After hydrogenation at 520°C the recombination in the space-charge region is reduced. For the passivated sample at 620°C, the current can be fitted, consisting only of J_{01}=1.7×10⁻⁴ mA/cm².
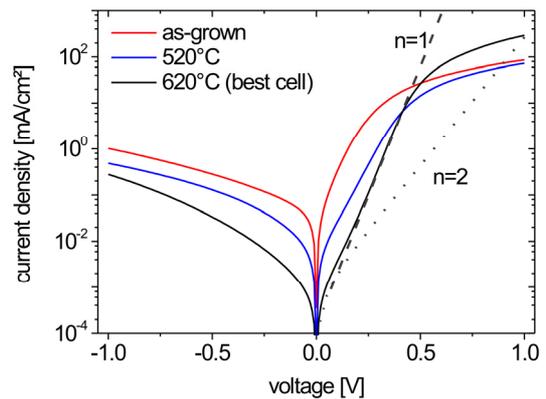
Figure 6: Dark I-V characteristic of i) an as-grown cell (red), ii) after hydrogenation at 520°C (blue) iii) the best cell, passivated at 620°C (black).

4 DISCUSSION

4.1 Influence of hydrogenation

In this work the effect of hydrogenation on poly-Si solar cell structures was investigated. In comparison also fine-grained fc-Si was hydrogenated. In both cases the open circuit voltage V_{OC} is strongly affected by the hydrogen treatment. Compared to the poly-Si sample the fc-Si has a very poor device characteristic in the untreated case. This can be attributed to the smaller grain size resulting in far more grain boundaries and thus higher defect densities for the fc-Si samples.

After hydrogenation the V_{OC} of the fine-grained films improved strongly up to 319 mV. This is almost the same value as is reached for our poly-Si material. It seems that after hydrogen passivation is applied the limiting factor is not the grain size anymore [21]. For a high temperature approach, it was already shown that fine-grained solar cells can also reach the same high V_{OC}'s and cell efficiencies as large-grained cells [11, 22]. Further it was found, that the poly-Si films contained a high amount of intra-grain defects that were electrically active [21]. A high intra-grain defect density was also observed for the poly-Si films presented here [6]. It needs to be investigated, if these intra-grain defects are deleterious for the solar cell performance and under which conditions they can be passivated by hydrogenation.

For the poly-Si cells the influence of the passivation temperature was investigated in the range from 400-600°C. J_{SC} is improved by hydrogenation but no influence on the temperature is seen. On the other hand V_{OC} increases steadily for temperatures higher than 500°C. The highest values were reached for the maximum temperature of 620 °C. One possible explanation could be that hydrogen diffusion is enhanced due to higher temperatures. Hence within a limited time hydrogen can advance deeper into the sample at higher temperatures and passivate more defects. To compensate the effect of smaller diffusion length at lower temperatures it would be necessary to expose the samples to atomic hydrogen for a longer time.

The investigations here were done by only changing the temperature and keeping all other parameters including the plateau time of 10 min constant. After hydrogenation high average V_{OC}'s of >330 mV were

reached for poly-Si films. With temperatures above 500°C the V_{OC} increases steadily to an average value of 385mV. This demonstrates that for a passivation time of 10 min, higher temperatures are in fact favorable for a good cell performance with the best result achieved for the maximum temperature of 620°C. However it has to be emphasized that this could be also an indication for limited hydrogen diffusion at lower temperatures. The actual effect of the hydrogenation has to be investigated in more detail. In addition from first secondary ion mass spectrometry (SIMS) analysis it was found that after hydrogen passivation at 520°C for 10 min the sample contained only low concentrations of hydrogen, equal or below 10^{18} cm^{-3}. At similar temperatures concentrations of $>10^{19}$ cm^{-3} were found [12]. This means that the hydrogenation process is not yet optimized, concerning for example hydrogen pressure or plasma power density.

5 SUMMARY AND CONCLUSIONS

A new hydrogen plasma tool was established, capable of high temperatures and fast ramping. The effect of hydrogenation on poly-Si solar cells was investigated. The solar cell performance could be enhanced significantly by hydrogen passivation. The open circuit voltage improved steadily with higher temperatures above 500°C. The best V_{OC} reported here is 396 mV after the exposure to a hydrogen plasma at a maximum temperature of 620°C. The corresponding active area cell efficiency is 2.7%.

For comparison fine-grained (fc-Si) solar cells were introduced. After passivation similar high values of V_{OC} were observed. Therefore it seems, that for the seed layer concept at this stage after hydrogenation grain size does not seem to be the dominating factor for the solar cell device. Rapid thermal annealing at high temperatures was omitted in this work but has also shown to be beneficial [10]. It is expected that the combination of rapid thermal annealing and hydrogenation and the implementation of light trapping will lead to a further improvement in cell efficiency. The beneficial effect of hydrogenation at high temperatures was clearly demonstrated.

6 ACKNOWLEDGMENTS

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