IMPROVEMENT OF EPITAXIALLY GROWN POLY-SI THIN-FILM SOLAR CELLS ON GLASS BY RAPID THERMAL ANNEALING

Hahn-Meitner-Institut Berlin, Kekuléstr. 5, D-12489 Berlin, Germany
*phone: +49 30 8062-1329, fax: +49 30 8062-1333, email: bjoern.rau@hmi.de

ABSTRACT: The impact of rapid thermal annealing (RTA) on large-grained polycrystalline Si thin-film solar cells on glass was investigated. The solar cells consist of absorber layers homo-epitaxially grown at 600°C by electron beam evaporation on polycrystalline Si seed layers. Due to the thermal limitations of the preparation processes by the glass the absorber layers suffer from a structural imperfection. Short high-temperature treatments improve the structural properties of the layers and therefore the solar cells. Here, we discuss the influence of the RTA temperature and duration on the solar cell, especially the open-circuit voltage. Annealing temperatures between 800 and 1000°C were applied for 5 to 300 s. The balance between high temperatures and their duration is very important and best results were achieved using 950°C for 200s as plateau parameter. We also studied the impact of RTA on the contamination levels determined by secondary ion mass spectrometry. Only a slight influence of the RTA was found on the levels of boron, aluminium and oxygen.

Keywords: Rapid Thermal Processing, Polycrystalline, Si-Films

1 INTRODUCTION

The epitaxial thickening of a thin large-grained polycrystalline Si (poly-Si) film (seed layer) on a foreign substrate like glass is a promising approach to realize the absorber layer of a poly-Si thin-film solar cell on glass [1]. Basically, such cell concept combines the benefits of crystalline Si wafers and the high potential for cost reduction of a thin-film technology.

Using glass as a transparent low-cost substrate all process steps of the solar cell preparation are generally limited by its thermal stability to about 600°C. This is a big challenge especially for the formation of a poly-Si seed layer on glass as well as its epitaxial thickening. Both process steps have been investigated intensively during the last years. Beside laser-crystallisation [2,3], the aluminium-induced crystallisation (AIC) of amorphous Si [4,5] was found to be suitable for large-grained poly-Si seed layers on foreign substrates like glass. For the subsequent growth of absorber layers, several growth techniques like electron-cyclotron resonance chemical vapour deposition (ECRCVD) [6,7], Hot-wire CVD [8] and electron-beam evaporation based deposition techniques [9-11] have shown, that Si can be grown epitaxially at temperatures ≤ 600°C. Especially the simple electron beam evaporation (without the commonly used additional ionisation stage) has recently shown its potential to grow Si epitaxially at these low temperatures on crystalline templates such as Si wafers or poly-Si thin-films [12].

But in contrast to Si films grown by conventional CVD at high temperatures (~1100 °C) [13], at this low temperatures the structural quality of the epitaxial growth is reduced and depends strongly on the properties of the underlying crystal structure (e.g. crystal orientation and defect density of Si seed layer or bulk material). This results typically in a higher density of crystal defects in the grown films leading to enhanced recombination losses in solar cells.

It is a well known fact, that the quality of Si films can be improved by post-deposition treatments like defect annealing and hydrogen passivation. For instance high-temperature annealing can improve the structural quality of such a film by re-arranging the crystal structure (e.g. point defect removal, doping activation) [14,15]. In general, the limitation by the glass substrate to temperatures of about 600°C does not allow long high-temperature treatments. Only very short annealing treatments as in rapid thermal annealing (RTA) processes can be applied. Enhanced RTA processes showed already the potential for significant improvements on thin-film technologies like crystalline Si thin-film solar cells on glass [15-17].

In this paper, we discuss the influence of RTA treatments on the performance of poly-Si thin-film solar cells with absorber layers grown epitaxially by e-beam evaporation on poly-Si seed layers on glass.

2 EXPERIMENT

2.1 Solar cell structure

We prepared solar cells on poly-Si seed layers on glass. The seed layers were prepared directly on Schott Borofloat® 33 glass by the aluminium-induced layer exchange (ALILE) process. The thickness of the glass...
was 0.7 mm. Details of this preparation can be found in [18]. Prior to the absorber deposition, the seed layers were treated by chemical-mechanical polishing (CMP). The resulting poly-Si film (about 200 nm thick) on glass is p'-type due to doping with Al. It is characterised by large grains (average grain size 7 μm) and a preferential (100) orientation (about 60% of all grains are tilted less than 20° relative to (100)) [19].

The absorber layers were grown by evaporating high purity (FZ quality) Si with an e-gun at a substrate temperature of 600 °C to a film thickness of about 1.6 μm. The p-type doping was realized by co-evaporation of boron from a high-temperature effusion cell. The free carrier concentration of the absorber layer is about 4×10^{16} cm\(^{-3}\). The base pressure was in the range of 10\(^{-4}\) Pa and the residual gas pressure during deposition was around 10\(^{-4}\) Pa. No additional post-ionisation stage has been used, and the substrates were held at ground potential. [20]

Figure 1 shows the complete process sequence as well as the schematic design of the solar cells under investigation. No light trapping was applied to this test structures. In order to study the direct impact of RTA on the solar cell performance no hydrogenation was applied in the work presented here. The influence of the hydrogenation is discussed separately, showing \(V_{OC}\)'s of about 400 mV already without defect annealing [21]. The solar cells were prepared using a slightly p-type absorber layer grown on the poly-Si seed layer (p'-type). A highly phosphorous doped hydrogenated amorphous Si (a-Si:H) layer was deposited as emitter (thickness: 10 nm) by plasma-enhanced CVD (PECVD). An 80 nm thick ZnO:Al film was used as transparent conductive oxide. No diffusion barrier (e.g. SiN) between glass and seed layer was used in this study. Device separation (mesa-etching) and metal grid definition (Al lift-off) was realised by photolithography. The cells had an interdigitating grid and a cell area of about 4 × 4 mm\(^2\) (emitter area = 8.6 mm\(^2\)). The sample size (7 cells per sample) was of about 1 inch × ½ inch cut from 1 square inch samples after absorber epitaxy.

We prepared two series of solar cells each consisting of samples prepared in the same runs of deposition for the individual layers. This allows a direct comparison of the samples of one series focussing on the influence of the RTA treatment only. For comparison of the different samples, the average of the open circuit voltage (\(V_{OC}\)) of all cells of one sample was used.

2.2 Rapid thermal annealing

The RTA treatments were carried out under nitrogen atmosphere in a rapid thermal processing (RTP) system (Heatpulse 210T from AG Associates) consisting of a quartz chamber, two banks of tungsten-halogen lamps and a microcontroller unit. A graphite wafer was used as sample carrier in order to avoid gluing of the glass substrates on the carrier.

Beside annealing temperature and duration, it is necessary to adapt the annealing profile to the properties of the glass. Therefore we used different heating and cooling rates for different temperature ranges. The crucial temperature range for an RTA treatment of a glass based sample is around the transformation temperature \(T_g\) of the glass (\(T_g\) Borofloat® 33: 525°C). The so called transformation range of Borofloat® 33 is between the 518°C (Strain point) and 560°C (Annealing point) [22]. Below the Strain point the thermal expansion coefficient of Borofloat® 33 closely matches that of Si. Above the Annealing point the glass softens slightly and therefore the stress which would in principle increase between glass and Si is less effective. Between both points, the expansion coefficient of the glass changes non-linearly and slow heating and cooling rates are required to relax the glass and avoid cracking. We applied a heating rate of 0.7 K/s and a cooling rate of -1 K/s for the transformation range.

Figure 2 shows schematically the RTA profiles applied in this work. The annealing started in the pre-heated chamber (around 100°C) directly after sample loading. The samples were pre-heated to about 620°C with a slow rate through the transformation range (1), immediately followed by a fast ramp (14 K/s) (2) to the final annealing step (3) with different plateau temperatures and durations. The samples were cooled down afterwards again with a reduced rate through the transformation range (4). The annealing chamber was opened at 250°C. The samples were removed from the RTP system at about 100°C. The complete cool down process took place in about 700 s.

3 RESULTS & DISCUSSION

In order to compare the influence of RTA treatment on the absorber layer the \(V_{OC}\) is a good parameter. The results do not depend on the cell design (like contacts and series resistance). In addition, we analysed complete solar cell test structures using a solar-simulator under standard test conditions (AM1.5). For these measurements a black padding was used in order to have defined conditions with only one light path through the sample.

3.1 Variation of annealing temperature and duration

We investigated the influence of the RTA plateau properties on the cell performance. For this we applied RTA profiles as shown in Fig. 2 with different plateau temperatures and durations (Fig. 2, step 3). The effect of this treatments on the \(V_{OC}\) is illustrated in Fig. 3. In principle, error bars are plotted on all data points to show
the variation over the 7 cells per sample. But, due to the 
good homogeneity of the samples, the error bars are 
mostly smaller than the plot size of the data points.

Two cell series are shown with different as-grown 
properties. The first series (solid symbols) has an average 
as-grown $V_{OC}$ of 166 mV (star). Samples of this series 
were annealed between 800°C and 875°C for 300s 
(squares) or 875°C and 900°C for 200s (circles), 
respectively. A clear improvement of the $V_{OC}$ was 
obtained with increasing annealing temperature. But for 
300s annealing time the $V_{OC}$ is decreased at 875°C 
compared to 850°C. However, by applying a reduced 
plateau time (200s) at 875°C, the $V_{OC}$ is increased even 
to a higher level as reached with 850°C. Therefore we 
treated one sample at 900°C for 200s also. This further 
 improves the $V_{OC}$ to 254 mV.

The second sample series (open symbols) has 
initially an average $V_{OC}$ of 135 mV (star) which is lower 
than the as-grown sample of the first series. The reason 
for this can be for instance a some lower doping level of 
the absorber layer as a result of a slight change in the 
growth rate or also a slight variation of the seed layer 
properties (different ALIIE and CMP processes). 
Nevertheless, by applying a 950°C treatment for 200s the 
$V_{OC}$ more than doubles to a average value of 288 mV. 
Applying 950°C for only 100s resulted only in a $V_{OC}$ of 
246 mV.

3.2 Short time annealing at 1000°C

From the results shown in Fig. 3, no temperature 
opimum could be concluded. Therefore we increased the 
plateau temperature further and treated samples of the 
second series (open symbols in Fig. 3) using 1000°C. 
But, in order to avoid a complete melting of the glass, we 
applied only very short annealing times of 5 to 20s. The 
dependence of the $V_{OC}$ on the annealing time is shown in 
Fig. 4. Also these treatments let to a significant 
improvement of the $V_{OC}$ whereas an optimum process 
duration was found to be around 15s. Here the $V_{OC}$ 
improves from 135 mV to 237 mV. This results are 
comparable to data published by Terry e. al [16]. They 
also found an optimum RTA duration of about 15s for a 
1000°C annealing for a similar cell structure. 
Nevertheless, we found, that the improvement of the $V_{OC}$ 
by the 1000°C anneal was much less effective compared 
to the annealing at 950°C for 200s obtained on the same 
sample series.

This shows, that both temperature and duration of an 
RTA treatment have a strong influence on the poly-Si 
films on glass. The balance between high temperatures 
and duration of their application has to be optimized. So 
far, a treatment of about 950°C for 200s seems to give 
the best results. But further optimizations are necessary.

3.4 Contaminations and diffusion

We investigated the contamination levels of O, C, B, 
and Al in dependence on the RTA treatment. For this

Fig. 3. Open circuit voltages of two sample series as a 
function of plateau temperature annealed with different 
process durations.

Fig. 4. Open circuit voltage as a function of annealing 
time for a 1000°C RTA treatment.

Fig. 5. SIMS results for O, C, B, and Al contaminations 
in dependence on the RTA treatment. Solid line: no RTA 
as-grown, dashed line: RTA 800°C, 300s, dotted line: 
RTA 900°C, 200s. The vertical line marks the interface 
between AIC seed layer and epitaxial grown film.
secondary ion mass spectrometry (SIMS) was carried out on three samples of the first sample series (solid symbols of Fig. 3). Figure 5 shows the depth profiles of the four elements for the as-grown sample (solid line) as well as the samples with the lowest (800°C) (dashed line) and the highest (900°C) (dotted line) annealing temperature of this series, respectively. The vertical dotted line marks the interface between AIC seed layer and epitaxial grown absorber. The interface between seed layer and glass is directly placed at the right border of the graph. An additional interface about 450 nm above the seed layer was found. Here, the levels of O and Al are increased, whereas B and C were not accumulated. The origin of this growth irregularity is still unclear.

Principally, the Al content seems to be rather high \((10^{17} - 10^{18} \, \text{cm}^{-3})\) already direct after epitaxy. Different samples showed different Al levels. Further investigations are needed to clarify the origin. Nevertheless, results can be used to investigate the influence of RTA on the Al level also. Although no diffusion barrier was used in the samples, RTA did not influence the contamination levels significantly. Only an increased B diffusion profile was observed within the absorber layer. Already the as-grown sample showed a slight diffusion of boron, as well as a rather high B level within the seed layer. This level, originally of about \(5 \times 10^{19} \, \text{cm}^{-3}\) after the ALILE process [23], seems to be strongly increased by a diffusion of B from the glass. The RTA process drives this diffusion further, which can be seen in the increased diffusion profile. Nevertheless, on the major part of the absorber layer, the B level (about \(6 \times 10^{16} \, \text{cm}^{-3}\)) remains independent on the RTA process.

In principle, the high Al concentration observed in all samples can also give an explanation for the increased \(V_{OC}\). An RTA treatment on these samples could lead to an electrical activation of Al resulting in an increased acceptor concentration within the absorber. This also would result in a higher \(V_{OC}\). Further investigations will be carried out in order to identify the processes occurring during RTA in detail.

As mentioned above, all three samples belong to the same series of preparations. But, whereas the as-grown sample and the sample treated at 800°C came from exact the same piece of glass, the sample annealed at 900°C was prepared on another piece. Therefore we can not exclude a slight variation of the seed layer properties due to inhomogeneties of the preparation process (e.g. CMP). Beside the higher temperatures during RTA, this can also be an explanation for the increased levels of O, Al and partly C in the sample annealed at 900°C.

Due to the fact, that the highest \(V_{OC}\) was achieved at 950°C, further experiments will be carried out in order to examine the diffusion at these elevated temperatures. In the next future, we will also investigate the influence of a diffusion barrier between glass and seed layer on the contamination of the Si films by elements from the glass.

3.5 Solar cell results

The impact of an RTA treatment on the complete solar cell is exemplarily shown in Fig. 6. Here, the current-voltage curves of the best solar cells from two samples of the second series are presented (as-grown and 950°C, 200s). To calculate the current density, the emitter area was taken into account. Note: neither hydrogenation was applied to this samples nor any light trapping is included.

Although the highest \(V_{OC}\) was obtained with this particular sample series the annealing influences the short-circuit current density \((J_{SC})\) only marginally. But, in most of the series, we investigated, the \(J_{SC}\) is affected more noticeable by an RTA treatment.

Beside the already describe improvement of the \(V_{OC}\), the improvement of the shunt resistance, \(R_{sh}\), is similar. Figure 7 shows \(R_{sh}\) as a function of plateau temperature for the samples of the first series (solid symbols in Fig. 3). A clear increase of \(R_{sh}\) was achieved with increasing temperature. Nevertheless, the values are still quite low and efforts have to be made to improve \(R_{sh}\) further. No change of the series resistance was found by the RTA treatment.

4 CONCLUSIONS

A strong improvement of the open-circuit voltage was obtained by rapid thermal annealing of poly-Si thin-film solar cells grown by electron-beam evaporation on AIC seed layers on glass. The balance between high plateau temperatures and the annealing duration is very
important. The highest open-circuit voltage of 288 mV was achieved at a temperature of 950°C applied for 200s. These results are promising taking into account, that no hydrogenation was applied in this study.

The combination of an optimized RTA treatment with an efficient hydrogenation process has the potential for high open-circuit voltages, much higher than about 400 mV as already reached for hydrogenation only.

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6 REFERENCES