INFLUENCE OF POST-DEPOSITION TREATMENTS OF ABSORBER LAYERS ON POLY-SI THIN-FILM SOLAR CELLS ON GLASS GROWN BY ECRCVD

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ABSTRACT: The epitaxial thickening of a thin polycrystalline Si (poly-Si) film (seed layer) is a promising approach to realize an absorber layer of a poly-Si thin-film solar cell on glass. Such cell concept combines the benefits of crystalline Si and the high potential for cost reduction of a thin-film technology. Here, we discuss the influence of post-deposition treatments on solar cells with absorber layers grown by electron-cyclotron resonance chemical vapour deposition (ECRCVD). Defect annealing was used to improve the structural quality of the absorber layers. For this, we used rapid thermal annealing (RTA) processes. Annealing times (up to 400 s) were applied at temperatures of up to 950°C. Defect passivation treatments were carried out at temperatures of about 350°C to passivate the remaining defects in the films by hydrogen. The impact of both treatments on the solar cell parameter will be discussed focusing on RTA. Open-circuit voltages of up to 361 mV were achieved without hydrogenation showing the potential of ECRCVD-grown absorbers. Applying both treatments resulted so far in an increase of V_{OC} to about 400 mV. Because of the fact, that both post-treatments (particularly hydrogenation) are still not yet optimized, further improvements can be expected.

Keywords: Rapid thermal processing, Si thin-film, Solar cells

1 INTRODUCTION

An attractive low-temperature route to a poly-Si thin-film solar cell on a low-cost substrate like glass bases on the seed layer concept [1]. In such a cell concept, we use a thin large-grained poly-Si seed layer on glass formed by aluminium-induced crystallisation (AIC). The absorber layer is grown on this seed layer in a subsequent epitaxial deposition process.

The epitaxial growth process is limited by the glass to temperatures of about 600°C. At these low temperatures it becomes necessary to apply deposition techniques which provide additional non-thermal energy to the surface of the growing film in order to obtain epitaxial growth. A possible solution is the use of ion-assisted deposition techniques. Several growth techniques like electron-cyclotron resonance chemical vapour deposition (ECRCVD) [2,3] and electron-beam evaporation based deposition techniques [4-6] have shown, that Si can be grown epitaxially in this temperature regime. But in contrast to Si films grown by conventional CVD at high temperatures (~1100 °C), at 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. In case of ECRCVD-grown Si films the density of extended defects is 4×10^8 cm^{-2} for films grown on Si(100) and increases strongly on other crystal orientations [7]. Another feature of this deposition method is a very low effective doping level compared to the amount of incorporated boron [8].

It is a well known fact, that the presence of crystal defects influencing the performance of an electrical device can be reduced by post-deposition treatments of the Si films. For instance high-temperature annealing can improve the structural quality of such a film by rearranging the crystal structure (e.g. point defect removal, doping activation) [9]. The limitation to temperatures below 600°C by the glass substrate for all process steps generally does not allow such 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 [10]. In this paper, we present results of solar cells with absorber layers epitaxially grown by ECRCVD on poly-Si seed layers on glass treated by different RTA procedures.

2 EXPERIMENT

2.1 Solar cell structure

We prepared solar cells on poly-Si seed layers on glass. The seed layers were prepared by the aluminium-induced layer exchange (ALILE) on Corning 1737F. Details of this preparation can be found in [11]. Prior to the absorber deposition, the seed layers were treated by chemical-mechanical polishing (CMP). The resulting poly-Si film (about 200 nm thickness) on glass is p^+-type due to doping with Al. It is characterised by large grains (up to 20 µm) and a preferential (100) orientation (about 75% of all grains are tilted less then 20° relative to (100)) [12].

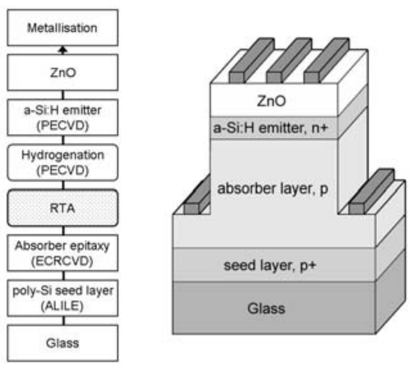

Fig. 1. Process sequence and schematic design of a Si thin-film solar cell test structure.

The crystalline Si absorber layers were grown in an ECRCVD system with a RR 250 PQ (Roth & Rau, Germany) plasma source decomposing silane (SiH_4) and diborane (B_2H_6) by an H_2 plasma. The thickness of the absorber layers was about 2 µm. The premix gas ratio used for doping was $[B_2H_6]/[SiH_4]$ = 100 ppm resulting in an as-grown effective doping level of about 3×10^{15} cm^{-3} [8]. The very low effective doping level can be explained in part by a compensation of the n-type base-doping. But this result also suggests that part of the boron has been incorporated on non-doping sites. The substrate temperature was about 600°C. The resulting growth rate amounted to 20 nm/min. More details can be found elsewhere [13].

Figure 1 shows the complete process sequence of the solar cell test structures under investigation. The solar cells were prepared using a slightly boron-doped absorber layer grown on the poly-Si seed layer. A highly phosphorous doped hydrogenated amorphous Si (a-Si) layer was deposited as emitter (thickness: 20 nm) by plasma-enhanced CVD (PECVD). An 80 nm thick ZnO:Al film was used as transparent conductive oxide. Device separation (mesa-etching) and metal grid definition (Al lift-off) was realised by photolithography. The cells had a non-interdigitating grid and a cell area of about 4 × 4 mm² (emitter area = 0.122 cm²). No light trapping was applied to this solar cell structures.

2.2 Post-deposition treatments

Two kinds of post-deposition treatments of the absorber layer were used. RTA processing was 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 Si wafer was used as sample carrier. In order to avoid the sticking of the glass to the Si, the carrier was graphite-coated. As annealing procedures simple temperature profiles were used (see Fig. 2). The annealing started in the pre-heated chamber (around 280°C after sample loading) (1), immediately followed by a mid-temperature annealing phase (400°C, 40 s) (2) and (3) the final annealing step with different temperatures (850°C - 950°C) and duration (200 s - 400 s). To reach the final plateau temperature we used a ramp up rate of about 120 K/s. The unloading process took place in about 200 s (4). No special annealing phases (e.g. low rate) were used to pass the transformation temperature of the Corning 1737F (Tg = 675°C) in these experiments.

In addition to RTA, we applied hydrogenation to most of our samples in order to reduce electrically active defects in the absorber layers by passivating them by atomic hydrogen. This treatment was carried out in a parallel-plate PECVD system at 350°C for 15 min. The process pressure and the power density amounted to 0.75 to 1 mbar and 15 mW/cm², respectively. The hydrogenation was finished by a unloading from the chamber. The samples were kept in vacuum. After cooling down the PECVD system, the samples were transferred into the same chamber in order to proceed with emitter deposition. Note: the hydrogenation of our layers is still a non-optimized process.

3 RESULTS & DISCUSSION

In order to compare the influence of different post-deposition treatments on the absorber layer the open-circuit voltage is a good parameter to characterize the quality of this layer. The results do not depend on the cell design (like contacts and series resistance). We analysed complete solar cell test structures using a solar-simulator under standard test conditions (AM1.5).

In Fig. 3, the influence of post-deposition treatments of the absorber on the solar cell performance is shown as an example. For a good comparison, the samples (b) and (c) are treated in the same annealing process. All emitter layers were processed in the same run of deposition. The as-grown V_{OC} is about 215 mV. Due to a 900°C anneal for 300s, the V_{OC} increased to 314 mV. This corresponds to an increase of 46%. By the additional application of hydrogenation the V_{OC} increased further to 354 mV in this particular example. The total improvement of V_{OC} amounts to 65%. This shows not only the strong improvement of the absorber layer by an annealing treatment but also the positive effect of hydrogenation on the V_{OC}. In addition, a large increase of J_{SC} was observed due to the hydrogenation. In this particular solar cell example, the post-deposition treatments led finally to an improvement of the solar cell efficiency by a factor of 3.5.

3.1 Influence of annealing temperature

We investigated the influence of the plateau temperature on the cell performance. For this, we applied

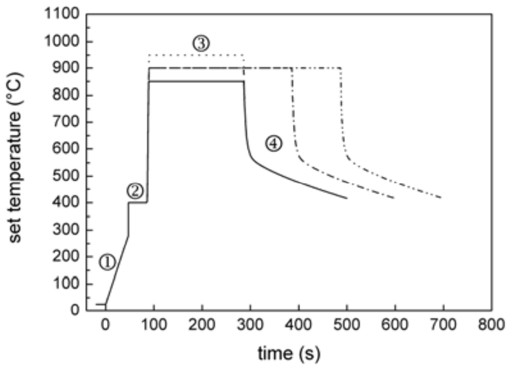

Fig. 2. RTA temperature profiles for post-deposition treatments of the poly-Si absorber layers grown on seed layer coated glass (Corning 1737F).

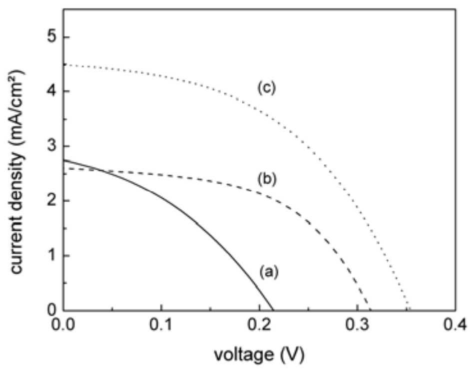

Fig. 3. Current-voltage characteristic of solar cells with different absorber layer treatments. (a) as-grown, (b) RTA treatment (900°C, 300 s), (c) RTA treatment and hydrogenation.

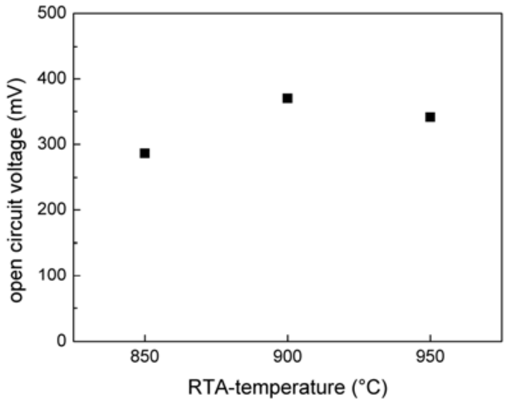

Fig. 4. Open-circuit voltage V_{OC} of solar cells with different RTA plateau temperatures.

850°C, 900°C or 950°C as constant annealing temperature for 300 s to a series of samples. All samples were hydrogenated in the same experiment afterwards. The results are shown in Fig. 4. We observed a significant increase of V_{OC} of 30% from 286 mV to 370 mV by increasing the temperature from 850°C to 900°C. In agreement with Terry et al. [10] a slight decrease of V_{OC} using higher temperatures was obtained. A (visible) deformation of the glass and the Si layers and a resulting increase of stress by the increased thermal budget could be a possible explanation for this.

For comparison, we also carried out experiments on Si(100) wafers instead of seed layers on glass. Here, we also observed an increase of V_{OC} by increasing the RTA temperature from 850°C to 900°C. But a further increase of the temperature (950°C) did not result in a decrease of V_{OC}. Instead of this, a stabilization of the V_{OC} value was observed. These results support the assumption, that the decrease in V_{OC}, observed for the glass-based samples is related to thermally influenced effects in the Si layer/glass stack and not in the absorber layer itself.

The total effect of V_{OC} improvement of films on Si(100) wafers is smaller compared to the films on seed layers. As an example, we observed only an increase in V_{OC} of about 6% from 436 mV (850°C) to 462 mV (950°C). This corresponds to the fact, that the films deposited on Si(100) are monocrystalline films grown on “ideal” substrates. These films have the lowest density of extended defects. The best cells on Si(100) have reached about 500 mV. The absorber layers grown on the seed layers are polycrystalline and consist of different grains with different crystal orientations. Although the seed layers have a preferential (100) orientation the structural quality of the absorber layers is reduced. Therefore and in combination with the grain boundaries, the potential for cell improvement is higher in these films.

3.2 Influence of annealing time

We analysed the influence of the plateau time on the solar cell performance. Samples were annealed at 900°C for 200 s, 300 s, and 400 s, respectively. No hydrogenation was applied. We observed only a slight increase of V_{OC} from 344 mV to 361 mV with increasing plateau time. This is in fair agreement with the detailed study of Terry et al. [10]. They also reported about a small improvement of V_{OC} in this plateau time region.

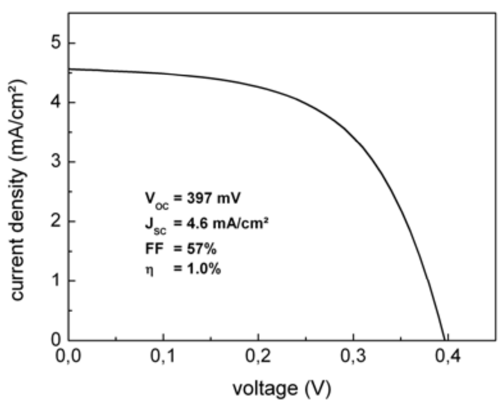

Fig. 5. Current-voltage characteristic of our best solar cell in terms of V_{OC}. It consist of a 2 µm thick absorber layer grown by ECRCVD on a poly-Si seed layer on glass. The absorber was treated by defect annealing and hydrogen-passivation.

Further investigations on Si films on glass with a larger number of temperature values and RTA plateau times will be carried out in the next future in order to find the optimum RTA process parameter. The focus will be the development of an enhanced RTA profile, e.g. taking into account the glass transformation temperature.

3.3 Best solar cell results

Table I summarizes the best solar cell results in terms of V_{OC} in dependence on the post-deposition treatment. All cells have comparable properties (e.g. 2 µm absorber layer, 100 ppm B_2H_6/SiH_4). As reported previously, the best as-grown solar cell we achieved, had an V_{OC} of 284 mV. This result was obtained with a higher diborane/silane ratio (200 ppm) [8]. It shows, that beside the optimisation of post-deposition treatments there is still some potential in optimising the as-grown doping level.

Table I: Best open-circuit voltages in dependence on the post-deposition treatment (2 µm absorber, 100 ppm).

	V_{OC} (mV)
as-grown	215
post-annealed	361
post-annealed and hydrogenated	397

The V_{OC} of 361 mV for an non-hydrogenated, 2 µm thick poly-Si film on glass is a remarkable result. It shows, that very promising solar cell results can be achieved for a poly-Si film on glass already prior to an additional hydrogenation. The reason seems to be the positive effect of the hydrogen plasma to the layer structure by the ECRCVD process. Despite of the high deposition temperature of about 600°C there is obviously still a certain in-situ defect passivation.

The current-voltage characteristic of the same sample with hydrogenation is shown in Fig. 5. The cell results are V_{OC} = 397 mV, J_{SC} = 4.6 mA/cm², FF = 57%, η = 1.0%. Compared to previously reported results [14], we achieved an increase of V_{OC} of about 20 mV and a strong increase of the fill factor. This was obtained by only the improvement of the RTA process. All other

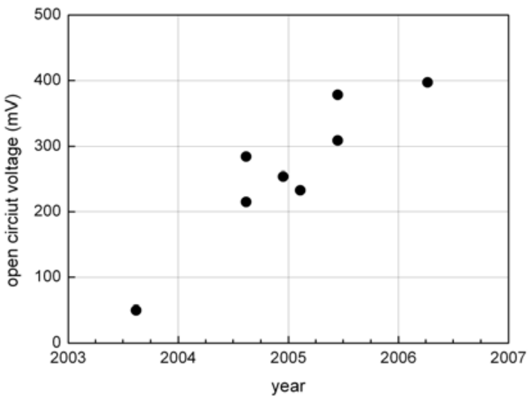

Fig. 6. Evolution of open-circuit voltage of our solar cells following the concept of epitaxial thickening of a poly-Si seed layer on glass by ECRCVD.

process parameter (for deposition and hydrogenation) are comparable to [14].

Unfortunately, the J_{SC}, reported here, is reduced by about 25%. The reason for this reduction is still unclear but was observed by the complete set of samples processed in the same run of cell production. The low J_{SC} itself can be explained by the used cell design. So far, no light trapping was applied to our solar cells.

3.4 Evolution of open-circuit voltage

Good progress has been achieved in recent years of research on our solar cell concept at HMI. Figure 6 shows the evolution of V_{OC} in the last four years following the concept of the epitaxial thickening of an poly-Si seed layer by ECRCVD. The importance of absorber layer treatments like defect annealing and passivation for such kind of cell concept are clearly visible. The stepwise increase of V_{OC} was achieved by the separate introduction of doping (mid 2004), annealing and hydrogenation (beginning of 2005) and by the ongoing improvement and combination of these treatments. Further progress can be expected from the development of an efficient hydrogenation procedure, the introduction of a light trapping scheme and an optimised solar cell design.

4 CONCLUSIONS

By following a seed layer concept, crystalline Si thin-film solar cells were prepared in a complete low-temperature process on glass substrates. Encouraging open-circuit voltages of 361 mV without hydrogenation and 397 mV with a first hydrogenation procedure were achieved on the seed layers on glass. This shows the potential of this solar cell concept. Further efforts have to be made in order to improve the solar cells. Beside the development of an efficient hydrogenation procedure as well as of a light trapping, the further optimisation of the RTA process in terms of annealing temperature, duration and profile will play an important role.

5 ACKNOWLEDGEMENTS

The authors would like to thank M. Muske, K. Jacob, C. Klimm, and T. Weber for technical assistance. This work was supported by the European Commission, project METEOR (ENK5-CT-2001-00543).

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