POLYCRYSTALLINE SI THIN-FILM SOLAR CELLS ON GLASS BY EPITAXIAL THICKENING OF SEED LAYERS USING ECRCVD

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ABSTRACT: The seed layer concept is an attractive approach towards a polycrystalline Si (poly-Si) thin-film solar cell on a low-cost substrate like glass. In such a concept, the solar cell absorber is grown epitaxially on a thin large-grained poly-Si seed layer. We prepared large-grained poly-Si seed layers on glass by aluminium-induced layer exchange (ALILE). Due to the use of glass as substrate the temperature of the epitaxial growth process is limited to temperatures below the softening point of the glass (< 600°C). In order to form the p-type absorber layers the seed layers were epitaxially thickened by electron-cyclotron resonance chemical vapour deposition (ECRCVD) from silane/diborane gas mixtures. The quality of the absorber layers strongly depends on the properties of the seed layer grains in particular on the crystalline orientation and the morphology. First $p^+/p/n^+$ solar cell structures were prepared using an a-Si:H(n^+) emitter. An open circuit voltage of 284 mV was obtained without additional treatments of the absorber layer. The reference solar cell on a p^+ type Si(100) achieved an efficiency of 4.24 %.

Keywords: Epitaxy, Polycrystalline Si, Si thin-film

1 INTRODUCTION

An attractive low-temperature route to a polycrystalline Si (poly-Si) thin-film solar cell on a low-cost substrate like glass bases on the seed layer concept. 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 substrate temperature during growth is limited by the glass to temperatures below its softening point ($T_S < 600$ °C). In order to realise epitaxial growth at such low temperatures additional non-thermal energy has to be provided to the surface of the growing Si-film. It was demonstrated that ion-assisted deposition techniques like electron-cyclotron resonance chemical vapour deposition (ECRCVD) [1] or ion-assisted deposition (IAD) [2] are in principle suitable for such a process. Apparently in particular ECRCVD requires a preferential (100) orientation of the grains in the seed layer. Recently, first successful epitaxial growth of Si on AIC seed layers was achieved by both methods [3,4].

In this paper we report on the epitaxial growth of Si by ECRCVD to form the absorber layer on a poly-Si seed layer on glass. Since Si films deposited from pure silane are n-type we used diborane for compensation although it is well known that the presence of boron may make epitaxial growth more difficult. First solar cell structures are presented and their performance is compared with reference cells grown on p^+-type Si(100) wafers.

2 EXPERIMENTAL PROCEDURE

2.1 Specimen characterisation

Scanning and transmission electron microscopy (SEM and TEM), electron-backscattered diffraction (EBSD) and secondary ion mass spectrometry (SIMS) were applied to analyse the structural properties of the grown films. We used a Hitachi S4100 (25 keV) SEM equipped with a cold field emission cathode and the EBSD system ORKID of ThermoNORAN. For these measurements the samples were tilted by an angle of 70 ° to the electron beam. The crystal orientations were determined by the standard analysis of the Kikuchi pattern. For a detailed investigation of the sample, cross-section transmission electron microscopy (TEM) experiments were carried out with a TENCAI F20 ST at the TU Vienna. Capacity-voltage (C(V)) measurements were used for electrical characterisation of the absorber layers. Current-voltage characteristics of the solar cells were measured under AM1.5 standard test conditions.

2.2 Seed layer preparation

The seed layers were prepared by the aluminium-induced layer exchange (ALILE) process in which a glass/Al/a-Si stack is transformed into a glass/poly-Si/Al(+Si) stack by annealing (500 °C, 2 h) below the eutectic temperature of the Al/Si system. Details of the seed layer preparation can be found in [5]. Prior to the absorber deposition the remaining Al layer with Si inclusions, Al(+Si), on top of the layer stack was removed by wet-chemical treatments and chemical-mechanical-polishing. The resulting poly-Si film (about 200 nm) on glass is p-type due to high doping with Al. It is characterised by large grains (about 20 µm) and a (100) preferential orientation (about 75% of all grains are tilted less then 20° relative to (100)) [6].

2.3 Epitaxial growth

The crystalline Si films discussed here 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. Seed layers and p^+-type Si(100) wafers (2-5 mΩcm) were used as substrates. They were treated by a standard RCA cleaning process and a final HF dip (30 s, 2 % HF:H_2O solution). In the process chamber, prior to the deposition, the substrates were held in hydrogen atmosphere (mTorr-range) for 20 min to obtain stable thermal process conditions. The substrate temperature was about 580 °C. A microwave power of 1000 W was used and the total pressure amounted to about 8 mTorr. The resulting growth rate was 20 nm/min. The process gas consisted of 10 sccm SiH_4 and 10 sccm H_2. For doping we used B_2H_6 solved in H_2 with 5000 ppm (for high doping levels) or 10 ppm

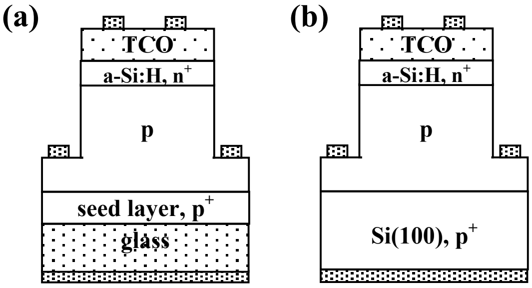

Fig. 1: Schematic structures of Si thin-film solar cells with epitaxial grown absorber layers on the ALILE seed layer (a) and on p^+-type Si(100) wafer (reference cell) (b). On top of the absorber layer a thin n+ type a-Si:H emitter is deposited followed by a ZnO layer acting as TCO.

(for low doping level). The base pressure of the system was about 4×10^{-7} Torr at the process temperature.

The influence of post-deposition treatments like defect annealing and H-passivation of the absorber layers was investigated. Some samples were annealed at 850°C in a preheated quartz tube for about 4 min under N_2 atmosphere. The H-passivation was performed in a standard PECVD system at 400°C for 15 min. A power density of 15 mW/cm² at a pressure of 0.6 mbar was used. Prior to the passivation the samples were HF-dipped in 2% $HF:H_2O$ for 30 s.

2.4 Solar cell preparation

We prepared solar cells on both seed layers and p^+-type Si(100) wafers. Fig. 1 shows the schematic structures of these solar cells. About 2 µm thick absorber layers were grown either on a 200 nm thick poly-Si seed layer on glass (a) or on a p^+-type Si(100) wafer (b). To form the pn-junction of the solar cell a phosphorus-doped a-Si:H emitter layer (20 nm, 2000 ppm phosphine in the gas phase) was deposited by PECVD. Prior to this deposition the samples were treated in 2% $HF:H_2O$ for 30 s to remove the native oxide. On top of the emitter a 80 nm thick ZnO layer was used as transparent conducting oxide (TCO). The area of the cells (about 4 × 4 mm²) was defined by photolithography and wet-chemical mesa-etching. After the mesa-etching Al contacts were deposited on both the TCO and the absorber (the absorber was contacted around the mesa). In addition, in both cell configurations Al was also deposited on the back sides of the substrates. This allows also a vertical measurement of the solar cells on the wafer. In case of glass substrate samples this acts as a simple mirror.

3 RESULTS

3.1 Epitaxial growth of absorber layers

Si films with high crystallographic quality can be grown on Si(100) wafers by ECRCVD up to film thicknesses above 2 µm. However, substrate orientations different from (100) lead to epitaxial films with a high degree of disorder or even complete fine-grained poly-Si films [7]. From these investigations it follows, that a preferential (100) orientation of the seed layer is favourable for epitaxial thickening. However, it also became clear that preferential (100) orientation is not the only requirement for epitaxial growth. The success of epitaxy obviously depends also on the detailed structure of the seed layer grain surface, for instance on the presence of terraces [3].

Fig. 2 shows a TEM cross-section image of a 400 nm thick Si film grown (without B-doping) on a seed layer. On the bottom the glass substrate is shown covered with the seed layer. One grain boundary of the seed layer (GB) is marked in Fig. 2 (known from images with higher magnification). The image presents four typical growth situations. (1) The left part of the film is grown completely fine-grained due to a seed layer grain with a non-suitable crystal orientation. (2) The seed layer grain right from the grain boundary is (100) orientated and therefore completely epitaxially thickened [3]. (3) Locally the epitaxy failed due to crystal defects in the seed layer grain or a local surface contamination. Finally (4) shows the breakdown of epitaxy during the growth e.g. influenced by the accumulation of stress in the growing film. The last case can be caused by a crystal orientation different from (100) and/or the formation and accumulation of crystal defects like dislocations and stacking faults. In order to obtain absorber layers with a high degree of epitaxially thickened grains the most

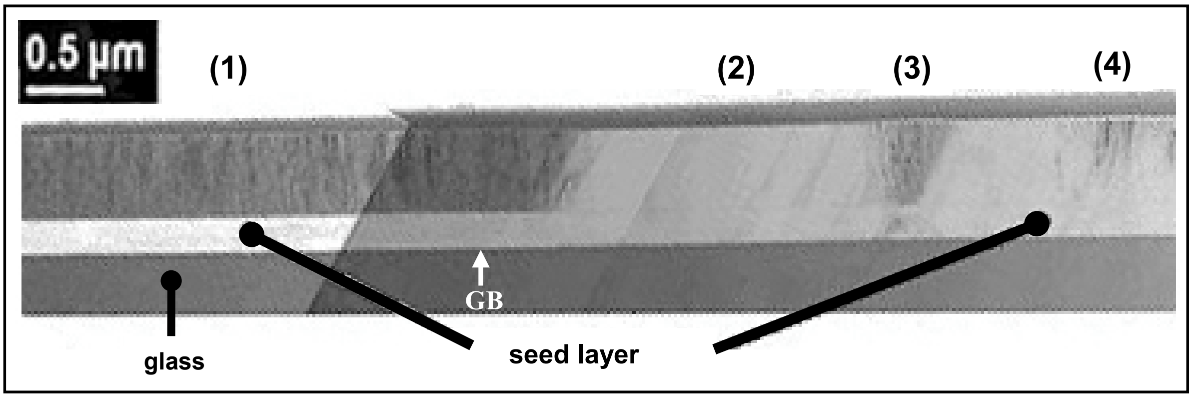

Fig. 2: TEM cross-section (landscape image) of a 400 nm thick Si film grown on an ALILE seed layer. On the bottom the glass substrate is shown covered with the seed layer. The grey region on top of the Si film is glue used in TEM preparation. One grain boundary of the seed layer (GB) is marked (known from images with higher magnification). The image presents four typical growth situations: (1) completely fine-grained growth, (2) completely epitaxially growth, (3) locally failed epitaxy and (4) breakdown of epitaxy during growth.

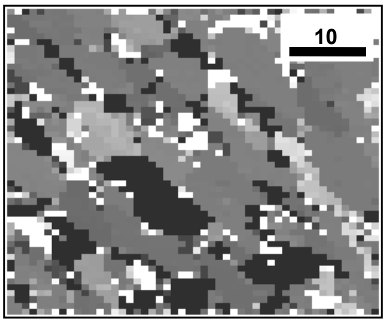

Fig. 3: EBSD orientation map of an about 1.55 µm thick boron-doped (200 ppm) Si film grown mostly epitaxially on an ALILE seed layer (83% of total area). Non-black regions: epitaxial growth. Black: fine-grained Si.

important requirement is a crystal orientation which is as close as possible to (100). As shown in [6] the preferential orientation of the ALILE seed layer can be controlled by the annealing temperature allowing to prepare seed layers with a very high fraction of preferential (100) orientation.

Unintentionally doped Si film grown in our system are always n-type (due to e.g. oxygen contamination). In order to realise a p+/p/n+ cell structure (seed layer/absorber/emitter) the absorber was deposited from silane/diborane gas mixtures. It is known that the presence of boron makes the epitaxial Si growth more difficult. By keeping the substrate temperature as high as possible and by minimising the dopant concentration films could be grown on Si wafers with defect densities comparable to unintentional doped Si films [8].

Both the high degree of preferential (100) orientation and an optimised growth mode for boron-doped films leads to films grown on seed layers with good structural quality even at a thickness of about 1.55 µm. Fig. 3 shows an EBSD crystal orientation map of such a Si film deposited at a boron concentration of 200 ppm [B_2H_6]/[SiH_4]. The regions with different shades of grey are grains where we a crystal orientation could be identified by the method used. The corresponding seed layer grains are completely epitaxially thickened. The black regions are grains where no crystal orientation could be determined. They are of a fine-grained poly-Si structure on the surface as a result of either a completely fine-grained thickened grain or from a well oriented grain where the epitaxy broke down during the growth. From this EBSD map we conclude that the sample is epitaxially thickened on 83% of the area. This is a strong improvement in comparison to previous published results [9]. Even though this sample was grown in the presence of boron.

Fig. 4 shows SIMS depth profiles of B and Al. The sample surface is on the left whereas the seed layer is on the right part of the diagram. The glass substrate is not shown. Boron is incorporated homogeneously in the major part of the film volume. Near to the seed layer and in the seed layer the concentration is considerably enhanced. This profile of B may be explained by the diffusion of boron from the glass (Corning 1737F, $C_B < 5\%$ [10]) into both layers.

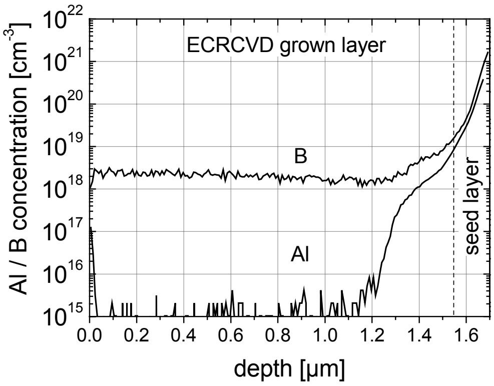

Fig. 4: SIMS depth profiles of B and Al of the 1.55 µm thick Si film (200 ppm [B_2H_6]/[SiH_4]) on ALILE seed layer. The sample surface is on the left whereas the seed layer is on the right part. The glass substrate is not shown.

Boron is incorporated in about the concentration in the gasphase ($3 \times 10^{18} cm^{-3}$). C(V) measurements led to the conclusion that the hole concentration in the p-type film amounts to 3×10^{15} cm^{-3} only. In part this is due to the compensation of the n-type base doping (10^{16} cm^{-3} for non-intentionally doped films) but this result also suggests that part of the boron has been incorporated on non-doping sites.

Beside the incorporation of B the diffusion of Al from the seed layer into the absorber was analysed. The possible diffusion of Al is a very crucial question for this solar cell concept. From the Al profile in Fig. 4 it can be seen, that Al diffusion leads only in the first 300 nm of the grown film to an Al concentration above $10^{15} cm^{-3}$ (detection limit). It is therefore concluded, that the Al diffusion is not a critical aspect.

3.2 Solar cell results

Solar cells were prepared on both seed layers and p^+-type Si(100). We deposited 2 µm thick absorber layers with both a low (5 ppm; $T_S = 590°C$) and a high (on seed layers: 100 ppm, on Si(100): 200 ppm; $T_S = 580°C$) doping level in the premix gas configuration.

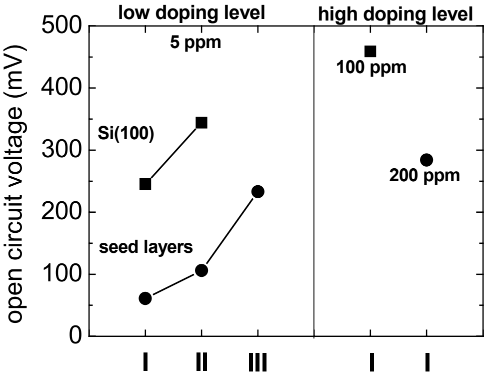

Fig. 5: Open circuit voltage V_{OC} of thin-film solar cells with different absorber doping levels. The absorber layers have been grown by ECRCVD on ALILE seed layers (circles) and Si(100) wafers (squares) with a boron doping ([B_2H_6]/[SiH_4]) of 5 ppm ($T_S = 590°C$) and 100 ppm (on seed layers) or 200 ppm (on Si(100)) ($T_S = 580°C$). The substrate/absorber stacks have been treated differently: state I – as grown; state II – annealed (850 °C, 4 min); state III – annealed (850°C, 4 min) and H-passivated (400°C, 15 min).

Fig. 5 shows the open circuit voltages V_{OC} of both types of solar cells. On ALILE seed layers (circles), as-

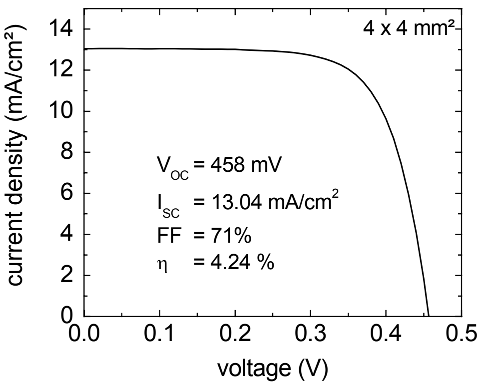

Fig. 6: Current-voltage characteristic of a solar cell consisting of an about 2 µm thick epitaxially grown absorber layer on a p+ type Si(100) wafer (reference system). The pn-junction was formed by a 20 nm thick a-Si:H emitter.

grown (state I) open circuit voltages of 61 mV and 284 mV were obtained with 5 ppm and 200 ppm, respectively. For comparison, using IAD for the epitaxial growth an as-grown V_{OC} of 220 mV was reported [11]. Only the sample with a doping level of 5 ppm has received additional treatments after the absorber layer deposition. A defect annealing step prior to the emitter deposition resulted in an increase of V_{OC} from 61 mV to 106 mV (state II in Fig. 5). The V_{OC} was further increased to 233 mV (state III) by an additional hydrogen passivation step. This shows clearly that additional treatments (defect annealing and defect passivation) are necessary to obtain reasonable open circuit voltages.

Under this aspect, the as-grown V_{OC} of 284 mV obtained at the higher doping level is a very promising result. It is expected that additional treatments and the optimisation of the doping level will lead to a strong increase of the V_{OC}.

Fig. 5 also includes the results obtained for the reference system on Si(100) (squares). As can be seen, the as grown V_{OC} (state I) of the solar cells with the low doping level increases from 245 mV to 344 mV through a defect annealing treatment. At a higher doping level (100 ppm) we obtained a V_{OC} of 458 mV even without any treatment of the absorber layer. The corresponding I-V curve of the solar cell is presented in Fig. 6. The efficiency of this cell is 4.24% at a short-circuit current (I_{SC}) of 13.04 mA/cm² and a FF of 71%. These results, especially the FF are very encouraging and proving the concept of ECRCVD grown absorber layers for low-temperature preparation of solar cells.

4 SUMMARY AND CONCLUSIONS

In summary, we studied the epitaxial growth of solar cell absorber layers deposited by ECRCVD at temperatures below 600°C. On poly-Si seed layer made by ALILE we obtained a high degree of epitaxially thickened grains (83% of total area) even at 1.55 µm thickness and the presence of boron. The incorporation profiles of B and Al were investigated by SIMS showing a mostly homogeneous boron profile and an only insignificant Al diffusion profile from the seed layer into the absorber.

Solar cells were prepared using an a-Si:H emitter (n^+) and different absorber doping levels. Promising open circuit voltages of up to 284 mV were achieved for higher doping concentration even without any additional absorber layer treatment. The potential of such treatments has been shown for solar cells with low absorber doping leading to an increase of V_{OC} from 61 mV to 233 mV. Therefore, it is expected that the application of additional treatments together with the optimisation of the boron doping level will lead to much higher V_{OC}'s.

Solar cell results of the reference system using p^+-type Si(100) wafers as substrates for epitaxy have also been presented. A solar cell efficiency of 4.24% was achieved by a V_{OC} of 458 mV for a sample without any absorber treatments. These encouraging results are proving the concept of ECRCVD grown absorber layers for low-temperature preparation of solar cells.

In addition to post-treatments of the absorber layers the optimisation of the seed layers towards an as high as possible fraction of preferential (100) orientation and an as perfect as possible crystal structure are important tasks to increase the cell performance of the solar cells grown on ALILE seed layers.

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