Strasbourg (France)

MANUSCRIPT COVER PAGE FORM

E-MRS Symposium : Symposium F: Thin film and nano-structured materials for photovoltaics
Paper Number : F-II.01
Title of Paper : LARGE-GRAINED POLYCRYSTALLINE SILICON ON GLASS FOR THIN-FILM SOLAR CELLS

Corresponding Author : S. Gall

Full Mailing Address : Hahn-Meitner-Institut Berlin
Kekuléstr. 5
12489 Berlin
Germany

Telephone : +49 30 8062 1309
Fax : +49 30 8062 1333
E-mail : gall@hmi.de

LARGE-GRAINED POLYCRYSTALLINE SILICON ON GLASS FOR THIN-FILM SOLAR CELLS

S. Gall [1 *], J. Schneider [1], J. Klein [1], K. Hübener [1 **], M. Muske [1], B. Rau [1], E. Conrad [1],
I. Sieber [1], K. Petter [1], K. Lips [1], M. Stöger-Pollach [2], P. Schattschneider [2], W. Fuhs [1]

[1] Hahn-Meitner-Institut Berlin, Kekuléstr. 5, D-12489 Berlin, Germany
[2] Technische Universität Wien, Wiedner Hauptstr. 8, A-1040 Wien, Austria

We have investigated the formation of large-grained polycrystalline silicon (poly-Si) films on glass for thin-film solar cells using the ‘seed layer concept’ which is based on the epitaxial thickening of a thin large-grained poly-Si template (seed layer). Due to the glass substrate all process steps are limited to a temperature of about 600 °C. The aluminium-induced layer exchange (ALILE) process based on the aluminium-induced crystallisation (AIC) of amorphous Si has been used to prepare p^+-type seed layers featuring large grains and a high preferential (100) orientation of the surface. The seed layers have been thickened by electron cyclotron resonance chemical vapour deposition (ECRCVD) to form the p-type absorber of the solar cell. First poly-Si thin-film solar cell structures have been prepared by deposition of an n^+-type a-Si:H emitter. So far an open circuit voltage of 284 mV has been reached without any additional treatments like defect annealing and defect passivation.

---

[*] Corresponding author: Stefan Gall, Hahn-Meitner-Institut Berlin, Kekuléstr. 5, D-12489 Berlin, Germany, phone/fax: +49-(0)30-8062-1309/1333, e-mail: gall@hmi.de

[**] Present affiliation: Freie Universität Berlin, Germany

INTRODUCTION

The production of solar cells has grown dramatically during the last decade. In 2004 the world wide production of solar cells reached about 1.23 GWp [1] corresponding to a growth rate of about 67 % as compared to 2003. With a share of more than 90 % wafer-based crystalline silicon solar cells are dominating the market. In order to maintain high growth rates in the future significant cost reductions are necessary. This can be achieved by reduction of the silicon thickness because thin crystalline Si solar cells have the potential for high efficiencies, too. The potential has already been demonstrated by the preparation of a solar cell with an efficiency of 21.5 % on a thinned-down monocrystalline Si wafer with a thickness of 47µm [2]. Unfortunately this is not a real Si thin-film technology but still a Si wafer technology. It is expected that on a long term a real Si thin-film technology, which uses deposition methods on large-area low-cost glass substrates, has a higher potential for cost reduction. Such a thin-film technology requires the preparation of high quality Si layers (i.e. comparable to the wafer-based material) on glass by an industrially applicable process. The Si thin-film solar cells available on the market today are based on hydrogenated amorphous Si (a-Si:H) and microcrystalline Si (µc-Si:H). The big advantage of both technologies is that the Si films can be prepared at very low temperatures (below 300 °C) using plasma enhanced chemical vapour deposition (PECVD). At these low temperatures hydrogen from the gas phase passivates defects already during the deposition. Although reasonable efficiencies have already been reached in the laboratory (e.g. 10 % with µc-Si:H [3]) both materials do not have the potential for very high single-junction efficiencies because the structural quality is relatively poor. To overcome the efficiency limits the material quality has to be improved strongly. Large-grained polycrystalline Si (poly-Si) characterised by both (i) a grain size much larger than the film thickness and (ii) an intra-grain quality comparable to wafer-based Si seems to be a suitable material for high efficiency Si-based thin-film solar cells on glass. The preparation of such large-grained poly-Si films is a big challenge because the glass substrate limits the process temperatures to about 600 °C. Several concepts have been studied to prepare large-grained poly-Si films on glass. Due to the fact that the direct deposition of Si on glass below 600 °C always results in material with a grain size much smaller than the film thickness, the techniques investigated so far are all based on a two step process. In a first step an amorphous Si (a-Si) film is deposited and in a second step this a-Si film is crystallised. For example, the a-Si layer can be crystallised thermally at about 600 °C (solid phase crystallisation - SPC). At such low temperatures the process is relatively slow and the Si films formed by SPC feature a grain size comparable to the film thickness (about 1µm). In the early nineties the company Sanyo investigated this technique for the preparation of Si thin-film solar cells. In 1995, Sanyo reached a cell efficiency of 9.2 % on 1 cm^2 in the laboratory [4]. Recently the company Pacific Solar developed mini-modules based on SPC featuring module efficiencies of above 8 % [5]. However, it remains questionable whether Si films prepared by SPC are suitable for thin-film solar cells with very high efficiencies. Therefore ongoing research is necessary to develop suitable large-grained poly-Si films. In 1998, O. Nast et al. presented a new technique to prepare poly-Si films on glass [6-8]. The corresponding process is called aluminium-induced layer exchange (ALILE). The resulting poly-Si films feature large grains (much larger than the film thickness) and a high preferential (100) orientation of the surface of the grains [9]. Due to the fact that Al is incorporated into the poly-Si film during the ALILE process (Al is an acceptor in Si) the resulting poly-Si film is heavily doped (p^+-type) [10]. The hole concentration is in the order of 10^{18} cm^{-3}. Because of the high doping level and the resulting low minority carrier lifetime the poly-Si films prepared by the ALILE process are not suitable as absorber layers of solar cells. But due to the large grain size and the high preferential (100) orientation these poly-Si films are very attractive as template (seed layer) for a subsequent epitaxial thickening process. A high preferential (100) orientation of the seed layer is favourable for the epitaxial thickening at low temperatures. Such a ‘seed layer concept' allows the preparation of large-grained absorber layers for Si thin-film solar cells. The epitaxial thickening of a seed layer at temperatures as low as 600 °C requires deposition techniques which provide additional non-thermal energy to the surface of the growing film. It has been demonstrated that techniques like electron cyclotron resonance chemical vapour deposition (ECRCVD) [11] or ion assisted deposition (IAD) [12] make low-temperature Si epitaxy possible. However, the quality of the grown films has to be improved. We have grown p-type absorber layers by ECRCVD onto the p^+-type seed layers (prepared by the ALILE process). In this configuration the p^+-type seed layer acts as back surface field (BSF). After the growth of the absorber layer an n^+-type a-Si:H emitter, a transparent conductive oxide (TCO) and metal contacts are deposited to form a solar cell structure. The corresponding scheme of such a large-grained poly-Si thin-film solar cell is shown in Fig. 1. In the present paper we describe the development of large-grained poly-Si films on glass for Si thin-film solar cells using the above mentioned 'seed layer concept'. The corresponding results will be presented in the sections 'seed layer formation' and 'low-temperature epitaxy'. Afterwards we will report on 'first solar cell structures'. The concept presented here is characterised by a high risk due to many scientific and technological questions which are not yet answered. But in case of success this concept could lead to high efficiency Si thin-film solar cells on glass with a high potential for cost reduction.

SEED LAYER FORMATION

In this section the seed layer formation by the aluminium-induced layer exchange (ALILE) process is described. The process is based on the aluminium-induced crystallisation (AIC) of amorphous Si. The starting point for the ALILE process is a glass/Al/a-Si stack. For our experiments we have used cleaned glass substrates (Corning 1737F). Both layers (Al and a-

Si) have been deposited in the same chamber by dc magnetron sputtering. The ALILE process requires a thin permeable membrane between the Al and the a-Si layer which controls the diffusion of Al and Si [13]. Usually the membrane consists of an Al oxide layer formed by exposure to air of the Al-coated glass substrate prior to the a-Si deposition. Our standard oxidation time is 2 hours. The thickness of the deposited films is about 300 nm and 375 nm for Al and a-Si, respectively. The excess of Si compared to Al is necessary for the preparation of continuous poly-Si films on the glass substrate. Annealing of the initial glass/Al/a-Si stack at temperatures below the eutectic temperature of the Al/Si system (T_{eu} = 577 °C) leads to a layer exchange and a concurrent crystallisation of Si resulting in a glass/poly-Si/Al(+Si) stack (Fig. 2). The membrane stays in place during the entire ALILE process (indicated by a grey line in Fig. 2). Thus, the thickness of the resulting poly-Si film (seed layer) is determined by the thickness of the initial Al layer. The Al layer on top of the seed layer contains some Si inclusions (‘Si islands’).

The ALILE process starts with the diffusion of Si across the permeable membrane into the Al layer. This leads to an increase of the Si concentration within the Al layer until the critical concentration for nucleation is reached. Then, Si nuclei are formed within the Al layer. These nuclei grow in all directions until they are confined vertically between the glass substrate and the permeable membrane. Afterwards the growth continues laterally only. The continuous formation of new nuclei and their growth reduces the Si concentration until it drops below the critical concentration for nucleation. By this mechanism further nucleation is suppressed such that the final poly-Si films feature large grains. Due to the fact that the Al layer is still supersaturated (i.e. the Si concentration exceeds the saturation concentration) the growth of existing grains continues in lateral direction until adjacent grains touch each other and finally form a continuous large-grained poly-Si film on the glass substrate. Using the Al/Si phase diagram and thermodynamic considerations the ALILE process and especially the suppression of nucleation as a characteristic feature can be understood [14].

The samples have been annealed at temperatures between 400 °C and 550 °C (i.e. well below the eutectic temperature of the Al/Si system). The annealing temperature has a strong effect on the ALILE process: The higher the annealing temperature the higher is the nucleation density resulting in smaller grains and the shorter is the process time. For example, at 500 °C it usually takes less than 30 minutes to form a continuous poly-Si film on the glass substrate.

The nucleation and the subsequent growth can be observed directly during the ALILE process using an optical microscope equipped with a heating stage. The samples are placed upside down onto the heater such that the initial glass/Al interface can be studied through the transparent glass substrate. Due to the different reflectivity of Al and Si it is possible to distinguish between these two materials. Figure 3 shows an optical micrograph of a sample during the layer exchange process (after about 4 days at 400 °C). The almost round-shaped dark spots correspond to Si grains grown out of a single Si nucleus and the bright areas correspond to Al which is still on top of the glass. Almost all dark spots show the same size (already about 100 µm in diameter). This can be put down to the fact that the nucleation has taken place at about the same time and that thereafter nucleation is almost entirely suppressed. The nucleation density determined from the number of dark spots in the optical micrograph here amounts to about 67 mm^{-2}. This very low nucleation density has been caused not only by the low annealing temperature of 400 °C but also by a special preparation of the permeable membrane. The membrane of this sample has not been formed by exposure to air for 2 hours at room temperature (‘normal Al oxide layer’ – our standard process) but in a furnace by exposure to an oxygen atmosphere for 2 hours at 560 °C (‘thick Al oxide layer’). Compared to our standard process such a ‘thick Al oxide layer’ leads to both a lower nucleation density and a longer process time. For the specimen shown in Fig. 3 it took more than 6.5 days to complete the layer exchange. These extreme conditions have been chosen to demonstrate that the ALILE process can lead to very low nucleation densities. Of course, such a slow process is technologically not interesting. But, if desired, the process time can be reduced to less than 2 hours by increasing the annealing temperature from 400 °C to 540 °C [15]. Aiming at a low nucleation density the usage of a ‘thick Al oxide layer’ is very appealing.

In the introduction of this paper the importance of a high preferential (100) orientation of the seed layer for the subsequent epitaxial growth at low temperatures has been mentioned. Therefore, we have investigated the orientation of the grains of the poly-Si film using electron back scatter diffraction (EBSD). Figure 4 shows the inverse pole figure of an EBSD orientation map of a poly-Si film formed by the ALILE process. The agglomeration of EBSD measurement points close to the (100) corner of the inverse pole figure is clearly visible. About 75 % of the area under investigation is tilted by less than 20 ° with respect to the perfect (100) orientation. In Fig. 4 the corresponding region of the inverse pole figure is indicated by a dashed line. We have used this definition (less than 20 ° tilt with respect to the perfect (100) orientation) to quantify the preferential (100) orientation $R_{(100)}$ of our samples. Kim et al. have shown that the preferential (100) orientation can be influenced by the annealing temperature [16]. With decreasing annealing temperature the preferential (100) orientation increases. In our experiments we have observed the same behaviour. We have been able to change the preferential (100) orientation $R_{(100)}$ from about 40 % to about 70 % by decreasing the annealing temperature T_A from 550 °C to 450 °C (Fig. 5, solid circles). However, decreasing the annealing temperature always results in an undesired increase of the process time. We have found that the preferential (100) orientation is not only influenced by the annealing temperature but also by the way the permeable membrane has been formed. The results in Fig. 5 (solid circles) have been observed on samples with a membrane formed by exposure to air for about 2 hours at room temperature. Samples with a membrane formed in a furnace at 560 °C by exposure to an oxygen atmosphere for about 2 hours show a different behaviour (Fig. 5, open circles). Using the same annealing temperature these samples feature a much lower preferential (100) orientation. $R_{(100)}$ has been reduced from about 70 % to about 30 % at 450 °C and from about 40 % to about 10 % at 550 °C. This means that reducing the annealing temperature always leads to an increase of $R_{(100)}$, even for the samples with a ‘thick Al oxide layer’. Unfortunately, the reason for the preferential (100) orientation and the dependence on both the annealing temperature and the way the permeable membrane has been formed is not fully understood. First ideas have been developed which are based on energetic considerations during nucleation [17]. Due to the fact that a high preferential (100) orientation of the seed layer is favourable for the subsequent epitaxial thickening process the focus for further investigations has not been set on ‘thick Al oxide layers’ but on ‘normal Al oxide layers’.

At termination of the ALILE process the continuous poly-Si film is covered by the permeable membrane and the Al(+Si) layer containing ‘Si islands’ (see Fig. 2). Both layers have to be removed completely prior to the subsequent epitaxial thickening process. We have applied chemical mechanical polishing (CMP) to remove these layers.

A drawback of the ALILE process (Fig. 2) and the related scheme of a Si thin-film solar cell (Fig. 1) is that the conductivity of the resulting thin p^+-type seed layer is not high enough to achieve a low series resistance of the final solar cell structure (the current has to flow laterally within the seed layer to reach the next metal contact of the absorber layer - not shown in Fig. 1). From that point of view it would be desirable to have a metal layer between the glass substrate and the p^+-type seed layer. This can be reached for example by the ‘inverse’ ALILE process. In contrast to the ‘normal’ ALILE process described above the ‘inverse’ ALILE process starts with a glass/a-Si/Al stack. The thickness of the a-Si and Al layers is 375 nm and 300 nm, respectively (as for the ‘normal’ ALILE process). During an annealing step below the eutectic temperature this stack is transformed into a glass/Al(+Si)/poly-Si stack. This means that the required metal layer between the glass substrate and the p^+-type seed layer is automatically formed. Another advantage of the ‘inverse’ ALILE process is that the seed layer is directly accessible for the subsequent epitaxial thickening process. The ‘inverse’ ALILE process requires a permeable membrane, too. This membrane can also be prepared by exposure to air at room temperature. But this time a Si oxide layer is formed. In comparison with the creation of an Al oxide layer the Si oxide layer formation takes much longer (days instead of hours), because a-Si is not as reactive as Al regarding oxide formation. It is very remarkable that the layer exchange takes place even if completely different permeable membranes are used.

To investigate the nucleation and the subsequent growth during the ‘inverse’ ALILE process the glass side of the samples is placed onto the heater of the optical microscope. Thus, the surface of the sample (initially Al) is observed. The optical micrographs recorded during the ‘inverse’ ALILE process have been transformed into binary black and white images. The ratio of the black areas (corresponding to crystalline Si) to the total area is called crystallised fraction R_C. During the layer exchange process the crystallised fraction increases gradually from 0 % (only Al at the surface) to 100 % (continuous poly-Si film at the surface). In Fig. 6, the crystallised fraction R_C is shown as a function of the annealing time t_A for a sample where the Si oxide layer has been formed by exposure to air for 7 days (dashed line) (please note that the annealing time is shown on a logarithmic scale). At 480 °C, which is a moderate annealing temperature, it took less than 10 min to form a continuous poly-Si film on top of an Al(+Si) layer. Although the sample has been oxidised already for 7 days the nucleation density has still been relatively high (normally long oxidation times result in low nucleation densities). Therefore we have also studied thermal oxidation of the initial a-Si layer. This has been carried out in a furnace by exposure to an oxygen atmosphere for 2 hours at the oxidation temperature T_{ox} (the oxidation temperature mentioned here is the target temperature - the real temperature is to a certain extent lower than the target temperature). The oxidation temperature T_{ox} has been varied between 450 °C and 590 °C. The corresponding results of the crystallised fraction are shown in Fig. 6 (solid lines) for an annealing temperature of 480 °C. With increasing oxidation temperature the process time increases. For T_{ox} = 450 °C the layer exchange took less than 20 min (left solid line) while for T_{ox} = 590 °C it took about 400 min (right solid line). In comparison to the sample naturally oxidised for 7 days at room temperature (dashed line) the process times are longer, even for the sample thermally oxidised for 2 hours at only 450 °C. The poly-Si films prepared by the ‘inverse’ ALILE process feature a preferential (100) orientation, too. For example, the preferential (100) orientation $R_{(100)}$ of a sample thermally oxidised for 2 hours at 500 °C and annealed at 420 °C is about 85 % (using the 20 ° tilt definition mentioned above). This value is even higher than the values obtained using the ‘normal’ ALILE process. For the ‘inverse’ ALILE process the temperature of subsequent processes is limited to the eutectic temperature of the Al/Si system (T_{eu} = 577 °C) because both Al and Si are present in the glass/Al(+Si)/poly-Si structure. This makes the subsequent epitaxial thickening very challenging. Furthermore, the existence of Al reduces dramatically the possibilities of the application of chemicals (e.g. hydrofluoric acid) during the following processes. Based on these disadvantages we have decided to focus on the ‘normal’ ALILE process to form p^+-type poly-Si seed layers suitable for the subsequent low-temperature epitaxy step.

LOW-TEMPERATURE EPITAXY

We have studied the epitaxial growth of Si at low temperatures (below 600 °C) on both Si wafers (mono- and multicrystalline) and poly-Si seed layers (prepared by the ALILE process). Prior to the growth the substrates (Si wafers and poly-Si seed layers) have been cleaned by a standard RCA procedure. A final dip in hydrofluoric acid (HF (2 %)) has been applied to remove the native oxide. The films have been grown by ECRCVD using hydrogen (H_2) as excitation gas and a mixture of silane (SiH_4), diborane (B_2H_6) and hydrogen (H_2) as process gas. In the ECRCVD process additional non-thermal energy is provided to the surface of the growing film which supports epitaxial growth at low temperatures. However, at low temperatures the structural quality of the grown Si films depends strongly on the crystallographic orientation of the substrate. Best results have been obtained on Si(100) wafers, where Si films have been grown epitaxially with a thickness of up to 2.5 µm [18]. On some substrates (e.g. on Si(311) wafers) epitaxial growth has been observed only at the beginning of the deposition process. After a certain critical thickness the growth has changed to fine-crystalline growth. On Si(110) and Si(111) wafers no epitaxial growth has been observed. The dependence of the Si growth on the substrate orientation is clearly visible in Fig. 7 showing a scanning electron microscopy (SEM) image of the surface of a 760 nm thick Si film grown without boron doping at 510 °C on a multicrystalline Si wafer. Three regions with completely different morphologies of the grown Si film are visible. The difference of the morphology is caused by different orientations of the underlying grains of the multicrystalline Si wafer. The surface of the grown Si film in region 1 is smooth indicating good epitaxial growth. In region 2 the surface consists of both smooth and rough parts. This corresponds to the fact that the underlying grain has been thickened epitaxially (smooth parts) but the growth has locally changed to fine-crystalline Si (rough parts). Within the growing film these fine-crystalline Si regions are shaped like an inverse pyramid with the tip at or close to the substrate/film interface (not shown here) [19]. At the surface these regions are square-shaped with pyramid-like extensions sticking out of the smooth parts (roughly visible in Fig. 7). In region 3 the complete surface is rough due to fine-crystalline growth. The underlying grains of the regions 1, 2, and 3 are orientated close to (410), (210), and (221) corresponding to a tilt with respect to the (100) orientation of about 8 °, 27 °, and 48 °, respectively. This means that only the (410) orientation is within the crystallographic region we have used for the quantification of the preferential (100) orientation. To get more information on the structural quality of the films we have carried out Secco etch experiments (HF (50 %) : 0.15 mol $K_2Cr_2O_7$ mixed 2:1). Fig. 8 shows an SEM image of a sample surface Secco-etched for 10 s. The Si film under investigation has been grown epitaxially onto a Si(100) wafer at 580 °C using boron doping ($[B_2H_6]/[SiH_4]$ = 100 ppm). The thickness of the film is about 2.1 µm. The large square-shaped etch pit 'P' shown in Fig. 8 corresponds to the already mentioned pyramid-shaped defect region. The inverse pyramid within the film is confined by stacking faults or twins in (111) planes. On a (100) surface this leads to lines in <110> directions which define the square-shaped etch pit 'P'. The density of etch pits 'P' is about 1.2 x 10^5 cm^{-2}. In addition three other types of etch pits have been observed ('L', 'E', and 'R' in Fig. 8). The line-shaped etch pit 'L' is caused by stacking faults in (111) planes leading again to lines in <110> directions on the (100) surface (the density is about 5 x 10^6 cm^{-2}). The elliptical ('E') etch pits are caused by line-shaped defects, mainly dislocations. The round ('R') etch pits correspond probably also to line-shaped defects but orientated in directions nearly perpendicular to the surface. The density of etch pits 'E' and 'R' is about 6 x 10^8 cm^{-2} and 5 x 10^6 cm^{-2}, respectively. Further investigations are necessary to identify all observed etch pits. The Secco experiments show clearly that the structural quality of the films has to be optimised further, even on Si(100) wafers.

We have grown Si films not only on Si wafers (which have been used as reference substrates only) but also on poly-Si seed layers. Figure 9 shows a transmission electron microscopy (TEM) cross section of a 400nm thick Si film grown at 560 °C on a seed layer/glass structure (the film deposited by ECRCVD has not been doped with boron) [20]. Two seed layer grains are shown (the corresponding grain boundary is marked). The surface orientation of these grains has been determined by analysis of the electron diffraction patterns. The surface of the grain on the right hand side is (100) orientated. This grain has been epitaxially thickened. The surface of the grain on the left hand side is tilted by 7.8 ° with respect to (100). On this grain fine-crystalline Si has been grown. This shows clearly that a relatively small tilt with respect to (100) can already lead to fine-crystalline growth of Si. This means that not all seed layer surfaces tilted by less than 20 ° with respect to (100) can be thickened epitaxially.

EBSD investigations of a boron-doped Si film ($[B_2H_6]/[SiH_4]$ = 200 ppm) grown at 580 °C have shown that approximately 83 % of the surface has been thickened epitaxially. Considering the strong dependence of the growth on the orientation of the underlying grains, epitaxial growth on 83 % of the seed layer surface is an excellent result. Due to the fact that a thin-film solar cell based on such a material can be considered as a parallel connection of both a high and a low quality solar cell, the remaining fine-crystalline Si (about 17 %) limits not only the short circuit current but also the open circuit voltage of the device.

Figure 10 shows the concentration of boron (C_B) and aluminium (C_{Al}) within this sample. The depth profiles have been measured using secondary ion mass spectrometry (SIMS). Light and deep grey correspond to absorber layer and seed layer, respectively. At $[B_2H_6]/[SiH_4]$ = 200 ppm the boron concentration within the absorber layer is about 2-3 x 10^{18} cm^{-3}. However, the effective doping level obtained by capacitance-voltage (C-V) measurements (using a Schottky diode) is only about 3 x 10^{15} cm^{-3}. The large difference is probably caused by a low doping efficiency (inactive boron atoms) and the compensation of the n-type behaviour usually observed for samples without boron doping. The boron concentration increases towards the glass substrate due to boron diffusion out of the glass substrate. Roughly the same behaviour has been observed for the aluminium concentration (the seed layer and the glass substrate act as a source for aluminium diffusion into the absorber layer). However, the aluminium concentration within the main part of the grown film is below the detection limit of about 10^{15} cm^{-3}. Consequently the diffusion of aluminium should not pose a problem for the solar cells.

FIRST SOLAR CELL STRUCTURES

Based on the ‘seed layer concept’ described above we have prepared first Si thin-film solar cells on glass. The basic structure (see Fig. 1) consists of a p^+-type poly-Si seed layer (about 200 nm), a p-type poly-Si absorber (about 2000 nm), an n^+-type a-Si:H emitter (about 20 nm), and a TCO window layer (about 80 nm ZnO). The area of the solar cells (about 4 mm x 4 mm) has been defined by photolithography and wet-chemical mesa etching. After the mesa etching metal contacts (Al) have been deposited on both the TCO and the absorber (the absorber has been contacted around the mesa). A solar cell with a boron-doped absorber of 5 ppm ($[B_2H_6]/[SiH_4]$) grown at 590 °C has shown an open circuit voltage V_{oc} of only 61 mV (state I – as grown). The quality of the absorber can be improved by a very short ‘high temperature step’ (which is far above the deposition temperature of the absorber). Such a defect annealing step (4 min at 850 °C) of the glass/seed layer/absorber stack prior to the emitter deposition has led to an increase of V_{oc} to 106 mV (state II – annealed). The V_{oc} has been further increased to 233 mV by an additional hydrogen passivation step in a PECVD chamber (state III – annealed and passivated). The passivation step (15 min at 400 °C) has been carried out after the annealing step (4 min at 850 °C) and prior to the emitter deposition. The passivation of defects by hydrogen is a very important separate step during the preparation of poly-Si thin-film solar cells because at deposition temperatures of about 600 °C almost no hydrogen remains in the poly-Si films and thus the defects are not passivated.

Although the V_{oc} has been increased strongly by the application of both defect annealing and defect passivation the obtained open circuit voltage is still very low. We have found that the boron doping we used for the above mentioned solar cells is insufficient. Therefore we have increased the boron doping from $[B_2H_6]/[SiH_4]$ = 5 ppm to 200 ppm (the effective doping level at 200 ppm is only about 3 x 10^{15} cm^{-3}, see above). Using an absorber grown at 580 °C with a boron doping of 200 ppm we have reached an open circuit voltage of 284 mV. This result has been obtained without any additional treatments – neither defect annealing nor defect passivation (state I – as grown). The results described here are summarised in Fig. 11 showing the beneficial effect of both additional treatments (from state I, via state II to state III) and an increased boron doping (from 5 ppm to 200 ppm). Using IAD for the epitaxial growth of the absorber layer Aberle at al. have reached an as-grown V_{oc} of 220 mV [21]. Considering the early stage of the development the as-grown V_{oc} of 284 mV we have obtained using ECRCVD is a very promising result. It is expected that the actual V_{oc} can be improved significantly applying both defect annealing and defect passivation.

SUMMARY AND CONCLUSION

This paper describes the development of large-grained poly-Si films on glass by the ‘seed layer concept’. We have investigated the preparation of seed layers by both the ‘normal’ and the ‘inverse’ ALILE process. It has been shown that the permeable membrane plays a significant role controlling the process time, the nucleation density (i.e. grain size) and the preferential (100) orientation. Therefore it is a key element for further optimisation of the seed layer. The importance of a high preferential (100) orientation of the seed layer for the subsequent epitaxial growth at low temperatures has been emphasised. Using our definition we have observed so far a preferential (100) orientation of up to 75 % and 85 % for the ‘normal’ and the ‘inverse’ ALILE process, respectively. This has to be optimised further because the growth of Si by ECRCVD depends strongly on the orientation of the underlying grain. The dependence of the Si growth on the orientation of the substrate has been studied using Si wafers. Using Secco etch experiments we have investigated the structural quality of Si films grown epitaxially on Si(100) wafers. Several types of etch pits have been found and partly identified. The experiments show clearly that the epitaxial growth has to be improved, even on Si(100) surfaces. We have grown Si by ECRCVD on seed layers prepared by the ‘normal’ ALILE process. Approximately 83 % of the surface has been thickened epitaxially. This has to be enhanced, too. The aluminium diffusion into the absorber layer from both seed layer and glass substrate seems to be no problem for the development of solar cells. Using the ‘seed layer concept’ first solar cells have been prepared. With a non-optimised boron doping we have reached an as-grown open circuit voltage of 284 mV. Applying both defect annealing and defect passivation it is expected that the V_{oc} improves significantly. The preparation of large-grained poly-Si films suitable for high efficiency thin-film solar cells on glass remains a big challenge. However, considering the early stage of the development the results obtained so far are encouraging.

ACKNOWLEDGEMENTS

The authors would like to thank K. Jacob, S. Kreutzmann, and C. Klimm from HMI for technical assistance during sample preparation. This work has been financially supported by the European Commission (METEOR project, contract N°: ENK5-CT-2001-00543).

REFERENCES

[1] M. Schmela and J. Siemer, Photon (German version) 4/2005 (2005) 28.

[2] J. Zhao, A. Wang, S.R. Wenham, and M.A. Green, Proc. of the 13th European Photovoltaic Solar Energy Conference, Nice, France (1995) 1566.

[3] K. Yamamoto, M. Yoshimi, T. Sazuki, Y. Tawada, Y. Okamoto, and A. Nakajima, Proc. of the 2nd World Conference on Photovoltaic Energy Conversion, Vienna, Austria (1998) 1284.

[4] T. Matsuyama, N. Terada, T. Baba, T. Sawada, S. Tsuge, K. Wakisaka, and S. Tsuda, J. Non-Crystalline Solids 198-200 (1996) 940.

[5] P.A. Basore, Proc. of the 19th European Photovoltaic Solar Energy Conference, Paris, France (2004) 455.

[6] O. Nast, T. Puzzer, L.M. Koschier, A.B. Sproul, and S.R. Wenham, Appl. Phys. Lett. 73 (1998) 3214.

[7] O. Nast and S.R. Wenham, J. Appl. Phys. 88 (2000) 124.

[8] O. Nast and A.J. Hartmann, J. Appl. Phys. 88 (2000) 716.

[9] O. Nast, T. Puzzer, C.T. Chou, and M. Birkholz, Proc. of the 16th European Photovoltaic Solar Energy Conference, Glasgow, UK (2000) 292.

[10] O. Nast, S. Brehme, S. Pritchard, A.G. Aberle, and S.R. Wenham, Solar Energy Materials & Solar Cells 65 (2001) 385.

[11] J. Platen, B. Selle, I. Sieber, S. Brehme, U. Zeimer, and W. Fuhs, Thin Solid Films 381 (2001) 22.

[12] R.B. Bergmann, C. Zaczek, N. Jensen, S. Oelting, and J.H. Werner, Appl. Phys. Lett. 72 (1998) 2996.

[13] S. Gall, J. Schneider, M. Muske, I. Sieber, O. Nast, and W. Fuhs, Proc. of PV in Europe – From PV Technology to Energy Solutions, Rome, Italy (2002) 87.

[14] J. Schneider, J. Klein, A. Sarikov, M. Muske, S. Gall, and W. Fuhs, Mat. Res. Soc. Symp. Proc. 862 (2005) in press.

[15] J. Schneider, J. Klein, M. Muske, A. Schöpke, S. Gall, and W. Fuhs, Proc. of the 3rd World Conference on Photovoltaic Energy Conversion, Osaka, Japan (2003) 106.

[16] H. Kim, D. Kim, G. Lee, D. Kim, and S.H. Lee, Solar Energy Materials & Solar Cells 74 (2002) 323.

[17] J. Schneider, I. Sieber, A. Sarikov, J. Klein, M. Muske, S. Gall, and W. Fuhs, will be submitted to J. Crystal Growth.

[18] B. Rau, I. Sieber, B. Selle, S. Brehme, U. Knipper, S. Gall, and W. Fuhs, Thin Solid Films 451-452 (2004) 644.

[19] B. Rau, B. Selle, U. Knipper, S. Brehme, I. Sieber, M. Stöger, P. Schattschneider, S. Gall, and W. Fuhs, Proc. of the 3rd World Conference on Photovoltaic Energy Conversion, Osaka, Japan (2003) 1237.

[20] B. Rau, I. Sieber, J. Schneider, M. Muske, M. Stöger-Pollach, P. Schattschneider, S. Gall, and W. Fuhs, J. Crystal Growth 270 (2004) 396.

[21] A.G. Aberle, A. Straub, P.I. Widenborg, A.B. Sproul, Y. Huang, and P. Campbell, Progress in Photovoltaics: Research and Applications 13 (2005) 37.

LIST OF FIGURE CAPTIONS

Fig.1: Scheme of a large-grained polycrystalline Si (poly-Si) thin-film solar cell on glass. The structure consists of a p^+-type large-grained poly-Si seed layer, a p-type large-grained poly-Si absorber, an n^+-type a-Si:H emitter, a transparent conductive oxide (TCO), and metal contacts to the TCO and the absorber (not shown here).

Fig. 2: Schematic illustration of the ‘normal’ aluminium-induced layer exchange (ALILE) process. During an annealing step the initial glass/Al/a-Si stack is transformed into a glass/poly-Si/Al(+Si) stack. The permeable membrane between the layers (grey lines) stays in place during the ALILE process.

Fig. 3: Optical micrograph of the initial glass/Al interface recorded during the ‘normal’ ALILE process (after 4 days at 400 °C). The round shaped dark spots and the bright areas correspond to Si grains and Al, respectively. The dark spots feature a size of about 100 µm in diameter.

Fig. 4: Inverse pole figure of an electron back scatter diffraction (EBSD) orientation map of a poly-Si film prepared by the ‘normal’ ALILE process [20]. The high preferential (100) orientation of the grains is clearly visible. About 75 % of the area under investigation is tilted by less than 20 ° with respect to the (100) orientation (the corresponding region is indicated by a dashed line).

Fig. 5: Preferential (100) orientation $R_{(100)}$ versus annealing temperature T_A for two types of samples (the definition of $R_{(100)}$ is based on a 20 ° tilt with respect to the (100) orientation). The permeable membranes for the ‘normal’ ALILE process have been formed either by

exposure to air for about 2 hours at room temperature (solid circles) or in a furnace by exposure to an oxygen atmosphere for about 2 hours at 560 °C (open circles).

Fig. 6: Crystallised fraction R_C of the ‘inverse’ ALILE process versus annealing time t_A for samples with differently prepared permeable membranes. The membranes (Si oxide layers) have been formed by exposure to air for 7 days at room temperature (dashed line) and in a furnace by exposure to an oxygen atmosphere for about 2 hours at different oxidation temperatures T_{ox} (solid lines). The following oxidation temperatures have been used: 450 °C (left solid line), 500 °C, 530 °C, 560 °C, and 590 °C (right solid line). All samples have been annealed at 480 °C.

Fig. 7: Scanning electron microscopy (SEM) image of the surface of a 760 nm thick Si film grown by ECRCVD at 510 °C (without boron doping) on a multicrystalline Si wafer (the sample has been tilted by 30 °) [18]. Three regions with completely different morphologies of the grown Si film are visible. The underlying grains of the regions 1, 2, and 3 are orientated close (410), (210), and (221).

Fig. 8: Scanning electron microscopy (SEM) top view image of a sample surface Secco-etched for 10 s. The 2.1 µm thick Si film under investigation has been grown epitaxially by ECRCVD at 580 °C onto a Si(100) wafer using boron doping ($[B_2H_6]/[SiH_4] = 100$ ppm). Four different types of etch pits are indicated (‘P’, ‘L’, ‘E’, and ‘R’).

Fig. 9: Transmission electron microscopy (TEM) cross section of a 400 nm thick Si film grown by ECRCVD at 560 °C (without boron doping) on a seed layer/glass structure [20]. Two seed layer grains are shown. The seed layer grain on the right hand side has been thickened epitaxially while on the left hand side fine-crystalline Si has been grown.

Fig. 10: Boron concentration (C_B) and aluminium concentration (C_{Al}) versus depth d determined by secondary ion mass spectrometry (SIMS). Light and deep grey correspond to absorber layer and seed layer, respectively.

Fig. 11: Open circuit voltages V_{oc} of different Si thin-film solar cells. The absorber layers have been grown by ECRCVD at 590 °C and 580 °C with a boron doping ([B_2H_6]/[SiH_4]) of 5 ppm and 200 ppm, respectively. The glass/seed layer/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 passivated (400 °C, 15 min).

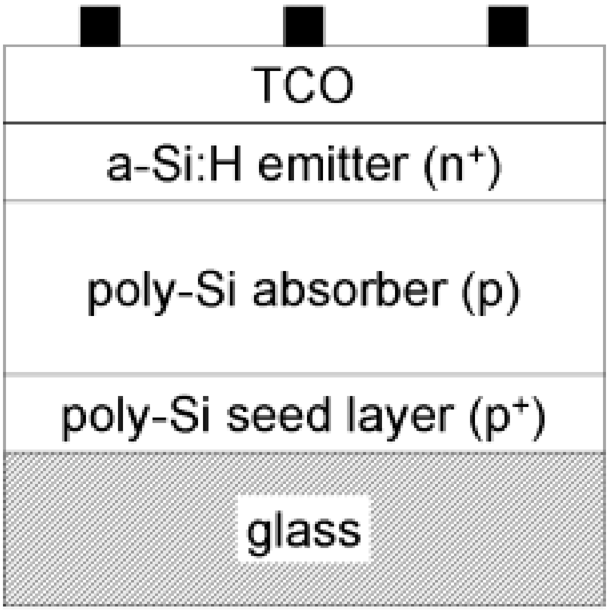
TCO
a-Si:H emitter (n+)
poly-Si absorber (p)
poly-Si seed layer (p+)
glass

Fig. 1

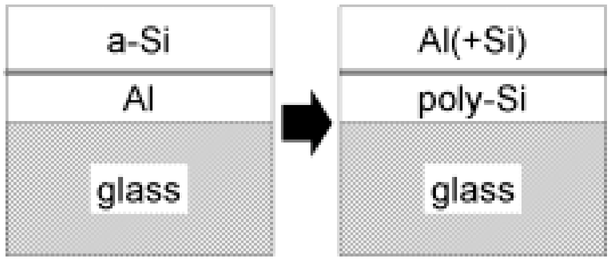

Fig. 2

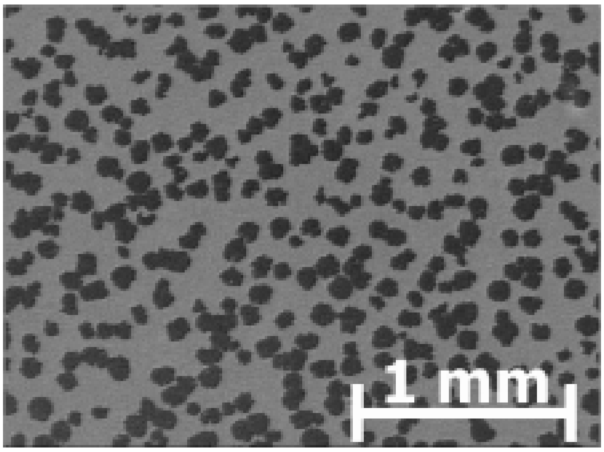

Fig. 3

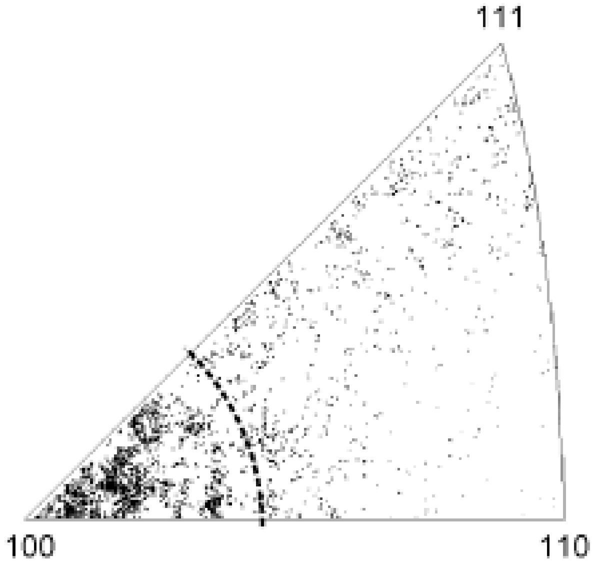

Fig. 4

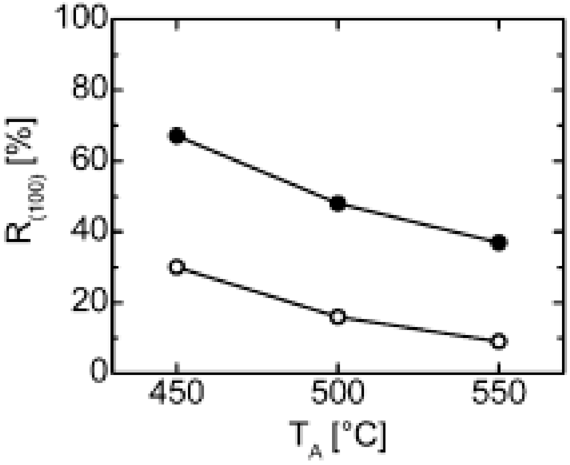

Fig. 5

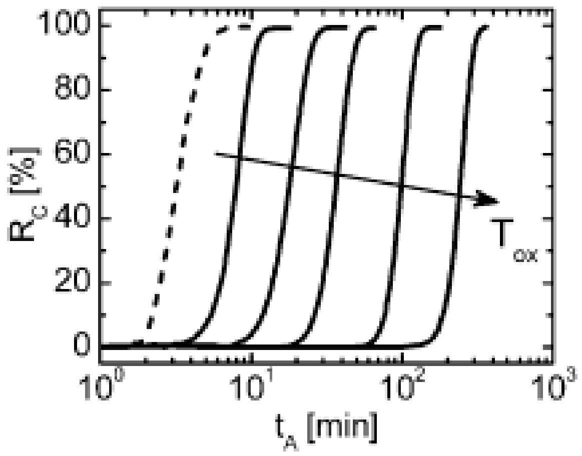

Fig. 6

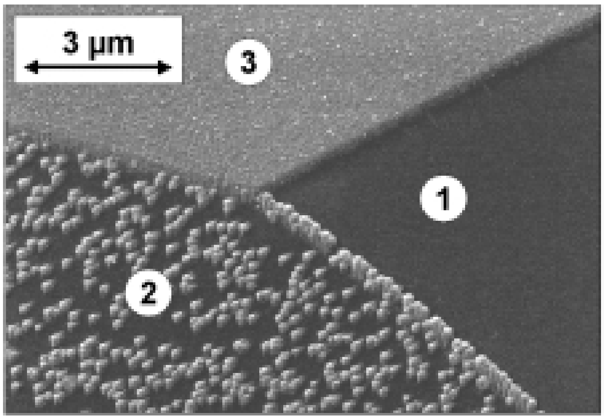

Fig. 7

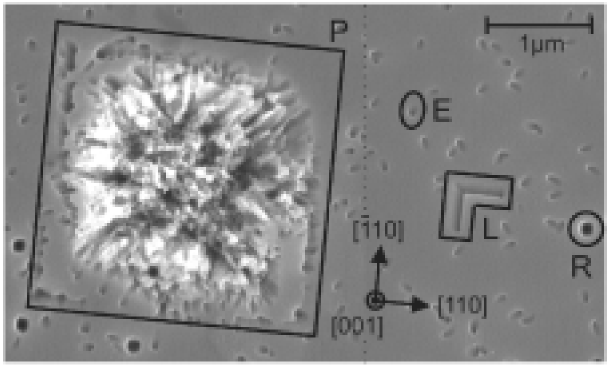

Fig. 8

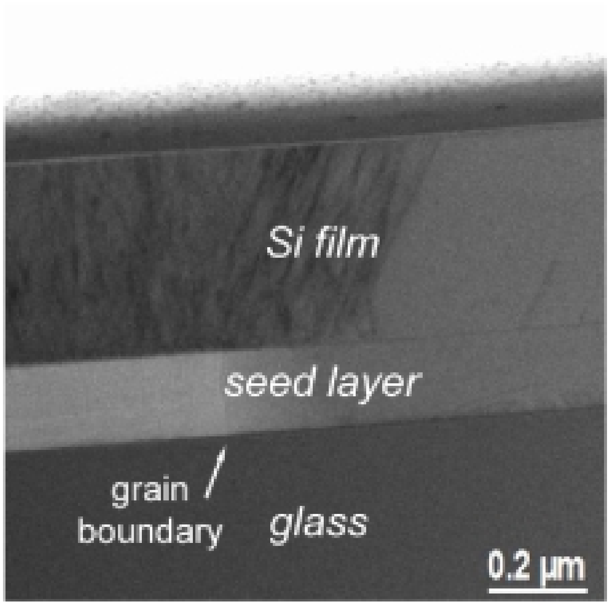

Fig. 9

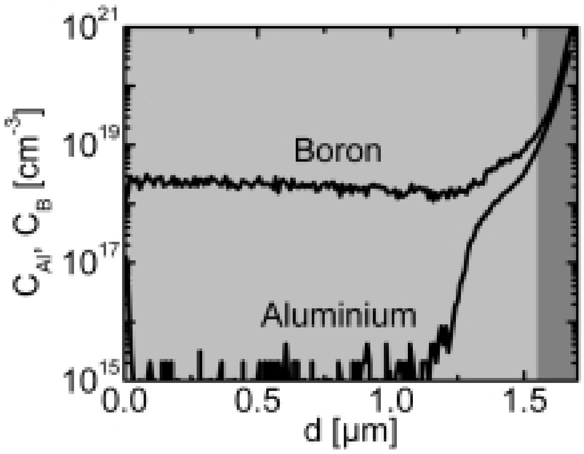

Fig. 10

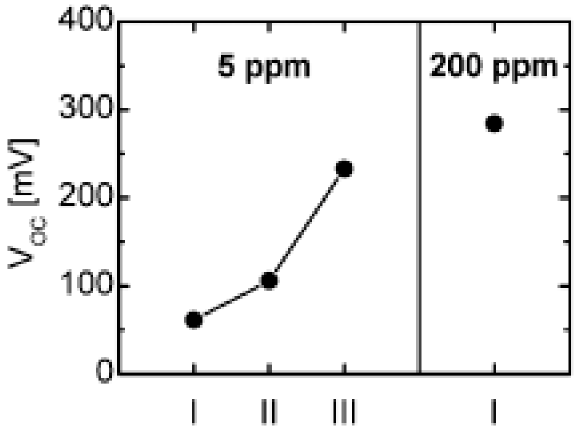

Fig. 11