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COARSE-GRAINED SI FILMS FOR CRYSTALLINE SI THIN-FILM SOLAR CELLS PREPARED BY ZONE-MELTING RECRYSTALLIZATION

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ABSTRACT: Zone-melting recrystallization (ZMR) is a technique which can dramatically improve the quality of Si films deposited on foreign substrates. Therefore this process also plays a key role for the fabrication of crystalline Si thin-film solar cells following the "high temperature route". The influence of substrate parameters on crystal quality is studied by ZMR experiments on different kind of Si wafers and on low cost Si ribbon material produced by the SSP (Silicon Sheets from Powder) process. The defect structure of recrystallized and epitaxially thickened Si films is correlated with crystal growth morphology observed *in-situ* during ZMR.

Thin-film solar cells prepared from Si films on multicrystalline Si and SSP substrates are characterized. Efficiencies reach up to 12.3% on mc-Si and 11.3% on SSP substrates. The improvement of solar cell parameters by an emitter passivation is quantified.

Keywords: Recrystallization - 1 -: Thin Film - 2 -: Substrate - 3 -

1. INTRODUCTION

Crystalline Si thin-film solar cells are promising candidates for next generation solar cell technology. Different methods have been employed in order to enlarge the grain size of Si films deposited on foreign substrates [1]. The zone-melting recrystallization (ZMR) technique which was developed since the 1960s in an effort to produce Si films on insulators (SOI) can lead to high-quality multicrystalline Si films. This technique has also been successfully applied for the preparation of Si thin-film solar cells. A group at Mitsubishi Electric Corporation demonstrated a remarkable efficiency of 16% for a solar cell processed by ZMR with an area of 10 x 10 cm^2 [2].

Our aim is the production of multicrystalline Si thin-films on ceramic or low cost Si ribbon substrates [3,4]. With these materials compromises concerning surface quality and flatness have to be made in order to be compatible with the cost goals. The impact of these parameters on crystal quality was studied using different types of Si substrates.

2. EXPERIMENTAL

2.1 Sample Structure

The Si substrates used for this investigation differ concerning flatness and surface roughness. Concentrating on Si materials the problem of matching the thermal expansion coefficient of active layer and substrate was avoided. Polished Czochralski Si (Cz-Si) wafers served as a reference substrate for studying the film growth by ZMR. Compared with them sliced and damage etched multicrystalline Si (mc-Si) wafers are characterized by higher surface roughness, which typically is in the micron range. Si ribbons produced by the Silicon Sheets from Powder (SSP) process at Fraunhofer ISE represented a low cost substrate. In addition to a surface roughness comparable to the mc-Si substrates the SSP substrates exhibit a wavy surface. Improvements concerning the flatness recently were made by changing the growth ambient resulting in a surface layer containing carbon and oxygen. These SSP wafers were used without any mechanical or chemical leveling of the surface. All wafers used had a thickness around 600 µm.

After cleaning the wafers were coated with an isolating intermediate layer. On the Cz-Si and mc-Si wafers 1.2–2.0 µm SiO_2 were deposited. On the SSP wafers a system of 1 µm SiO_2, 0.1 µm SiN_x and 1 µm SiO_2 was employed. A 5–10 µm highly Boron doped (approx. 1×10^{19} cm^{-3}) Si film was deposited onto the SiO_2 by CVD. Subsequently the Si film was coated with 2 µm SiO_2 deposited by PECVD. Without this "capping layer" the molten Si would ball-up during ZMR due to the high surface tension and the poor wettability of Si on SiO_2. After recrystallization the capping layer was removed with HF. After a slight CP-133 etch the Si film was epitaxially thickened by CVD. 5 µm Si at a p-type doping concentration of 1×10^{19} cm^{-3} and 30 µm at a concentration of 1×10^{16} cm^{-3} were deposited at 1100°C. By the change in doping concentration a back surface field (BSF) is implemented.

2.2 Zone-Melting Recrystallization (ZMR)

The ZMR system used was developed at Fraunhofer ISE [5]. The samples are heated up homogeneously with a field of halogen lamps while the molten zone is created by a single halogen lamp mounted in an elliptical reflector. The molten zone is scanned across the Si film by moving the heaters relative to the stationary substrate. For the investigations discussed a scanning speed of 10 mm/min was used. The shape of the molten zone and the morphology of the solid/liquid interface can be monitored *in-situ* with two CCD cameras integrated in the system. In addition the width of the molten zone is extracted from the camera images by digital imaging and used to automatically control the power of the focussed lamp. In this way an extremely fine temperature control is realized.

Defect structure of the recrystallized and epitaxially thickened films was studied at Secco etched cross and surface sections. Etch pit density was determined with the help of an image analysis software.

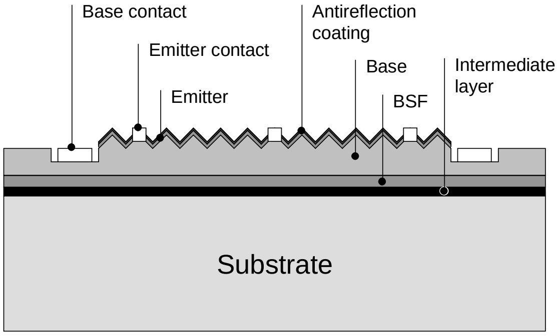

Figure 1: Structure of thin-film test solar cells. The base is contacted by a trench around the 10 x 10 mm^2 active cell area.

2.3 Solar Cell Process

Thin-film test solar cells were prepared from selected samples on mc-Si and SSP substrates using the structure sketched in Figure 1. The Cz samples have not been processed to solar cells yet. Light trapping was implemented by a combination of front surface texture with random pyramids and reflectance at the intermediate SiO_2 layer. Since thin Si films grown by ZMR are preferentially (100)-orientated [6] the surface texture could be realized by an easy to apply alkaline etching. The emitter was diffused from a $POCl_3$ source targeting a sheet resistivity of 80 Ω/□. Comparable samples were processed with and without passivation of the emitter by an 10 nm thick oxide. Since the intermediate layer is non-conducting, both emitter and base contact were formed on the front side using a mesa type diode structure. While the emitter grid was conventionally defined by photolithography the base was contacted by a trench around the active cell area as shown in Figure 1. The samples were passivated in a remote hydrogen plasma after emitter formation/oxidation and a second time after photoresist lift-off. The final solar cells were coated with a double layer antireflection coating.

3. RESULTS AND DISCUSSION

3.1 Growth Interface Morphology

A straight molten zone of constant width aligned perpendicular to the scanning direction is a prerequisite for ZMR films with low defect density. In this way the temperature gradient at the solid/liquid interface is constant along the molten zone and the projection of the gradient on the film plane coincides with the scanning direction. Ideally a cellular, facetted morphology develops as visible in the areas marked (ii) and (iii) in Figure 2.

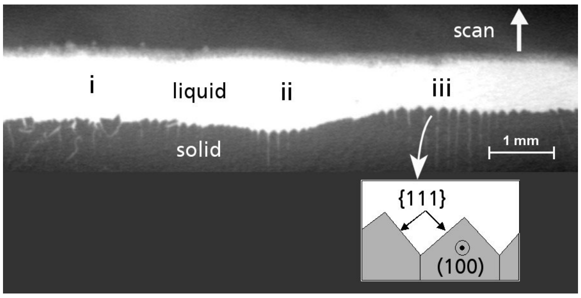

Figure 2: *In-situ* image of the molten zone during ZMR on a SSP ribbon substrate.

On none of the substrates examined solely the perfect cellular interface morphology was found. While on the Cz-Si substrates the cellular interface was clearly dominating on the mc-Si and especially on the SSP substrates more often other interface morphologies were found. On the SSP substrates the molten zone often had wave shape as shown in Figure 2 for an extreme case. This shape can be explained by an inhomogeneous lateral heat flow caused by variations in substrate thickness.

3.2 Crystal Properties

By ZMR large grains could be grown on all substrate types. Their typical length was between one cm and the length of the substrate (5–10 cm). Their width reached more than one cm on the Cz-Si substrates and usually was in the mm range for the mc-Si and SSP substrates. On some SSP substrates areas with untypical small grains with length and width around 1 mm were found. The microscopic analysis revealed that in this case the intermediate layer was locally destroyed and the uncovered parts of the SSP substrate acted as seeding crystals.

While grain size is not limiting the electrical performance of the Si films investigated subgrain boundaries (short: subboundaries) have a significant impact. These defects are a characteristic phenomena of Si films produced by the ZMR technique. They originate at the inner edges of the growth cells (see inset in Figure 2) and cause bunches of dislocations in the epitaxial layer (Figure 3). At preferentially etched surface sections of these films the end points of the dislocations are visible as dark stripes (Figure 4). The dislocation density measured at these stripes was in the range 10^7 cm^{-2} to 10^8 cm^{-2} while between two subboundaries the typical density was around 10^6 cm^{-2}. The distance between two subboundaries at the samples examined was between 50 and 200 µm. One strategy to decrease the harm of the subboundaries has been to increase their spacing [7]. Therefore one key for low defect films is a solid/liquid interface of large cells.

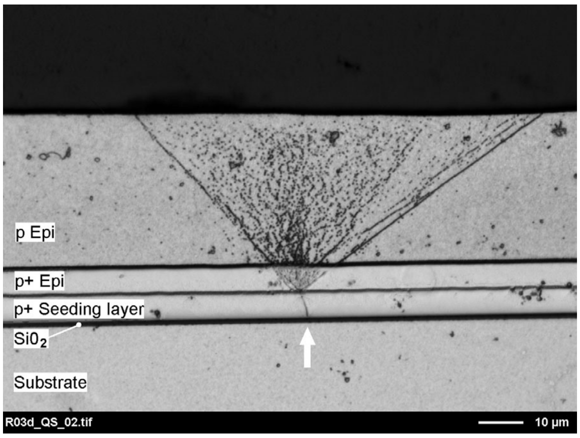

Figure 3: Cross section of a Si-film on a Cz-Si substrate. Defects originate from a subboundary (arrow) in the recrystallized seeding layer.

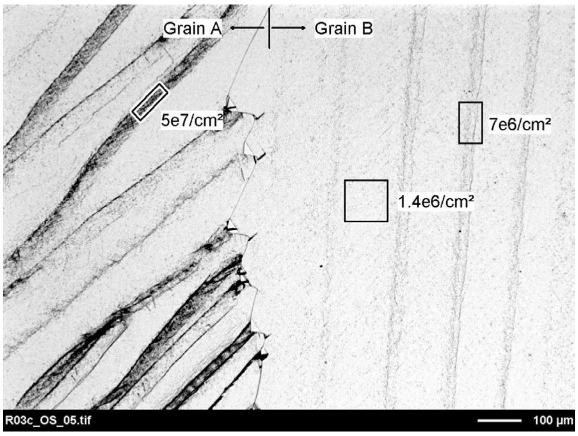

Figure 4: Surface section of an epitaxial layer on top of a recrystallized film showing two grains with different subboundary structure. A Cz-Si wafer was used as substrate.

This work indicates that the run of the subboundaries might be more important than their spacing. The dislocation density in the stripes above the subboundaries was found to vary in a wide range. Above parallel subboundaries pointing in scanning direction a much lower dislocation density was measured than in areas with a less regular run of the subboundaries. An example are the two grains marked A and B in Figure 4. A reason for this behavior might be that parallel subboundaries are produced by equilateral triangular growth cells with {111}-faces. This solid/liquid interface morphology is very stable in time. Other morphologies are less stable and more fluctuations were observed. This results in incorporation of a higher number of dislocations.

3.3 Solar Cell Results

The parameters of thin-film solar cells reflect the difference in crystal quality between Si films on mc-Si and SSP substrates. Short circuit current and (less pronounced) open circuit voltage of the solar cells on SSP substrate do not reach the values of those on mc-Si substrates (Table 1).

For both substrate types solar cells with and without passivation of the emitter have been characterized. A significantly improved overall performance is found for the solar cells with passivated emitter (Figure 5 top). The increase in conversion efficiency can be attributed to an enhanced open circuit voltage (Figure 5 bottom) as well as an increased spectral response for wavelengths up to 500 nm (Figure 6).

Table 1: Parameters of the best thin-film solar cells without and with oxidized emitter processed on mc-Si and SSP substrates.

Substrate	E.	V_{oc} [mV]	I_{sc} [mA/cm^2]	FF [%]	η [%]
mc-Si	–	580	25.3	77.1	11.3
mc-Si	ox.	594	26.9	77.2	12.3
SSP	–	563	23.6	79.2	10.5
SSP	ox.	578	25.7	76.4	11.3

E. = Emitter

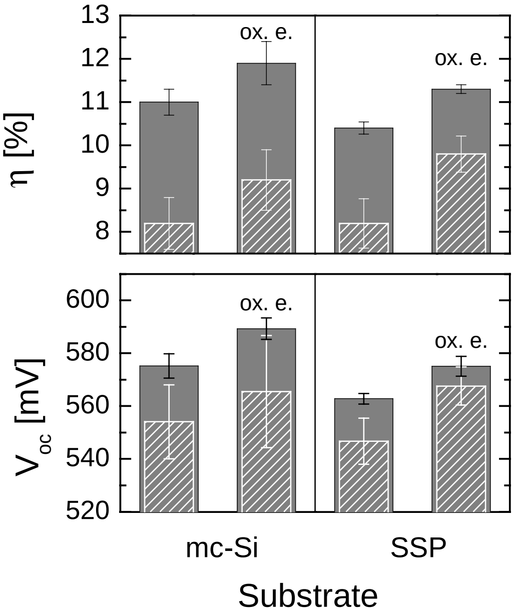

Figure 5: Average values of open circuit voltage V_{oc} and efficiency η for solar cells without (left) and with (right) oxidized emitter. Parameters were measured after photoresist lift-off (striped columns) and at the finished cells with double layer antireflection coating (solid columns).

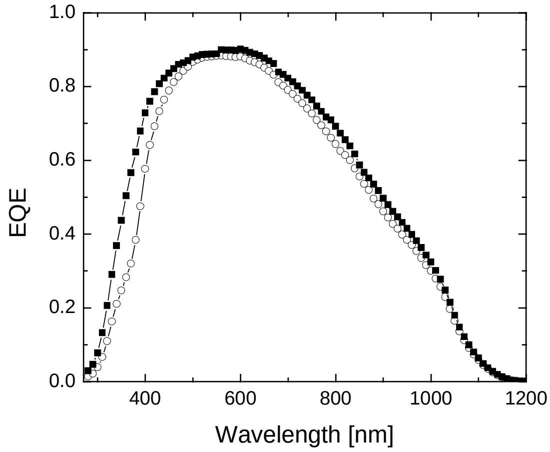

Figure 6: External quantum efficiency of solar cells without (○) and with (■) oxidized emitter made from the same recrystallized film.

4. CONCLUSION

Coarse grained Si-films have been prepared by ZMR on three different Si substrate types: polished Cz-Si wafers, mc-Si wafers and SSP ribbon material. The main defects found in epitaxially thickened Si films are dislocations originating from subboundaries in the recrystallized seeding layer. The impact of these subboundaries depends on their run. At parallel subboundaries pointing in scanning direction the dislocation density is lower than at those subboundaries running less regularly. This phenomena correlates with the morphology of the solid/liquid interface and its stability in time. The appearance of an interface with ideal morphology decreases with increasing roughness and unevenness of the surface. The main drawback of the SSP ribbon material is its inhomogeneous thickness.

The parameters of thin-film test solar cells on mc-Si and SSP substrates reflect the crystal quality of the films. However the difference between SSP and mc-Si substrates is not dramatic and improvements in fabrication of the SSP ribbons may bridge the gap in performance. An efficiency of 11.3% was demonstrated on a SSP ribbon substrate used without any mechanical or chemical leveling of the surface.

Low surface recombination is especially important for Si thin-film solar cell. For the back side of the test structure this requirement was realized by a back surface field. For the front side performance could be clearly improved by introducing an oxide emitter passivation.

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