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Structural and chemical investigations of adapted Siemens feed rods for an optimized float zone process

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Abstract

The optimization of the float zone process for industrial application is a promising way to crystallize high purity silicon for high efficiency solar cells with reduced process costs. We investigated two differently produced Siemens rods which should be used as feed material for the float zone process. The aim is to identify and to improve material properties of the feed rods which have a high impact to the float zone process. We show here microstructural and chemical analysis comparing feed rods manufactured under standard conditions and under float zone adapted conditions. To resolve the growth behavior of the grains SEM/EBSD mappings are performed at different positions. TEM analyses are used to investigate the interface region between the mono- and the multicrystalline silicon within the Siemens feed rod. Additionally, drilled cores are cut out from the feed rods containing the region of the slim rod. Afterwards, the drilled cores are crystallized with the float zone process. Finally, carbon and oxygen measurements with FT-IR spectrometry on different positions of the crystallized drilled cores of the Siemens feed rods show the influence of the slim rod material to the float zone process.

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Keywords: float zone process, Siemens process adaption

1. Introduction

The PV industry is facing the big challenge to reduce the material costs and to economize process steps with simultaneous enhancement of the solar cell efficiency. The float zone process is known for its potential to give high purity silicon material [1]. Despite of its requirements concerning round shaped crystalline feed silicon material, the float zone process has a great potential of cost reduction [2,3]. In this

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work optimized round shaped feed material produced in a modified Siemens process is investigated concerning its suitability for the float zone crystallization. For this purpose structural and chemical analyses are performed on standard run and process adapted feed rods. We show here for the first time microstructural investigations at Siemens feed rods in correlation to their production conditions giving insight into the crystal growth mechanisms and the interface between the slim rod at which the Siemens process usually starts and the deposited silicon. Moreover, the grain size distribution is analyzed which have an influence on the later float zone process as known from previous technology developments [4-6].

During the float zone crystal growth process the slim rod becomes a critical component of the feed rod, especially at the beginning of the crystallization, since it is the first molten silicon volume and it is necessary to transfer the polycrystalline feed rod into a dislocation free single crystal. So the slim rod itself has an influence regarding the material quality achieved later on concerning impurities and crystal defects which must be avoided.

The aim of the BMBF project FzSil is to establish the float zone method as economically viable method for the production of high quality monocrystalline silicon for solar cells. For this purpose it is important to understand the influence of parameters of the involved processes. In addition to the macroscopic morphology of the Siemens feed rod also the slim rod has a significant impact on the successful crystallization of monocrystalline float zone ingots. Therefore, three approaches were investigated in detail:

(i) Characterization of the microstructural transition region between slim rod and deposited silicon
(ii) Chemical impurities (especially oxygen and carbon content) of the slim rods
(iii) Evaluation of the slim rod production according to its feed crystal and to process parameters

In this publication, only the items (i) and (ii) are described in more detail. The oxygen and carbon content of the slim rods and its influence behavior during crystallization is showed by FT-IR measurements on crystallized cores drilled out of the Siemens feed rod. Concerning (i), we investigate the interface region, because it was not known from the adapted Siemens feed rods if there is an oxide layer which probably limits the crystallization and how the interface is microstructurally formed. The slim rod production also has a relevant influence on the successful float zone crystallization with the optimum properties of high purity and a monocrystalline crystal structure in <100> orientation [4]. We try to find a more efficient and economic process by producing multicrystalline slim rods in a shorter recrystallization time of the used multicrystalline Czochralski ingot as slim rod feed crystal. Just to mention the specific influence factors concerning (iii), it turns out that a high purity Czochralski ingot is needed to produce sufficient pure slim rods and also that a nitrogen containing process atmosphere is negative due to its potential of Si_3N_4 precipitate formation (data not shown).

2. Experimental work

Different analytical methods are applied to investigate the microstructural and chemical properties of the Siemens feed rods. To compare the grain structure and growth behavior of a standard feed rod run and a float zone optimized run, slices are sawed out of the Siemens feed rods using a diamond wire saw. After optical inspection and high quality polishing on three different positions, EBSD (electron backscatter diffraction) mappings are performed to depict the radial growth behavior using a SEM (scanning electron microscope) apparatus Hitachi SU70. Furthermore, TEM lamellae are prepared by the FIB (focused ion beam) technique with a Zeiss FIB Auriga at two position of the interface region between slim rod and deposited silicon. Afterwards, the lamellae are analyzed with the TEM (transmission electron microscope) apparatus FEI Tecnai G2 F20.

To verify the impurity influences of the slim rod material, drilling cores are prepared from different positions of the Siemens feed rod including the region of the slim rod. Afterwards they are crystallized in the float zone process. Then the chemical analyses to determine the carbon and oxygen content are performed with FT-IR (Fourier transform infrared) spectrometry measurements (using the standards DIN-50438-1 and DIN-50438-2) on samples from the top region of the small float zone crystal, from a region including the former slim rod and from the bottom region of the small float zone crystal.

3. Results and discussion

3.1. Macroscopic structure of Siemens feed rods

The sawing process of feed rod material on laboratory scale is a long term process, because mechanical stresses are present in the material, which can lead to an abrupt cracking of the feed rods while sawing. Nevertheless, about 1 cm thick slices of the two feed rods are prepared successfully. The optical inspections of the standard run feed rod showed a relatively rough “broccoli like” surface structure, which corresponds to a large total surface. Therefore, a cleaning etching can lead to incomplete or residual etching solution, which may induce complications during the float zone process. The standard feed rod also shows lot of micro cracks and voids inside the slice (see fig. 1. left), which would also limit the crystallization process. In contrast, the slice of the adapted feed rod process showed a less rough surface structure with no visible cracks and voids (see fig. 1 right). After varying process conditions for a float zone optimized run, we found out, that the deposition rate could intentionally be reduced by lowering the temperature of the Siemens process.

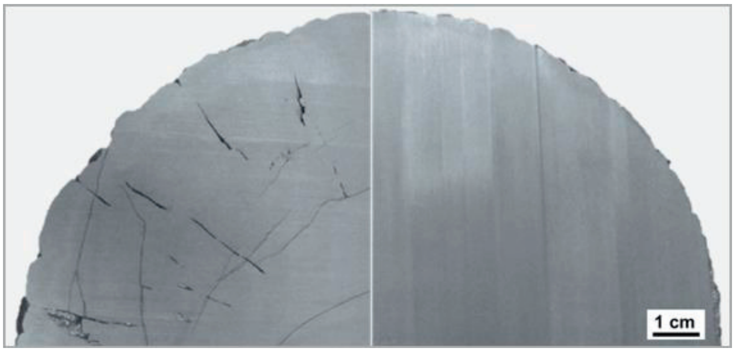

Fig. 1 Cross sections of a standard run feed rod (left) and an adapted feed rod process (right)

3.2. Microstructure of Siemens feed rods

The effects due to the reduced silicon deposition rate, which was applied on the adapted Siemens feed rod in comparison to the standard Siemens feed rod, is also investigated on microstructural scale. The Siemens process starts with the deposition of silicon on the heated slim rod substrate. A uniform growth rate is important for a uniform diameter increase. Under high pressure conditions in the reaction chamber the chemical vapor deposition starts with the thermic decomposition of gaseous trichlorsilane and hydrogen as a surface reaction of the heated slim rod [6]. The separated silicon atoms are deposited on the substrate surface and form crystallization seeds.

Fig. 2 depicts the SE (secondary electron) images for the interface region of the slim rod and standard run deposited silicon including the secondary ions (SESI detector, fig, 2 a)) and especially for the SE of first order (inlense detector, fig, 2 b)). It can be concluded that epitaxial growth occurs on the surface of the slim rod, which is very smooth and consists of relatively large crystal grains compared to the deposited silicon. The interface region appears furthermore in a darker contrast in fig. 2 b), which supports the interpretation as the first layers of deposited silicon.

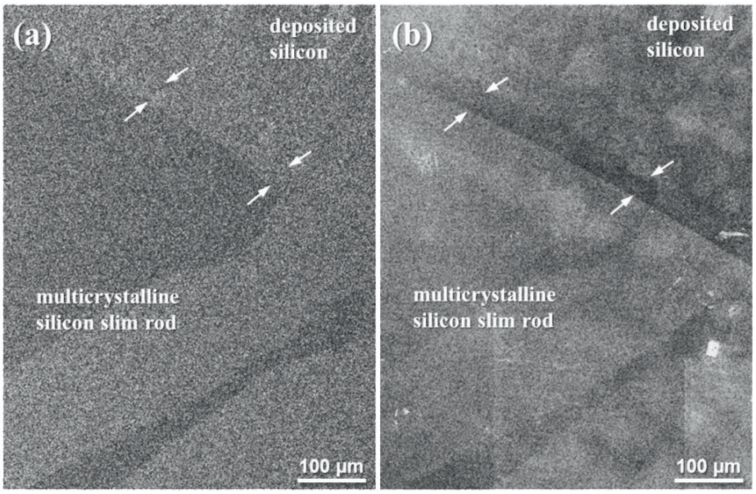

Fig. 2. SEM images at 3 kV with (a) SESI and (b) inlense detector of interface region of a standard slim rod and deposited silicon of an adapted Siemens feed rod

The epitaxially grown silicon layer follows the underlying crystal orientation given by the local grain orientation of the slim rod. In the following this region is called interface region because two interfaces are visible. The first interface exists between the slim rod surface and the epitaxial grown silicon and the second interface is formed by the epitaxial silicon with the given crystal orientation from the slim rod and the deposited nanocrystalline silicon. The thickness of the epitaxial layer is about 40 µm up to 90 µm before the deposited silicon appears in a different contrast (fig. 2 (b)). Afterwards two TEM lamellae are prepared on the two visible interfaces to clarify the presence of an oxide layer and how the interface is formed on nanometer scale.

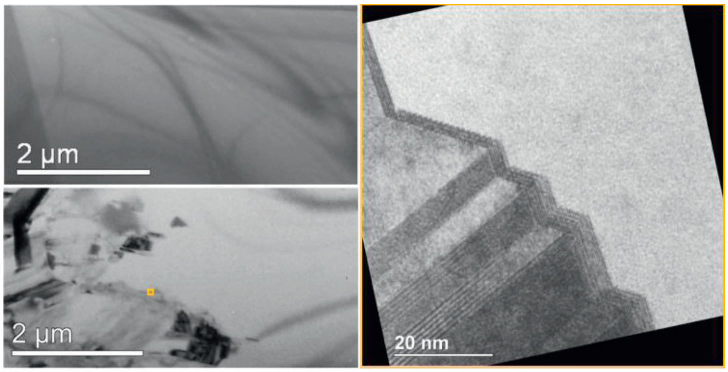

Fig. 3. TEM bright field images of TEM lamella at the interface between slim rod an epitaxial layer (top left) and at the interface between epitaxial layer and deposited nanocrystalline silicon (bottom left) with marked detail image (right)

The TEM lamella at the first visible interface between slim rod and epitaxially grown silicon clearly shows that the first layers deposited in the Siemens process continue the crystal structure from the slim rod and can be considered locally as monocrystalline (see fig, 3, top left). Neither a structural interface nor an oxide layer is visible here. The darker contrast in fig. 2 b) can be explained as doping difference contrast, because the slim rod material is doped by boron [7]. The TEM lamella at the transition from monocrystalline to nanocrystalline structure shows a rough interface (fig. 3, bottom left). At higher magnification of a detail (fig. 3, right) at the structural transition region the lattice planes of the silicon are visible, but also here an oxide layer is not present. In the nanocrystalline region especially small twin grains are observed.

After high quality polishing of three samples, SEM/EBSD mappings are performed each at the interface region of the slim rod and the deposited silicon, the middle radius of the deposited silicon and at the edge region. The EBSD mapping shown in fig. 4 exemplary represents the grain structure as inverse pole figure for a standard slim rod and a standard Siemens process.

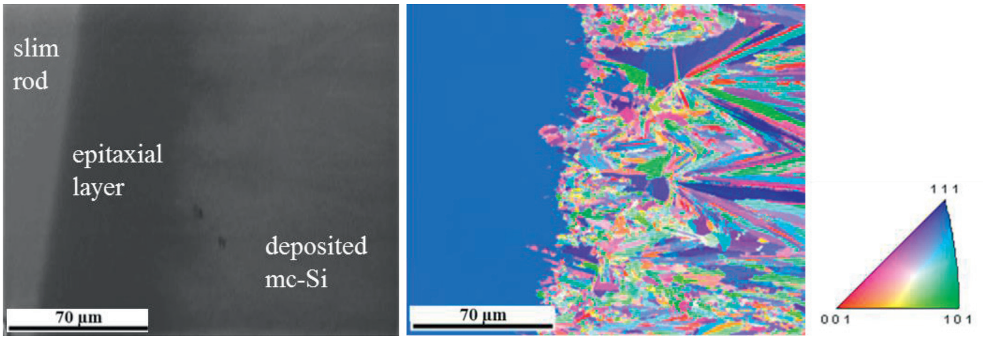

Fig. 4. SEM image (left) and inverse pole figure (right) of the interface region between slim rod and deposited silicon

The interface between epitaxial (locally) monocrystalline layer and nanocrystalline deposited silicon appears jagged and irregular as seen at the second TEM lamella. The multicrystalline grain growth starts with very small grains until the grains coarsen, which is followed by long narrow grains. The radial growth alternates between small and long narrow grains. The following diagram (fig. 5) depicts the radial grain size distribution for the standard run and the adapted run Siemens feed rod.

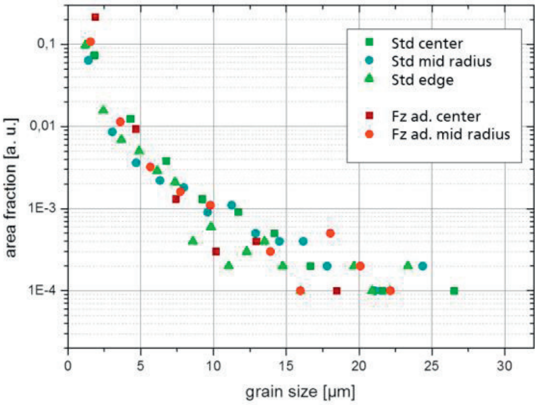

Fig. 5. Radial grain size distribution for standard and adapted feed rod

It turns out that no change is observable on micrometer scale neither for the radial grain size distribution nor for the both Siemens feed rods, which means we have a very uniform process for both cases.

3.3. Chemical analysis of crystallized Siemens feed rod material

In addition to the characterization of the microstructural transition region between slim rod and deposited silicon also the chemical impurities concerning the oxygen and carbon content of the slim rods itself are investigated. Therefore, the influence of these slim rod impurities is determined by preparing samples from the Siemens feed rods including the slim rod. The round shaped samples are drilled out perpendicular to the direction of the slim rods having about 2 cm in diameter and a length which corresponds to the rod diameter of the Siemens feed rods. These so called drilled cores are crystallized with the float zone process. Fig. 6 shows the interstitial oxygen content and the substitutional carbon content measured by FT-IR analyses on polished samples from the crystallized drilled cores at different positions. The impurity influence for the region previously corresponding to the slim rod material is clearly increased and an impact to afterwards crystallized regions is observed due to segregation. Accordingly, it can be concluded that the purity of the slim rod and hence the Czochralski feed rod purity has to be increased especially with respect to carbon.

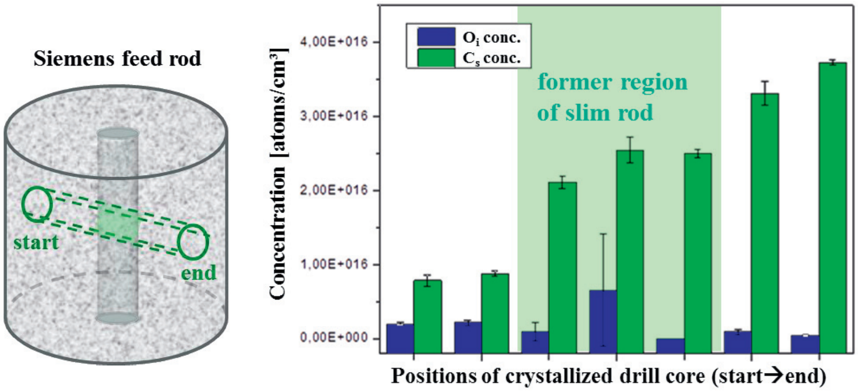

Fig. 6: FT-IR results of crystallized cores drilled out of standard run feed rod including region of slim rod

3.4. Float zone crystallization experiments of Siemens feed rods

Supplemental to the modifications of Siemens process concerning the reduced deposition rate (fig. 1) and the adaption of the slim rod material, float zone crystallization experiments are performed to evaluate its suitability or rather its potential in increasing material quality. It turns out that a dislocation free single crystal only starts to grow from Siemens feed rods with slim rod material of high purity from a pure Czochralski ingot and an adapted macroscopic structure without voids and cracks and a smoother “broccoli like” structure. So far, it was possible to grow a float zone crystal up to a diameter of 40 to 70 mm without any dislocations. For bigger diameters the saturation of the relatively small melting volume with contaminations becomes dominant [8]. Since no oxide interface is found, we assume that carbon plays an important role in this case. For this crystallized part a carbon concentration of 8×10^{16} atoms/cm^3 was determined. The concentration of carbon in the melt is then at least one order of magnitude higher, because the segregation coefficient is 0.07 in silicon. The solubility limit is

3.5×10^{17} atoms/cm³ [9]; that means the supersaturation in a small melting volume is reached soon. Moreover, the formation of SiC particles may occur when the solubility limit is exceeded, which prevents the further dislocation-free growth of the crystal in the float zone process.

4. Conclusion

In summary, important insights concerning as well the interface region of slim rod and deposited silicon as the grain growth behavior were obtained. We found, that no oxide interface is formed and that the silicon growth on the slim rod starts with an epitaxial layer of the same crystal orientation as the underlying slim rod. The silicon diameter growth continues with the transition of the locally considered monocrystalline to multicrystalline silicon. The interface is rough and shows some twin grains. We found that the transition is due to a critical crystal defect density of dislocations and stacking faults. The grain size distribution for the standard run and the adapted run of the Siemens feed rods seems to be the same on micrometer scale.

Also the influence of the slim rods concerning the chemical properties of the crystallized material by crystallization experiments with drilled cores containing the former slim rod material was investigated. We found a relatively high carbon content for the standard slim rods which have to be reduced. Nevertheless, we found that the adapted Siemens feed rod process has the potential to enable the crystallization of float zone silicon.

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