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Influence of slim rod material properties to the Siemens feed rod and the float zone process

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Abstract

The identification and understanding of material properties influencing the float zone process is important to crystallize high purity silicon for high efficiency solar cells. Also the knowledge of minimal requirements to crystallize monocrystalline silicon with the float zone process is of interest from an economic point of view. In the present study, feed rods for the float zone process composed of a central slim rod and the deposited silicon from the Siemens process are investigated. Previous studies have shown that the slim rod has a significant impact on the purity and suitability for further crystallization processes. In particular, contaminations like substitutional carbon and the presence of precipitates as well as the formation of oxide layers play an important role and are investigated in detail. For this purpose different slim rod materials were used in deposition and float zone crystallization experiments. Samples were prepared by cross sectioning and core drilling of Siemens rods, which were recrystallized with the float zone process. Recrystallized drilled cores are analyzed with FT-IR spectrometry concerning the carbon and oxygen content. To estimate the grain growth behavior on the slim rod surface in dependence of the used slim rod material, EBSD mappings inside a SEM are performed on squared and circular slim rods. TEM analysis was used to investigate the presence of an oxide layer at the interface between slim rod and deposited polycrystalline silicon. Additionally the influence of a nitrogen-containing gas atmosphere during the slim rod pulling is investigated by IR microscopy and ToF-SIMS regarding Si_3N_4 precipitation.

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1. Introduction

The float zone process is known for its potential to give high quality material and is therefore used also for the production of photovoltaic and electronic grade silicon ingots [1]. To optimize process steps for the material production of photovoltaic applications, limiting influence factors have to be identified [2]. In order to get suitable float zone feed silicon, the commonly used Siemens feed rods need to be of high purity of <1 ppb [3]. In this work Siemens feed rods are compared with the focus on different slim rod material quality. To estimate the influence of the slim rod purity independently of the silicon deposition parameters, squared slim rods and circular shaped slim rods produced from a Czochralski feed rod by a pedestal process are compared. Analyses are performed with regard to structural properties like the presence of precipitates, the formation of interface layers and the grain growth behavior. Also chemical properties concerning the carbon and oxygen content are studied. The correlation of microstructural and chemical properties of Siemens feed rods regarding the slim rod production conditions are investigated. The knowledge of the crystal growth mechanisms with respect to the interface region of slim rod and deposited silicon is important to realize the further float zone crystallization process. Some material depending technological connections between process steps involved in the float zone crystallization are shown in fig. 1.

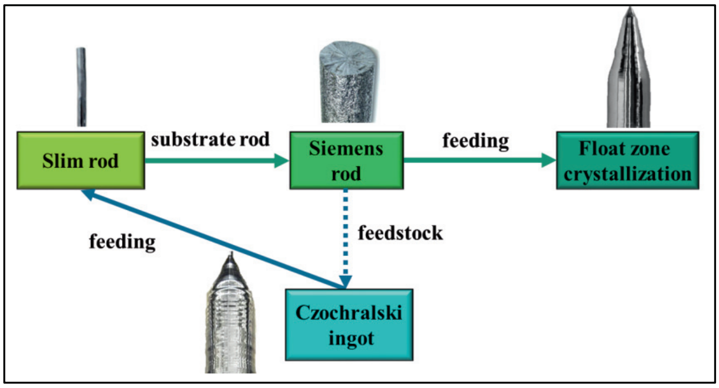

Fig. 1. Schematic silicon material flow connections between some process steps for the float zone crystallization.

2. Experimental work

Horizontal slices were sawn out of Siemens feed rods composed of different slim rods inside. After high quality polishing of these cross sections on the position of the structural transition from slim rod to deposited polycrystalline silicon, EBSD (electron back scattered diffraction) mappings inside a SEM (scanning electron microscope) were performed. Additionally, TEM (transmission electron microscope) lamellae were prepared by the FIB (focused ion beam) technique at this interface region. Line scans using the EDX (energy dispersive X-ray spectroscopy) analysis method inside the TEM were carried out to study the presence of an oxide interface layer. Additionally, cores were drilled out at different positions of a Siemens feed rod with a slim rod material which was pulled in the pedestal process using a Czochralski feed rod. The drilled cores were located at an axial position of the Siemens feed rod containing the total slim rod, at an axial position excluding the slim rod and at a radial position containing the slim rod in the central region. Afterwards the drilled cores were recrystallized with the float zone process. Thin slices of the top and bottom region of these recrystallized samples were removed and analyzed with the FT-IR (fourier transform infrared) spectroscopy with respect to the interstitial oxygen and the substitutional carbon content. So the contamination influence of the slim rod to the float zone process was investigated. To analyze the influence of the slim rod production to the slim rod purity some slim rods were produced from a Czochralski feeding ingot with a process atmosphere with a nitrogen concentration of a few atom percent. The so produced circular slim rods were investigated by transmitting light IR microscopy. Also the residual Czochralski ingot, which was the feeding ingot for these slim rods, was inspected on its cross section. The so located precipitates were identified by their morphology and stoichiometric characteristic with the help of ToF-SIMS (time of flight - secondary ion mass spectrometry) analysis. Characteristic intensity ratios of the measured secondary ion complexes can be used as reported [4] to identify the different types of precipitates in correlation to further material properties.

3. Results and discussion

3.1. Influence of slim rod feed material and production conditions to its purity

Microscopic IR transmission analyses of slim rods produced in a gas atmosphere containing a certain concentration of nitrogen were performed. As a result mainly rod shaped Si_3N_4 precipitates can be observed (see fig. 2). Also the surface of the remaining Czochralski crystal, which was used for the slim rod pulling shows precipitates. The chemical analysis performed by ToF-SIMS identifies these precipitates as hexagonal β-type Si_3N_4 needles and cubic 3C-SiC particles. The possibility to identify the precipitate types using ToF-SIMS was reported earlier [4]. During the slim rod pulling with the pedestal method [5] a certain volume of the surface of the Czochralski feeding crystal is molten and a seed crystal is used to pull and recrystallize slim rods. This process is usually optimized for high throughput. Therefore the following consequences have to be considered: First, incomplete mixing of the melt in the pulling time regime and secondly, the enrichment of the melt with nitrogen from the gas atmosphere and the local supersaturation leads to the formation of Si_3N_4 precipitates on the interface between gas atmosphere and silicon melt surface. The latter case occurs due to the local reduced free enthalpy by reduced surface formation energy which promotes the heterogeneous nucleation. If this happens, the incorporation of the slim rod with precipitates is unavoidable. The source of carbon contamination for the SiC precipitate formation could have its origin either also in the process gas atmosphere or in the high basic carbon content of the slim rod feeding material, which is more likely in this case.

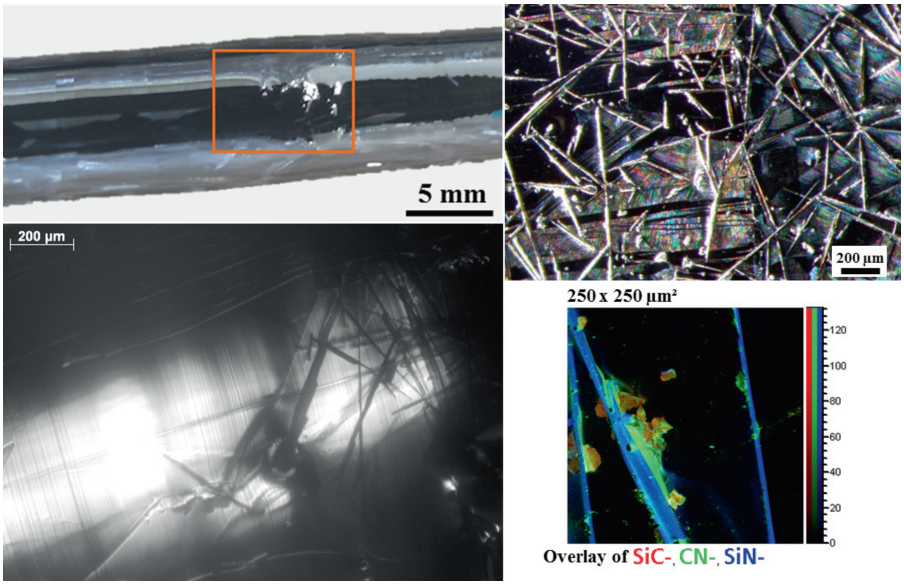

Fig. 2. Image of circular slim rod including precipitates (top left) visible by IR microscopy (bottom left). Precipitates also on surface of slim rod feeding crystal visible (top right) with negative ToF-SIMS ion imaging (bottom right) showing signals for SiC particles and Si_3N_4 needles [3].

The presence of precipitates has a significant influence on the float zone process. Slim rods are used as substrate material for the growth of polycrystalline silicon in the Siemens reactor. After mechanical treatment, the Siemens rods are used for the float zone process. For this purpose, one end is shaped conical. That means the first melting volume used in the float zone process has a high amount of slim rod material. The presence of precipitates prevents the growth of a dislocation free single crystal, because the precipitates cannot dissolve in the small melting volume during the float zone crystallization in time.

3.2. Influence of slim rod material properties on the initial Siemens process grain growth

Besides the pedestal pulling which results in circular slim rods also squared slim rods can be used in the Siemens process. Squared slim rods are produced by sawing of a feed crystal which can be silicon material of different quality. The surfaces of squared slim rods are usually cleaned by etching. The comparison of two slim rod materials used for silicon deposition by the Siemens process shows a different behavior in the grain growth of the deposited silicon close to the slim rod surface. The float zone crystallization of monocrystalline silicon using round shaped slim rod material was successful in several cases. Besides the geometric difference between circular and squared slim rods and the purity of the feed material also the surface smoothness is different for the two slim rod materials. In some cases the roughness of the sawed and etched squared slim rods led to the formation of cavities in the first micrometers of silicon deposition (see fig. 3 bottom). With the help of EBSD mappings for the square shaped slim rods it turns out, that a region with small grains of ~20-30 µm thickness can be observed for the investigated examples (see fig. 3). For the round shaped slim rods either epitaxial growth behavior (up to ~65 µm) can be observed for the first deposited silicon grains [2] or the directly growth of small silicon grains for a thickness of about 10-20 µm (see fig. 3 top). In the latter case, no oxide layer was observed, as published in [2].

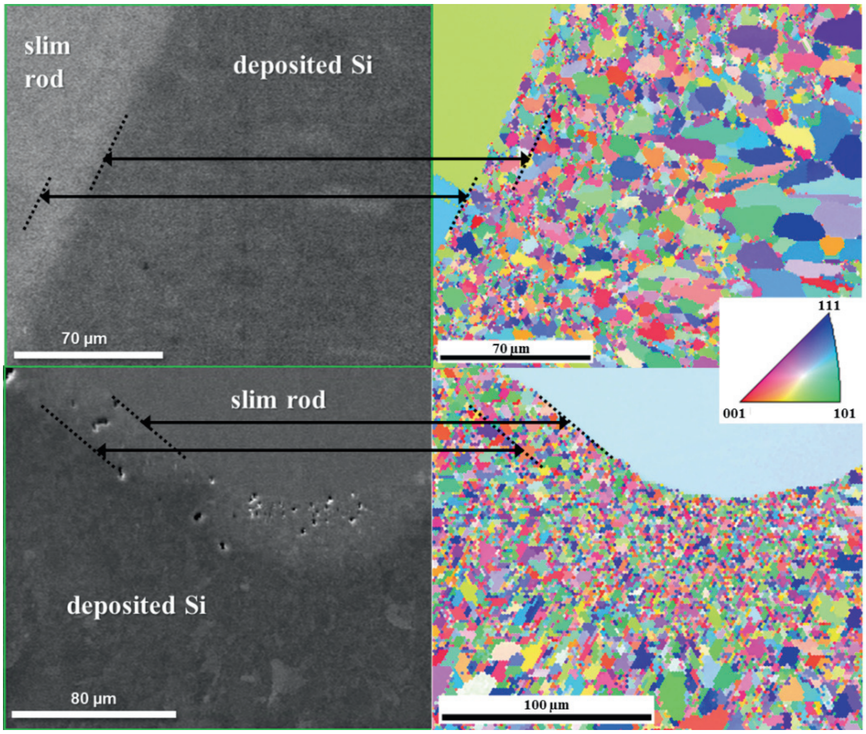

Fig. 3. SEM images with corresponding EBSD mappings of interface region from slim rod to deposited Si for a round shaped slim rod (top) and a square shaped slim rod (bottom) on a corner position.

The grain growth of the first layers of deposited silicon in the Siemens process becomes visible at the Siemens rod cross sections as a contrast region in the secondary electron image from the SEM analysis (see fig. 3). EBSD mappings support the characterization of grain growth behavior. For the squared slim rod a TEM lamella was prepared at the first visible transition between slim rod and deposited silicon, which is visible in the EBSD mapping as the beginning of small grain growth. It turns out, that on top of the slim rod a ~25 nm thick SiO_2 layer can be detected by an EDX line scan (see fig. 4) with ~66 at% O and ~33 at% Si. The Cu signal from the EDX line scan is caused by the Cu grid on which the lamella was transferred for the TEM investigation.

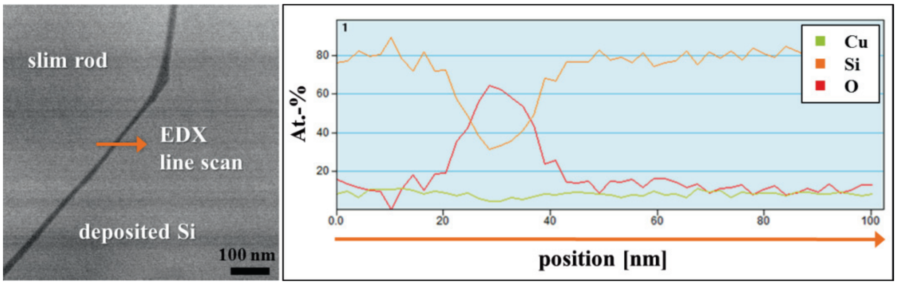

Fig. 4. STEM dark field image (left) with position of EDX line scan (right) between a squared slim rod and deposited silicon.

The float zone crystallization of Siemens feed rods including squared slim rod material for which an oxide layer was observed did not lead to a dislocation free single crystal in our experiments. Analogical to the assumptions made for the presence of precipitates, it has to be concluded, that the local high oxygen content on top of the slim rod may disturb the formation of a single crystal because the first melting volume recrystallized in the float zone process has a high amount of slim rod material. In general, oxide layers grow very easily on silicon surfaces and preferably on large rough surfaces. Therefore probably the oxide layers of slim rods with a rough surface disappear more slowly during the heating inside the Siemens reactor.

3.3. Contamination influence of slim rod material to the float zone process

To investigate the contamination influence of the slim rod material on the float zone process, cores with a diameter of about 2 cm were drilled out of Siemens rods on positions with varying slim rod content as depicted in fig. 5 (right). These drilled cores were recrystallized by the float zone process.

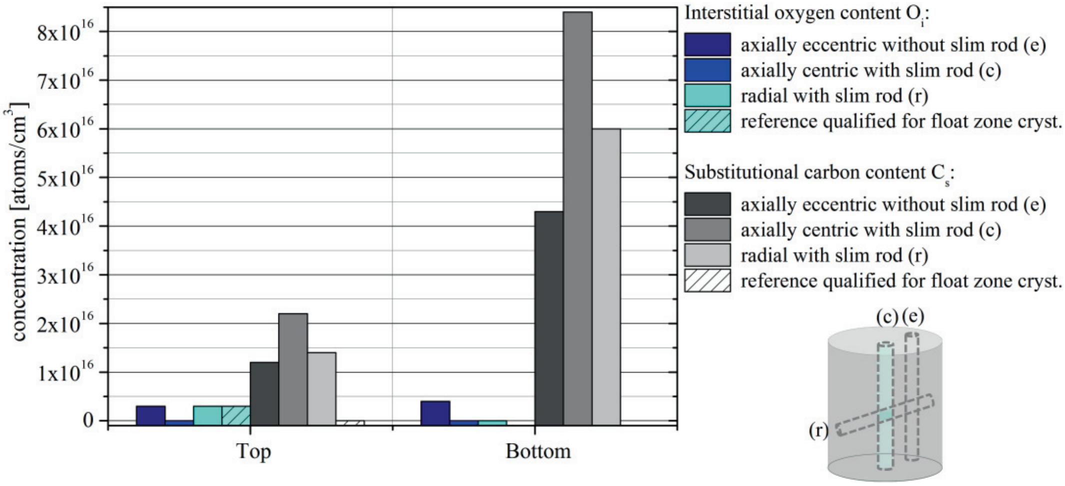

Fig. 5. FT-IR measurements of recrystallized drilled cores of different positions from a Siemens rod produced with float zone optimized deposition rate [2]. The drilled cores includes different quantities of circular slim rod material

FT-IR analyses of the recrystallized drilled cores each on a top and a bottom sample positions are performed. The results clearly show the influence of the slim rod material in particular for carbon with respect to the segregation mechanism ($k_{0,C} = 0,07$) [6]. It can be derived that the larger the fraction of the slim rod material, the higher the carbon content becomes. Reference materials with known float zone suitability show substitutional carbon contents below $1x10^{16}$ atoms/cm³. The interstitial oxygen content was close to the FT-IR detection limit of $1x10^{16}$ atoms/cm³ and therfore very low as expected for float zone silicon. It turns out, that the recrystallized drilled cores at the position axially eccentric without any slim rod material grow as dislocation free single crystal. In contrast the drilled cores from the position axially centric with total slim rod as well as from the radial position with a slim rod content showed a loss of the monocrystalline structure at some point of the recrystallization using the float zone process.

4. Conclusion

In summary, the influence of the chemical purity of the slim rod feeding material to the slim rod production, the influence of the used slim rod material for the Siemens process and to a subsequent float zone crystallization were obtained. The formation of an oxide layer between slim rod and depositied silicon from the Siemens process has to be avoided. The purity of the slim rod feeding material needs to be noticeably below a carbon content of $1x10^{17}$ atoms/cm³ and a gas atmosphere with low nitrogen content (only a few atom percent) is mandatory due to the potential of Si_3N_4 precipitate formation, which should be evaded. The here investigated limiting factors has to be considered for a successful crystallization of monocrystalline silicon by the float zone process.

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