ABSTRACT: The microstructure of SiC particles and SiC filament-type precipitates found in block-cast multicrystalline Si was studied in detail by transmission electron microscopy (TEM). TEM investigations showed that the SiC particles are monocrystalline and the SiC filaments are microcrystalline. Both types of precipitates consist of cubic SiC (3C polytype). However, a high density of planar defects was found in the filaments. High-resolution TEM analysis of the interface between SiC filaments and Si matrix revealed that the interface is rough and very wavy. SiC filaments do not show a special orientation relationship with respect to the Si matrix. The growth mechanisms of SiC precipitates are discussed. The influence of SiC inclusions in terms of device performance is also considered.

Keywords: Multicrystalline silicon (mc-Si); Solar cell; SiC; Transmission electron microscopy (TEM)

1 INTRODUCTION

Low cost mc-Si is mostly fabricated by a vertical freezing process [1]. During processing of block-cast mc-Si, SiC precipitates appear frequently in the top part of mc-Si blocks. There are two different types of SiC precipitates: 1) clusters of SiC particles (several tens of micrometers in size) mostly occurring on Si$_3$N$_4$ rods [2-11] and 2) SiC filaments mostly growing at grain boundaries of mc-Si [4-8]. The filaments have a size of several micrometers in diameter and of several hundred micrometers or even millimeters in length and grow in upward direction [5] (see also Fig. 1).

The SiC precipitates have already been well characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), IR-transmission microscopy (IRM), lock-in thermography (LIT), X-ray fluorescence and electron/light beam induced current methods [3,4,5,8,12]. However, due to the complexity of specimen preparation, only few reports were devoted to TEM characterization [4,13]. It is well-known that the different thinning rate in two phase materials, e.g. SiC embedded in mc-Si, is a common problem in the samples preparation for TEM investigation by conventional methods. This often leads to samples in which one phase is evenly polished while another phase is either etched out or stands proud of the surrounding material. This problem can be overcome by using focused ion-beam (FIB) in the preparation [14]. In addition, the most attractive feature of the FIB technique is its ability to accurately cut a TEM specimen at the area of interest.

Recently, the electrical properties of SiC precipitates found in mc-Si for solar cells were reported [8,13]. It was found that SiC filaments may cause strong shunts in the cells causing a degradation in the performance. The aim of the current study is to investigate in detail the microstructure and modifications of SiC particles and filaments by TEM.

2 EXPERIMENTAL

The samples studied in this work were commercial solar cells fabricated from block-cast mc-Si. The areas of interest were found by LIT shunt imaging over complete solar cells as described in Refs. 7 and 8. Figs. 2(a)-2(b) show typical SEM images of clusters of SiC particles and of SiC filaments, respectively. Cross-sectional and plan-view specimens for TEM investigations were prepared by FIB milling using a “lift-out” technique. A FEI Nova 600 NanoLab system equipped with micromanipulator was used for this work. To produce a plan-view sample a FIB lamella was cut parallel to the area of interest. To prepare a cross-sectional specimen a FIB lamella was cut perpendicular to the area of interest. Two types of cross-sectional specimens were prepared for the SiC filaments lying in grain boundaries of mc-Si. One type of cross-section was cut parallel to a grain boundary (the direction of cutting is shown by arrow “A” in Fig. 2(b)) whereas another type of cross-section was cut perpendicular to a grain boundary (the direction of cutting is shown by arrow “B” in Fig. 2(b)). TEM investigations were carried out in a conventional TEM CM 20 Twin (Philips, Netherlands) at a primary beam energy of 200 keV, and in a high-resolution TEM JEOL 4010 (JEOL, Japan) at a primary beam energy of 400 keV.
for TEM by FIB. The arrow “A” corresponds to the direction parallel to a grain boundary of mc-Si while the arrow “B” corresponds to the direction perpendicular to a grain boundary of mc-Si (see also text).

3 RESULTS

There are many different polytypes of SiC [15]. The polytypes arise from different periodic (stacking) sequence of tetrahedrally bonded Si–C bilayers. Identification of the polytype of SiC particles and SiC filaments precipitated in block-cast mc-Si was performed by the most adopted TEM methods, namely from selected area electron diffraction (SAED) patterns taken from a set of crystallographic directions and high-resolution TEM (HRTEM) images recorded along a low index zone axis.

3.1 Characterization of SiC particles

Fig. 3(a) shows a cross-sectional bright field TEM image of a SiC particle formed in mc-Si. Figs. 3(b) and 3(c) present two SAED patterns along two different zone axes of Fig. 3(a). The patterns were indexed as [101] and [001] zone axes of cubic SiC (3C polytype, a=0.435 nm), respectively. The angle between zone axis patterns (Fig. 3(b) and Fig. 3(c)) read from the tilting angle of the TEM specimen holder is 45°±1°, in good agreement with 45° estimated from a stereographic projection for cubic 3C-SiC. It should be noted that the characterization of SiC particles in mc-Si by electron back scatter diffraction [11] and by X-ray diffraction [9] showed also the cubic structure of SiC particles. In addition, SAED investigations of the SiC particle showed that the particle is monocrystalline. However, macroscopic defects like cracks were observed within the particles. No other defects have been found up to now in these SiC particles.

![Fig. 3: (a) Cross-section bright field TEM image of SiC particle and (b) and (c) SAED patterns of SiC particle taken along two different zone axes. The Pt layer seen in (a) is due to FIB sample preparation.](image)

3.2 Characterization of SiC filaments

Fig. 4(a) shows a typical plan-view bright field TEM image of a SiC filament embedded in a grain boundary of mc-Si. Figs. 4(b) and 4(c) present SAED patterns along [101] and [112] zone axes, respectively, of the region marked in Fig. 4(a). The patterns were indexed using the cubic unit cell of 3C-SiC. The angle between zone axis patterns (Figs. 4(b) and 4(c)) read from the tilting angle of the TEM specimen holder is 28°±1°, reasonable close to 30° calculated from a stereographic projection for cubic 3C-SiC. TEM investigations in dark and bright field of the several SiC filaments showed that the filaments are microcrystalline and consist of several parts (Fig. 4(a)). No accumulation of dislocations was found in the Si matrix around the filaments.

In order to check the presence of other polytypes of SiC in the filaments, SAED and HRTEM studies were performed on a cross-sectional sample cut along a grain boundary of mc-Si. Fig. 5(a) shows a typical bright field TEM image of SiC filaments embedded in a grain boundary of mc-Si. The TEM sample was cut parallel to a grain boundary of mc-Si (see arrow “A” in Fig. 2(b)). SAED investigations performed on the cross-sectional sample containing several filaments proved that the filaments consist of the 3C-SiC. However, the filaments contain a high density of planar defects (Fig. 5(b)) such as stacking faults and twins (Figs. 5(c)-5(d)). An SAED pattern recorded from representative region is shown in Fig. 5(d). The image shows weak diffuse streaks along <111> directions of cubic SiC, indicating the presence of stacking faults (see also Fig. 4(b)). The formation of defects is due to the large lattice mismatch between Si and 3C-SiC (19.9%). In addition, Fig. 5(d) contains extra reflections in 1/3 and 2/3 of the (111) SiC reflection, indicating a threefold periodicity. HRTEM investigations showed that the regions with threefold periodicity were always associated with {111} twin regions of cubic SiC (not shown). Similar regions were also found in other parts of the TEM sample. Previously, it was reported that the threefold periodic structure presented in SAED pattern or in the HRTEM image of cubic SiC is due to overlapping of twinned cubic SiC domains [16,17]. No indication for the presence of other polytypes of SiC was found by both SAED and HRTEM investigations.

![Fig. 4: (a) Plan-view bright field TEM image of SiC filament embedded in a grain boundary of mc-Si and (b) and (c) SAED patterns of SiC filament recorded along two different zone axes. The patterns were taken from the region marked in (a).](image)

![Fig. 5: (a) Cross-section bright field TEM image of SiC filaments embedded in a grain boundary of mc-Si. (b) HRTEM image of the region marked in (a). The image shows planar defects in SiC filament. (d) SAED pattern of SiC filament of the region marked in (a). The triangles show twin spots whereas the double arrows mark double diffraction spots.](image)
Fig. 6 shows a cross-section HRTEM image of the sample cut perpendicular to a grain boundary of mc-Si. The interface between SiC and Si matrix is rough and very wavy. HRTEM (see Fig. 6) and SAED investigations showed also that SiC filaments did not have a special orientation relationship with respect to the Si matrix.

The monocrystalline form of SiC with hexagonal structure and as β-SiC with cubic structure. However, the α-SiC has many polytypes [15]. In the present work, we identify only the β-modification of SiC without the presence of other polytypes of SiC. According to the thermodynamic data, the β-SiC has lower Gibbs energy of formation compared to the α-SiC (ranging from -67.633 kJ/mol to -59.629 kJ/mol at a temperatures between 700 K and 1700 K for β-SiC and ranging from -65.866 kJ/mol to -57.665 kJ/mol at a temperatures between 700 K and 1700 K for α-SiC) [18] and, thus, should be the most stable modification. However, the stability difference is actually small. Consequently, thermodynamics cannot explain why only the β-SiC precipitates in mc-Si solar material. Previously, it was shown that donors like nitrogen favor the formation of cubic SiC [19]. The precipitated SiC in mc-Si is n-doped by nitrogen [8,20]. The latter can explain the formation of SiC clusters and of SiC filaments with cubic structure (β-modification) observed in the current study. It should be noted that the presence of nitrogen in mc-Si is evidenced by the precipitation of Si$_3$N$_4$. The latter is frequently observed in mc-Si [2-11,20].

The formation of SiC precipitates in mc-Si is obviously due to carbon contamination of the Si melt which is probably caused by the graphite heaters in the high-temperature furnace [21]. We found that the microstructure of SiC particles is very different compared to the microstructure of SiC filaments. The particles are monocrystalline while the filaments are microcrystalline with a high density of planar defects. Consequently, we can assume different growth mechanisms of SiC particles and of SiC filaments. Below, we describe the possible formation mechanisms of SiC particles and of SiC filaments.

The monocrystalline form of SiC particles suggests that the particles are growing in the Si melt. Also SiC particles in mc-Si are frequently precipitated around Si$_3$N$_4$ rods [6-8,10,11] which are completely formed in the melt [6,10,11]. This is an additional argument that the formation of SiC particles occurs in the silicon melt. Previously, epitaxial β-SiC films were produced on Si substrates covered by silicon nitride buffer layers [22]. This fact can explain the precipitation of SiC particles around Si$_3$N$_4$ rods in the Si melt and the rods can act as nucleation sites for the formation of SiC particles. Thus, the nucleation of SiC particles is heterogeneous [23]. In contrast, SiC filaments are microcrystalline and their growth mechanism is different from the particles’ one. The SiC particles are frequently a starting point for the growth of SiC filaments (Fig. 1). The SiC filaments are frequently observed at grain boundaries of mc-Si [4-8]. Consequently, the growth of SiC filaments may start during crystallization of Si by diffusion of carbon from the melt into pre-forming grain boundaries of Si. In this case, the nucleation of the grain boundaries occurs at SiC particles. The latter acts also as nucleation center for the growth of SiC filaments. After the nucleation, the growth of the filaments proceeds in the crystallization direction of Si and the filaments multiply by branching. Alternatively, the filaments may also grow by solid state diffusion of dissolved carbon in the solid Si matrix into already pre-existing Si grains. In this scenario, the filaments should form by solid state reaction of C with Si. Thus, the Si should act as a template for the growth of the filaments and the reaction should lead to a defined orientation relationship between the template and precipitate as was already shown in many examples of solid state reactions conducted on single-crystalline substrates [24]. However, we found that the filaments did not have a special orientation relationship with respect to the Si matrix. Nevertheless, the highly disturbed crystal structure of the precipitates suggests that they at least increase in thickness inside the grown silicon ingot by solid state diffusion of dissolved carbon.

Now, we would like to discuss the influence of SiC inclusions in terms of device performance. In the starting material, the SiC filaments have a length up to several hundreds micrometers or even several millimeters [5]. The filaments are growing in crystallization direction of mc-Si. Thus, the filaments can go through several solar cell wafers and may electrically connect the emitter and the back contact of the solar cells. Consequently, the filaments may cause strong ohmic (linear) shunts in the cells [8,20] and thus decrease the efficiency of the cells. Depending on the degree of shunting, the absolute efficiency measured under standard conditions (1000 W/m$^2$, 25 °C) may be reduced by these SiC-induced shunts by ~ 0.5 to 1.5%. However, this degradation can be even higher reaching up to 5 % if the cell is working at reduced light intensity, as it is often the case in middle Europe [25]. On the other hand, SiC particles are lying isolated in the mc-Si material and are not expected to cause any shunts in the cells, as long as their size does not exceed the thickness of the solar cell.

5 CONCLUSIONS

The microstructure of SiC particles and SiC filaments occurring in mc-Si was investigated in detail by TEM. SAED investigations showed that the SiC particles are monocrystalline and the SiC filaments are microcrystalline. Both types of precipitates consist of cubic SiC (3C polytype). It is suspected that nitrogen presented in mc-Si favors the formation of SiC particles
and SiC filaments with cubic structure. A high density of planar defects like stacking faults and twins was found in the SiC filaments. The formation of defects is attributed to the large lattice mismatch between Si and 3C-SiC. Many regions containing a threefold periodic structure were observed within the 3C-SiC filaments, which is due to the overlapping of twinned cubic SiC domains.

Different formation mechanisms of SiC particles and of SiC filaments are assumed. The formation of SiC particles is supposed to grow in the Si melt contaminated by carbon. In contrast, SiC filaments are assumed to grow during crystallization of Si by diffusion of carbon from the melt into pre-forming grain boundaries of Si. However, the growth of the filaments in thickness is considered to occur by solid state diffusion of dissolved carbon in the Si matrix.

The influence of SiC inclusions in terms of device performance was also discussed. Since SiC filaments may be electrically connected both with emitter and back contact of the solar cell, they may cause strong ohmic shunts [8, 20] and thus decrease its efficiency.

ACKNOWLEDGMENTS

This work was supported by the Federal Ministry of Environment (BMU) under contract number 0327650D (Solar Focus). Q-Cells AG (Thalheim, Germany) is gratefully acknowledged for providing the material used for this investigation.

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