DISTRIBUTION AND FORMATION OF SILICON CARBIDE AND SILICON NITRIDE PRECIPITATES IN BLOCK-CAST MULTICRYSTALLINE SILICON

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ABSTRACT: In this paper the horizontal and vertical distribution of silicon carbide (SiC) and silicon nitride (Si₃N₄) precipitates in block-cast silicon is investigated in correlation to the shunting action of these precipitates. From these observations, several hypotheses are derived for the formation of these precipitates. The methods for the investigations are IR-transmission microscopy (IRM), lock-in thermography (LIT), and X-ray micro-fluorescence (µ-XRF). In good agreement with earlier results, we have found 3 different types of precipitates: (1) multicrystalline SiC filaments with a diameter of some microns, (2) Si₃N₄ fibres with a diameter of about 1 micron, appearing in bundles, and (3) straight hexagonal shaped Si₃N₄ rods, often containing SiC clusters around. For investigating the lateral distribution of precipitates, wafers and cells from different columns in the block have been compared. It was found that the columns in the corners and at the edges of the block show the highest concentration of precipitates, whereas the central columns shows the lowest one. The µ-XRF investigations on the precipitates showed nanoclusters consisting of FeSi₂ and Cu₃Si at the SiC filaments and some FeSi₂ at the Si₃N₄ rods. We suppose that Fe plays a role in the formation of the precipitates. The horizontal distribution of the precipitates may be a result of the convection flow in the melt.

1 INTRODUCTION

Material-induced shunts reduce the fill factor and open circuit voltage of solar cells, therefore shunts reduce the efficiency of the cells. In our earlier investigations on material induced shunts [1] we basically found 3 types of precipitates, which are (1) multicrystalline SiC filaments with a diameter of some microns, (2) Si₃N₄ fibres with a diameter of about 1 micron, appearing in bundles and (3) straight hexagonal shaped Si₃N₄ rods or tubes, often containing SiC clusters around. According to our analysis, only the SiC filaments may produce ohmic shunts in the cells. Meanwhile we have observed that the Si₃N₄ precipitates may cause non-linear (diode-like) shunts, but no ohmic shunts. In this contribution we are investigating the vertical and the lateral distribution of these precipitates across the silicon block. Based on these observations, we are suggesting hypotheses for the mechanism of the formation of these precipitates, with the final goal to avoid them or to reduce their detrimental effects on the efficiency of the solar cells. The 3-dimensional distribution of the precipitates in the block was investigated by IR-transmission microscopy (IRM) on horizontally and vertically cut and polished wafers, shunts were imaged by lock-in thermography (LIT) under forward and reverse bias to reveal their linearity, and metallic impurities in the precipitates were imaged by X-ray microfluorescence (µ-XRF).

2 EXPERIMENTAL RESULTS

2.1 Vertical distribution

The starting material for the analysis of the vertical distribution of the precipitates is presented in Fig. 1, where a multicrystalline silicon block was cut vertically. From this material, several small samples 20x20x1 mm³ in size have been prepared at different heights. The sample surfaces have been polished down to 250 nm roughness for the IRM measurements.

Figure 1: Image of the wafers cut vertically from a brick

It was found that most precipitates are concentrated in the upper third fraction of the block. Samples A, B, C, D, and F, denoted in Fig. 1, have been investigated by IRM. In samples D and F no precipitates were found, and sample C contained only a low amount of Si₃N₄ fibres. Most precipitates were concentrated in samples A and B.
Fig. 2 shows the overview IRM image of sample B. In good correspondence to earlier results [1, 3], we have found the above mentioned 3 different types of precipitates: (1) multicrystalline SiC filaments with a diameter of some microns, which are mostly found in grain boundaries and are usually branched, as shown in Fig 3a, (2) Si₃N₄ fibres with a diameter around 1 micron, which are appearing in bundles (Fig 3b), and (3) straight hexagonal shaped Si₃N₄ rods up to some 10 microns in diameter, often containing SiC clusters around (Fig 3c). Note that the identification of these precipitates has been done by EDX analysis and TEM diffraction analysis [1].

In these vertical views it was found that the SiC filament growth is often starting from SiC clusters, which are attached to Si₃N₄ rods (Fig 3c). The growth is continuing in crystallization direction, whereby the filaments multiply by branching and yield dense groups of these filaments. From our investigations on vertically cut samples we know that these precipitates are mostly growing in large-angle grain boundaries, but not in twins [1]. This leads to the speculation that the SiC clusters are forming if a Si₃N₄ rod crosses a grain boundary. Fig. 2 shows that, after some mm, the growth of the filaments stops, but later the growth may start again in the same way. Thus, the SiC filaments often appear vertically distributed in several successive rushes, as indicated by the dashed lines. Also Soiland et al. [2] have found that the carbon concentration may fluctuate vertically in the block.

2.2 Lateral distributions

For investigating the lateral distribution of precipitates, wafers and cells from different columns in another block have been compared. The methods used were lock-in thermography for the solar cells to investigate the shunting behavior, and IRM for inspecting the polished wafers.

Fig. 4a shows the arrangement of the bricks used for the lateral investigations. Fig. 4b shows a lock-in thermogram of a solar cell from the top of the corner brick A1 at 0.5V in forward bias and Fig. 4c in the same reverse bias. The comparison of the two images indicates that this cell is strongly linear shunted, the dominant heat source is the Joule heat in both bus bars. The uppermost cells of D2 behaved similarly. Only the innermost brick C3 revealed a high density of non-linear shunts at the uppermost cell (see Fig. 6a/b), but no linear shunts. Deeper lying cells showed either non-linear or no shunts.

IRM investigations of one of the top-most wafers in brick A1 have shown a high concentration of SiC filaments outside of grain boundaries and (c) a Si₃N₄ rod with SiC clusters

IRM investigations of the wafer on top of the brick A1 showing (a) a high concentration of SiC filaments outside of grain boundaries and (b) a high concentration of Si₃N₄ filaments in grain boundaries, and (c) a Si₃N₄ rod with SiC clusters.
of the SiC filaments in grain boundaries. This mechanism locally enrich, which would explain the preferred growth showing a groove. In this groove impurities like carbon may certain grain boundaries the solid-liquid-interface may after the formation of the grains. It is known [4] that at precipitates, hence they are growing during or/and shortly crystallization of silicon and to additional dissolution of SiC, leading to a lowered carbon slightly lower than the eutectic temperature of SiC. Then supersaturated by carbon may form at a temperature saturation limit, and then drops. We assume that silicon supersaturated by carbon may form at a temperature slightly lower than the eutectic temperature of SiC. Then the SiC precipitates, leading to a lowered carbon concentration in the silicon, until the precipitation stops. Then the carbon concentration increases again, due to the crystallization of silicon and to additional dissolution of carbon e.g. from the surrounding gas atmosphere, and the process may repeat.

The preferred appearance of the SiC precipitates in several successive rushes (Fig. 2) is pointing to certain instabilities in the supersaturation behavior of the melt. This is supported with the observation of Soiland et al. [2]. They observed that the concentration of the carbon in the solid phase increases gradually, attain values above the saturation limit, and then drops. We assume that silicon supersaturated by carbon may form at a temperature slightly lower than the eutectic temperature of SiC. Then the SiC precipitates, leading to a lowered carbon concentration in the silicon, until the precipitation stops. Then the carbon concentration increases again, due to the crystallization of silicon and to additional dissolution of carbon e.g. from the surrounding gas atmosphere, and the process may repeat.

The preferred appearance of the SiC filaments in grain boundaries is a strong indication that these are real precipitates, hence they are growing during or/and shortly after the formation of the grains. It is known [4] that at certain grain boundaries the solid-liquid-interface may show a groove. In this groove impurities like carbon may locally enrich, which would explain the preferred growth of the SiC filaments in grain boundaries. This mechanism would also explain the appearance of the SiC clusters if the Si$_3$N$_4$ rods are crossing grain boundaries (see below).

We observed that the starting point of the SiC filament are very often at SiC clusters at the silicon nitride rods (see Fig. 3c). A µ-XRF investigation was done on such a sample, which was polished until the Si$_3$N$_4$ rod appeared in longitudinal cross section. Figs. 7b and 7c showed Fe and Cu at the SiC clusters, which could be identified as FeSi$_2$ and Cu$_3$Si$[5]$. Note that also the Si$_3$N$_4$ rod itself contains measurable amounts of Fe and Ca, but no Cu. It is well known that metallic impurities favor the supercooling effect [6]. The presence of Fe and Cu are not surprising, since these are the most frequent metallic impurities in mc-Silicon [7,8].

3.2 Silicon nitride formation

We found two clearly distinct types of Si$_3$N$_4$ precipitates, the thin fibres and the large rod-like structures. The fibre structures have been observed also by other groups [3,9]. They consist of monocrystalline β-Si$_3$N$_4$. In contrast to the finding of Lawerenz et al [9], we did not see a preferential occurrence of these fibres at grain boundaries. Some fibres are ending at grain boundaries, but most of them are not. However, we have found from the vertically cut samples that all fibre bundles are roughly oriented and are branching in growth direction. This agrees with the assumption that the fibre bundles grew at the liquid-solid interface during crystallization [2,9]. The rod-like structures with perfect hexagonal shape have been observed also by Ferrara [3] and Soiland et al. [2]. For these objects we did not find any correlation to the growth direction. In our case we did not see any Si$_3$N$_4$ at the bottom of the block, unlike Soiland et al. [10]. This allows us to conclude that our melt is not saturated with nitrogen before the start of the crystallization. Obviously the impurity content of the melt is strongly dependent on the crystallization furnace and the process conditions used. In Fig. 7b and 7c we see that the Si$_3$N$_4$ rods contain also Fe but no Cu. In Fig. 7d, a large amount of Ca has been observed in the Si$_3$N$_4$ rods. It is known that Ca is a common impurity in commercial Si$_3$N$_4$ and plays an important role on the formation of β-Si$_3$N$_4$ [11]. Also Fe is used as a catalyst in the commercial production of Si$_3$N$_4$, this is why it is a major impurity in this material [12].

Based on these observations, Buonassisi [5] suggested a mechanism for the formation of Si$_3$N$_4$ fibres involving iron silicide that can be seen in Fig. 8. During crystal growth, the nitrogen and iron content in the liquid phase increases due to their low segregation coefficient (a). At a certain critical point, constitutional supercooling occurs, and liquid droplets of FeSi$_2$ are forming at the interface (b). Nitrogen, having a very high diffusivity both in liquid and high-temperature solid silicon, is dissolved atomically in these droplets. During cooling, nitrogen gets supersaturated in these droplets and precipitates out to form a monocrystalline rod or tube of β-Si$_3$N$_4$ growing in direction of its c-axis (c). As the solidification front advances, the Si$_3$N$_4$ fibre is more and more buried in the silicon crystal (d). This model explains why the fibres are obviously growing and branching upwards in growth direction of the silicon. The fact that the actual growth appears in the melt explains why these fibres are not or only little affected by grain boundaries. Obviously these fibres are frequently branching, leading to the observed bundles.
We believe that only the relatively long (several mm) and up to several 10 microns thick Si₃N₄ rods are real inclusions, hence they are completely forming in the melt, are sinking down to the solid-liquid-interface, and are overgrown by the silicon. One argument for this hypothesis is the large thickness of these rods, that cannot form solely by diffusion of nitrogen supersaturated in the solid silicon material. Maybe the actual growth mechanism is a similar one as shown in Fig. 8, but is completely appearing in the melt. We have not observed any branched Si₃N₄ rods yet, but in earlier investigations also cross-shaped Si₃N₄ complexes have been found [1]. We have observed that the diameter of the rods often gradually decreases over the length, so obviously they show a combined length- and thickness growth, which also indicates that they are growing in the melt. The fact that in the uppermost wafers no Si₃N₄ rods have been found [5] also indicates that they are growing in the melt. The fact that the SiC filaments are appearing preferentially in the edge region of the block. If a notable amount of carbon is dissolved at the surface of the melt from the surrounding gas atmosphere, the downward stream should be more carbon-rich.

3.3 Strategies to avoid the formation of the precipitates.

If the formation mechanism of these precipitates is known, certain strategies may be suggested to avoid the formation of these precipitates:
- Reduce the content of N and C in the melt, e.g. by reducing the amount of time the molten silicon is in contact with the crucible or by avoiding high C contents in the surrounding atmosphere.
- Addition of impurities during later stages of crystal growth that decompose Si₃N₄ and SiC, or form ternary/quaternary compounds. Kalejs et al. [13] found that the addition of Al in the melt reduces the formation of Si₃N₄ and SiC precipitates.
- Reduce the Ca or Fe content in the Si₃N₄ coating. If catalytic reactions should enhance the formation of these precipitates, especially of SiN₃ rods, this should reduce also the amount of these precipitates.

4. CONCLUSIONS.

The horizontal and vertical distribution of SiC and Si₃N₄ precipitates in cast solar silicon was investigated, and metallic impurities in these precipitates were imaged on a microscopic scale. It was found that most precipitates concentrate in the upper third part of the block. While the SiC filaments are present mostly in the uppermost part of the block, the Si₃N₄ precipitates are also appearing in somewhat deeper regions of the block. The SiC filament growth is often starting at a certain height from SiC clusters, which are attached to Si₃N₄ rods. The growth is continuing in crystallization direction, whereby the filaments multiply by branching, yielding dense groups of these filaments. After some mm, the growth of the filaments stops, but later on the growth may start again in the same way. Thus, the SiC filaments are vertically distributed in several successive rushes. We suppose that the horizontal distribution of the precipitates is a result of the convection flow in the melt, which is upwards in the center and downwards at the edges.

The µ-XRF investigations showed nanoclusters consisting of FeSi₂ and Cu₃Si at the SiC clusters attached to the Si₃N₄ rods. The chemical analysis revealed also Fe and a large amount of Ca dissolved in the Si₃N₄ rods. We suppose that the Fe may play a role in the formation mechanism at least of the Si₃N₄ precipitates. The appearance of the SiC precipitates in several successive rushes is pointing to certain instabilities in the supersaturation behaviour of the melt. Our hypothesis to the growth mechanism of the different precipitates is that the SiC filaments are growing at and/or shortly behind the liquid-solid-interface, where they experience the presence of grain boundaries. The Si₃N₄ fibres should grow slightly in front of the crystallization front still in the liquid silicon, maybe catalyzed by FeSi₂ droplets. For both defect types a further thickness growth may happen in the cooling phase by precipitation of impurities more and more supersaturated in the solid Si. We believe that only the large Si₃N₄ rods are real inclusions.

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REFERENCES