ABSTRACT: Silicon carbide and silicon-nitride precipitates appear often in the upper part of multicrystalline silicon blocks. It is well known that these precipitates may cause shunts in solar cells, but the electrical properties of the precipitates are unknown so far. To study their electrical properties, the precipitates were isolated from the Si bulk material. Silicon carbide filaments can cause severe ohmic shunts, so we concentrated on the investigations of the electrical properties of these filaments. It turns out that the filaments are highly conductive. Measurements of filaments, which are still embedded in the silicon bulk material, were also performed to study the heterojunction silicon carbide – silicon. The results show that there is only a low positive conduction band offset at the interface silicon – silicon carbide, hence it can be assumed that the shunt current flows inside of the filaments.

Keywords: EBIC, Multi-crystalline block-cast silicon, Shunts, Silicon carbide, Simulation

1 INTRODUCTION

Shunts can reduce the efficiency of silicon solar cells. Earlier investigations showed that these shunts often were material-induced and consist of silicon carbide (SiC) and silicon nitride (Si$_3$N$_4$) precipitates [1]. These precipitates are growing during the crystallisation process of the multicrystalline silicon (mc-Si) blocks and mostly appear in the upper part of these blocks [2,3]. Further investigations showed that SiC-filaments can cause severe ohmic shunts [4]. The SiC-filaments are growing in crystallisation direction of the mc-Si blocks and can have a length from some micrometer up to several millimeters. Therefore they can affect several solar cell wafers. The electrical properties of the SiC-filaments and the shunt mechanism were not proven so far. The goals of the investigations described in this paper are the isolation of the precipitates from the mc-Si bulk material, to investigate the electrical properties of the precipitates and to develop a model of the conduction mechanism of the ohmic shunts in mc-Si solar cells.

2 EXPERIMENTAL

2.1 Isolation of the precipitates

To investigate the electrical properties of the precipitates, it was necessary to isolate them from the Si bulk material. Søiland et al. dissolved the silicon material in a standard etching mixture, consisting of hydrofluoric acid (HF) and nitric acid (HNO$_3$). The SiC and Si$_3$N$_4$ precipitates are inert against this acid mixture and can be separated from the acid mixture by filtering the liquid. Unfortunately, the very thin and brittle SiC-filaments were not found or were destroyed with this method [2]. We increase the yield and decrease the destruction of the SiC and Si$_3$N$_4$ particles by dividing them from the acid mixture by a teflon funnel [5]. After dissolving a piece of a solar cell, which contains precipitates, the acid mixture was diluted with deionized water and decanted several times until the acid concentration was below 0.05%. After that, the residual liquid, which contains the SiC and Si$_3$N$_4$ particles, was put into a teflon funnel. The funnel was sealed by a piece of a monocrystalline Si-wafer with a 100 nm SiO$_2$ layer on its surface. By shaking and rotating the funnel one can concentrate the particles in the middle of the SiO$_2$-wafer (Fig. 1). The residual liquid evaporates.

Figure 1: Scheme of the isolating method

As can be seen in Fig. 2, SiC and Si$_3$N$_4$ particles can be found on the Si-wafer. The particles were divided into four different types:

1. Si$_3$N$_4$-rods
2. SiC-filaments, which appear in grain boundaries, as single precipitates, or grown from SiC-clusters
3. Si$_3$N$_4$-fibres (not shown in this paper)
4. SiC-clusters, which appear mostly on Si$_3$N$_4$-rods
2.2 Electrical measurements

This paper concentrates on the electrical properties of the SiC-filaments, which obviously cause severe ohmic shunts in mc-Si solar cells. The SiC-filaments are approximately 1 µm to 4 µm in diameter, therefore it is necessary to make the electrical measurements in a secondary electron microscope (SEM). To contact the SiC-filaments, we used two nanomanipulators (Kleindiek), which were equipped with platinum/iridium tips. The tips were produced by electro-chemical etching of Pt/Ir wires (80/20, 0.25mm diameter) after an etching method by Libioulle et al. [6]. Fig. 3 shows the manipulators.

For recording the current-voltage (I-V) curves we used a picoamperemeter (Keithley 6487) with an internal voltage source and computer control. The capacitance-voltage (C-V) measurements were done with a capacitance meter (Booton 7200). Two types of experiments were done.

1. Investigation of SiC-filaments, which were dissolved out of the Si bulk material as described in 2.1. On these SiC-filaments, two-point I-V measurements and four-point measurements were performed, as shown in Fig. 4.

2. Investigation of SiC-filaments, which were still embedded in the Si bulk material, as can be seen in Fig. 5a). For these measurements shunted areas of solar cells were located and cut out of the solar cell. After polishing the solar cell and etching the surface for only ten seconds by a HF+HNO₃ mixture, the SiC-filaments stick out of the wafer surface. On these samples I-V, C-V and electron beam induced current (EBIC) measurements were performed (see Fig 5). In Fig. 5a) a contacted SiC-filament, which sticks out of a grain boundary, is shown. Fig. 5b) shows an EBIC image of this SiC-filament.

3 RESULTS

Electrical measurements were also performed on Si₃N₄-roses, but it turned out that these precipitates are insulating, hence no further investigations on Si₃N₄-roses was performed.

3.1 Two-point and four-point investigations on isolated SiC-filaments

The two-point I-V characteristics of the SiC-filaments showed a linear behaviour. The resistance of the SiC-filaments is in the order of 10 Ω, as can be seen in Fig. 6. Regarding the dimensions of the SiC-filaments their resistivity was calculated to be ρ = 0.002 Ωcm. The four-point measurement showed, that the SiC-filaments are n-type. Assuming a mobility of the electrons µ = 400 cm²/Vs [7] leads to a carrier density of n = 8 x 10¹⁸ cm⁻³ [5].

![Figure 2: SiC and Si₃N₄ particles](image)

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![Figure 3: Two nanomanipulators with Pt/Ir-tips to contact the precipitates](image)

**Figure 3:** Two nanomanipulators with Pt/Ir-tips to contact the precipitates

![Figure 4: Two-point measurement a) and four-point measurement b) of SiC-filaments](image)

**Figure 4:** Two-point measurement a) and four-point measurement b) of SiC-filaments

![Figure 5: I-V measurement of a SiC-filament embedded in bulk Si a) and corresponding EBIC image b)](image)

**Figure 5:** I-V measurement of a SiC-filament embedded in bulk Si a) and corresponding EBIC image b)

![Figure 6: I-V curve of a SiC-filament corresponding to Fig. 4a)](image)

**Figure 6:** I-V curve of a SiC-filament corresponding to Fig. 4a)
3.2 Measurements of SiC-filaments embedded in bulk Si

For measuring SiC-filaments as they appear in mc-Si solar cells, an I-V measurement as seen in Fig. 5a) was performed. The base contact was made by rubbing on liquid gallium/indium to the backside of the Si substrate. Now it was possible to measure the I-V and C-V curves of the heterojunction n-SiC (the filament) – p-Si (the solar cell substrate material). Fig. 7a) shows the I-V curve. The characteristic is diode-like. From the C-V measurement, one can determine the diffusion voltage of the hetero pn-junction n-SiC – p-Si to be 1.1 V (Fig. 7b)). The EBIC investigation of this system p-Si – n-SiC showed current collection in the silicon around the filaments, as can be seen in Fig. 5b.

4 SIMULATION AND DISCUSSION

4.1 Simulation

The simulation of the hetero junction n-SiC – p-Si was done with AFORS-HET [8]. We fitted the I-V and C-V characteristics, which were simulated by AFORS-HET, to the experimental data, see Fig. 7.

![Figure 7: I-V curve a) and C-V curve b) of the hetero junction n-SiC – p-Si, the black curves are the experimental data, the red curves are the data simulated with AFORS-HET](image)

By using the parameter set, which make the best fit of the simulated data with the measured data, we calculated the band diagram of the heterojunction, which is shown in Fig. 8. It turns out, that the conduction band offset from the p-Si to the n-SiC is positive. The work function of the SiC (Φ_{SiC}) is not known exactly, but a slight change of this parameter did not lead to any change of the simulated characteristics. Therefore, we can not give an exact value for the height of the band offset. However, our simulation matches quite well to the experimental data in the range from Φ_{SiC} = 4.4 eV to Φ_{SiC} = 4.85, which are reasonable values for Φ_{SiC} [9]. The barrier height of the positive band offset turns out to be several 10 meV. Such a barrier height can easily be overcome by electrons. Therefore, electrons from the conduction band in the p-Si will enter the conduction band in the n-SiC, and the shunt current will flow in the SiC-filament.

![Figure 8: By AFORS-HET simulated band diagram of the heterojunction p-Si – n-SiC, the band offset is positive and the barrier height E_{BO} is low (here ≈ 60 meV)](image)

4.2 Discussion

The question whether the shunt current flows in an inversion layer [1] or in the SiC-filament was not clear so far. Using the new experimental data of the electrical properties of the SiC-filaments and the data of the system n-SiC – p-Si for the simulations, strong hints for the assumption that the shunt current flow inside the SiC-filaments are given. A second indication for a shunt current flow inside the SiC-filament is the estimation of the resistance of a possible inversion layer at the interface p-Si – n-SiC. By assuming a positive band offset of the conduction band, which is higher than expected from the AFORS-HET simulations, an inversion layer will form at the interface p-Si – n-SiC. Electrons can not overcome the barrier, and the shunt current will flow in this inversion layer [1]. An estimation shows that the resistance of this inversion layer is orders of magnitude higher than the resistance of the SiC-filaments. Hence, the shunt current obviously flows in the SiC-filaments and the simulation of the heterjunction presents a realistic description of the electronic properties at the p-Si – n-SiC interface.

5 SUMMARY

SiC and Si\(_3\)N\(_4\) precipitates, which appear in block-cast silicon for solar cells, were isolated from the Si bulk material. I-V measurements were performed on the precipitates. The Si\(_3\)N\(_4\)-rods are insulating. However, the SiC-filaments are highly conductive with a resistivity of 0.002 Ωcm. The filaments are n-doped with a carrier density of n ≈ 8 x 10\(^{18}\) cm\(^{-3}\). I-V and C-V measurements of SiC-filaments, which are still embedded in the p-Si bulk material were, also performed. The I-V characteristic of this heterojunction shows a diode-like behaviour. From the data of the C-V curve, a diffusion voltage of the heterojunction of 1.1 V was determined. The band offset between SiC-filaments and Si was determined by fitting the I-V and C-V characteristics simulated to the experimental data by AFORS-HET. It turns out that there is a low positive band offset of the conduction band of only some ten meV. Hence, the shunt current obviously flows inside of the SiC-filaments.
REFERENCES


