

Electronic activity of SiC precipitates in multicrystalline solar silicon

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In the upper part of block-cast multicrystalline silicon one often finds silicon carbide and silicon nitride precipitates and inclusions. These contaminants can cause severe ohmic shunts in solar cells and thus decrease the efficiency of the solar cells very strongly. It is well known that the silicon carbide precipitates cause the ohmic shunts. However, the electrical properties of the silicon carbide was unknown so far. To study the electrical properties of these silicon carbide particles we isolated them from the silicon bulk material and performed different electrical measurements on them. The measurements show that the silicon carbide precipitates are highly conductive. An investigation of the heterojunction silicon–silicon carbide was also performed and a simulation of this heterojunction leads to a new model of the ohmic shunt mechanism. It is concluded that the shunt current flows inside of the filaments.

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1 Introduction

The efficiency of multicrystalline silicon solar cells can be strongly reduced by material-induced shunts [1]. These shunts are caused by silicon carbide (SiC) precipitates [2], which were generated during the crystallisation of the multicrystalline silicon (mc-Si) ingot at the block-casting process [3]. It is well known that so-called SiC-filaments cause dangerous ohmic shunts in solar cells [2]. However, the electrical properties and the electronic activity of the SiC particles, which are embedded in the mc-Si, were unknown so far. Since the SiC-filaments can have a length up to some millimeters, they can damage several solar cell wafers, and it will be important to know more about the shunting mechanism. This paper concentrates on the electrical measurements of the SiC-filaments and the electronic activity of these precipitates in the mc-Si bulk material. A model of the shunt mechanism of material-induced ohmic shunts in mc-Si solar cells will be developed.

2 Experimental

2.1 Isolation of the precipitates

Since the SiC-filaments are embedded in the silicon bulk material they must be isolated from the silicon. We used a method by Søiland et al. [3], which we modified drastically to increase the yield of the fine and brittle SiC-filaments [4]. Briefly, we etched a piece of a solar cell wafer, which contains a large amount of precipitates and inclusions, in a mixture of hydrofluoric acid and nitric acid. After dissolving the Si, SiC and silicon nitride (Si₃N₄) particles remain in the acid. The acid mixture was diluted with

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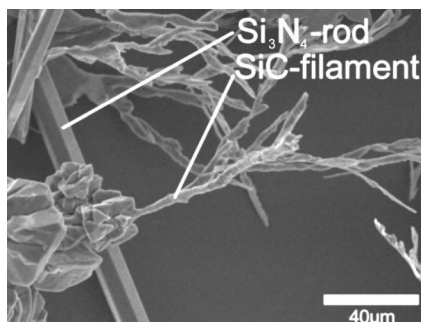


Fig. 1 SiC and Si₃N₄ particles isolated from the mc-Si bulk material.

deionised water and decanted until the acid concentration of the liquid reached <0.05%. The residual liquid with the SiC and Si₃N₄ particles in it was put into a funnel made by teflon. The funnel was sealed by a Si wafer, which has a 100 nm SiO₂ layer, to isolate the SiC and Si₃N₄ particles electrically from the substrate. After the liquid was evaporated the particles can be found on the Si wafer surface, as can be seen in Fig. 1.

2.2 Electrical measurements

The diameter of the SiC-filaments and Si₃N₄-rods are in the range of some micrometers. Thus it is necessary to use a scanning electron microscope (SEM) for all measurements. We applied two nanomanipulators (Kleindiek) in the SEM. These nanomanipulators are equipped with PtIr-tips, which were etched after a procedure of Libioulle et al. [5]. The nanomanipulators and a PtIr-tip can be seen in Fig. 2.

For measuring current–voltage (I – V) curves a picoamperemeter with an internal voltage source was used (Keithley 6487, ≤ 2 fA noise) to have the possibility to apply very low voltages and avoid the destruction of the fine and brittle SiC-filaments. Capacitance–voltage (C – V) characteristics were measured by using a Booton 7200 bridge. The 4-probe measurement was accomplished by a VEECO FPP-5000 instrument. To determine the type of conducting this instrument employs at first a rectification test on the specimen. If the rectification test is inconclusive the instrument uses a thermal test. In the case that none of the tests give a clear result the instrument will display both n- and p-type. For probing the SiC-filaments we attached a special microscopic 4-point probe (Capres) to one of the manipulators. We connected the 4-point probe to the VEECO instrument and contacted in that way the filaments for the type test.

Three types of electrical measurements were performed, which are 2-probe measurements of SiC-filaments and Si₃N₄-rods, 4-probe measurements of SiC-filaments, and measurements of SiC-filaments, which were still embedded in the Si bulk material (heterojunction between Si and SiC). In Fig. 3 all

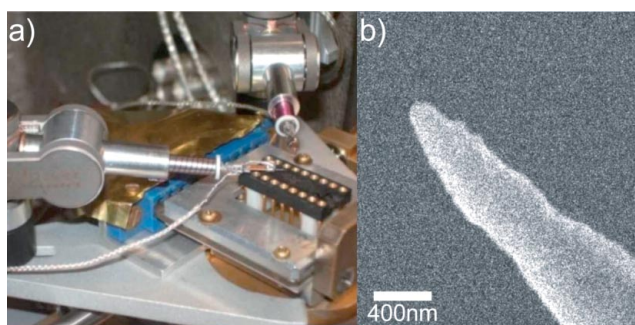


Fig. 2 (online colour at: www.pss-a.com) Nanomanipulators in a SEM (a) and one PtIr-tip, which is applied to the nanomanipulators for the electrical measurements of the precipitates (b).

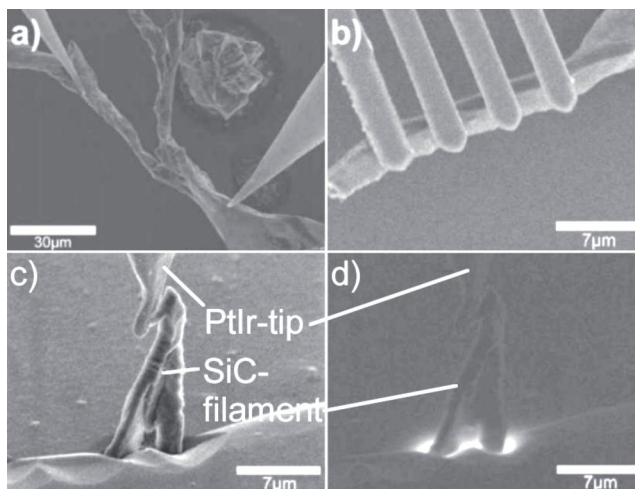


Fig. 3 Measurement methods: 2-probe measurement of a SiC-filament (a), 4-probe measurement of a SiC-filament (b), measurement of the heterojunction (c), and EBIC image of this heterojunction (d).

types of measurements are shown. Additional to the I – V and C – V characteristics electron beam induced current (EBIC) measurements were performed on SiC-filaments, which were embedded in Si bulk material. In Fig. 3d an EBIC image is shown.

3 Results

The resistivity of the Si_3N_4 -rods was measured to be above $4.7 \times 10^7 \Omega \text{ cm}$, therefore Si_3N_4 -rods are insulating and no further investigations were made on Si_3N_4 precipitates.

The I – V curve of the SiC-filaments is linear. The resistance of the SiC-filaments is in the order of 10Ω . Referred to the dimensions of the filaments their resistivity is $\rho = 0.002 \Omega \text{ cm}$, and the resistance of one $250 \mu\text{m}$ (= thickness of the solar cell wafer) long filament is about 710Ω . The 4-point probe measurement by the VEECO instrument shows reproducibly that the SiC-filaments are n-type conducting. Transmission electron microscopy (TEM) investigations on the SiC-filaments confirmed that the SiC-filaments consist of cubic SiC (3C-SiC) [1]. There is no indication for a graphite phase in the filaments, hence we suppose that the electrical properties of the filaments are dedicated by the 3C-SiC. Therefore we assume a carrier mobility of $\mu \approx 400 \text{ cm}^2/\text{Vs}$ [6] for the electrons in the SiC, thus the carrier density is approximately $n \approx 8 \times 10^{18} \text{ cm}^{-3}$ [4]. We have to mention that the value for μ is taken from Ref. [6], because unfortunately we have no measurement of the electron mobility. Therefore the value for

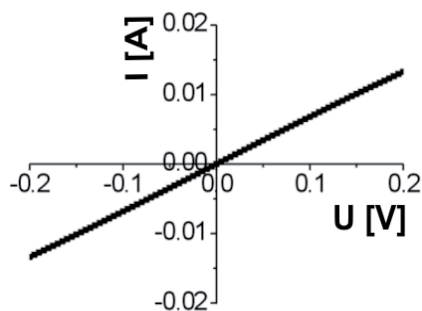


Fig. 4 Example of an I – V characteristic of a SiC-filament. The resistance of this measurement is $R \approx 15 \Omega$.

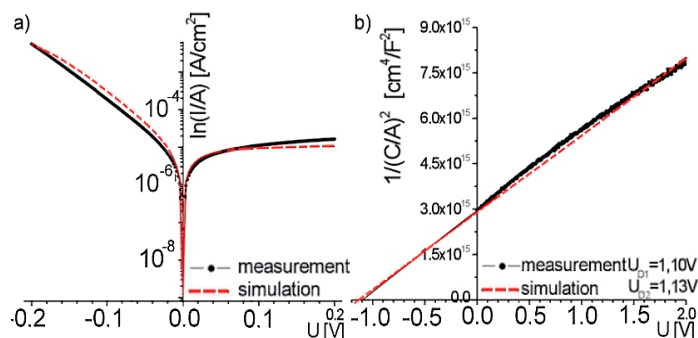


Fig. 5 (online colour at: www.pss-a.com) I – V characteristic (a) and C – V curve (b) of a SiC-filament, which is embedded in the Si bulk material. The black (solid) curves are the experimental data, the red (dotted) ones are simulated data, respectively.

n is the lower limit of the carrier density, because the mobility of the electrons could be lower than we assume. The 2-probe I – V characteristic of a SiC-filament is shown in Fig. 4.

The I – V and C – V measurements of a SiC-filament, which is embedded in the Si bulk material (see Fig. 3c), is shown in Fig. 5. The I – V curve is similar to that of a p–n junction with a well pronounced asymmetry. Here the n-type material is the SiC and the p-type material is the p-type Si substrate (the solar cell substrate). At the interface between the SiC-filament and the Si bulk material an EBIC signal appears (see Fig. 3d), so there should be a collecting barrier for electrons.

The C – V characteristic is also similar to that of a p–n junction. From the C – V curve one can determine the diffusion voltage of the heterojunction n-SiC – p-Si to $U_{\text{Diff}} = 1.1$ V (see Fig. 5b). The diffusion voltage of a normal p–n junction of a solar cell is approximately $U_{\text{pn}} = 0.9$ V. So there is obviously a separating layer between Si and SiC.

4 Simulation of the heterojunction

With the knowledge of the electrical properties of the SiC-filaments, a model of the shunt mechanism and the electronic activity of the SiC was developed.

For the simulation the computer program AFORS-HET [7] was used, which is a special program for the simulation of semiconductor heterojunctions. In AFORS-HET one can define an arbitrary system of semiconductor layers with different properties. For our simulation of the heterojunction system n-SiC – p-Si we defined a two layer system: One layer with the properties of the n-SiC and one layer with the well known properties of the p-Si solar cell substrate. The best fit of the experimental I – V and C – V data by the simulated data (see Fig. 5) occurs by defining the interlayer between p-Si and n-SiC as an intrinsic Si layer, which contains defects. These defects act as acceptors and donors. This is a weak point of the simulation, because nothing is known about the defect structure of the interface between Si and SiC. Another parameter in the simulation was the work function Φ_{SiC} of the SiC. However, a slight change of Φ_{SiC} in the range from $\Phi_{\text{SiC}} = 4.4$ eV to $\Phi_{\text{SiC}} = 4.9$ eV, which are reasonable values for Φ_{SiC} , does not change the simulated characteristics significantly. With the parameter set that shows the best match of the simulated data with the experimental data, a simulation of the band structure of the heterojunction was made. Figure 6 shows this band diagram. Obviously only a very low positive offset of the conduction band occurs at the interface between Si and SiC. The height of the barrier at interface depends mainly on Φ_{SiC} . By changing Φ_{SiC} from 4.4 to 4.9 eV, the barrier height changes from 0.47 to 2 meV. The best fit occurs at $\Phi_{\text{SiC}} = 4.85$ eV, which corresponds to a conduction band offset barrier height of 47 meV.

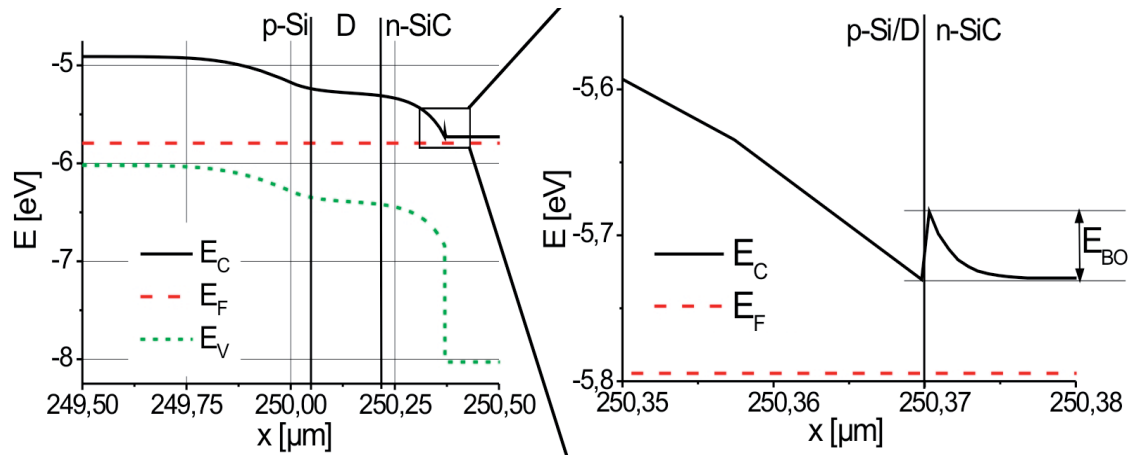


Fig. 6 Band diagram of the heterojunction Si–SiC, where D marks the defect layer, E_C is the conduction band, E_F the Fermi level, E_V the valence band, and E_{BO} the barrier height of the band offset.

5 Discussion

In [2] it was assumed that the shunt current flows in an inversion layer, which exists at the Si–SiC interface. However, the simulation of the electronic band structure of this heterojunction shows that only a low positive conduction band offset occurs at the interface. Electrons can easily overcome this barrier and can enter the conduction band of the SiC. Hence, we conclude that the shunt current flows in the SiC-filament.

We made a simple estimation of the resistance of a possible inversion layer. We found that for an electron concentration of 10^{16} cm^{-3} the resistance of the inversion layer should be orders of magnitude higher ($R_{\text{inv}} \approx 80 \text{ M}\Omega$) than the resistance of the SiC-filament ($R_{\text{fila}} \approx 710 \Omega$). Indeed, a shunt resistance of about 800Ω is compatible with measured shunt resistances of cells containing a known number of SiC-filament-induced shunts. This is the second argument that the shunt current flows in the SiC-filaments.

A new shunt model is presented in Fig. 7, which shows the hump of the defect layer in the silicon and a low positive conduction band offset between Si and SiC. Since the defect structure of the interface of the heterojunction is not well known yet, further investigations are necessary to improve the model.

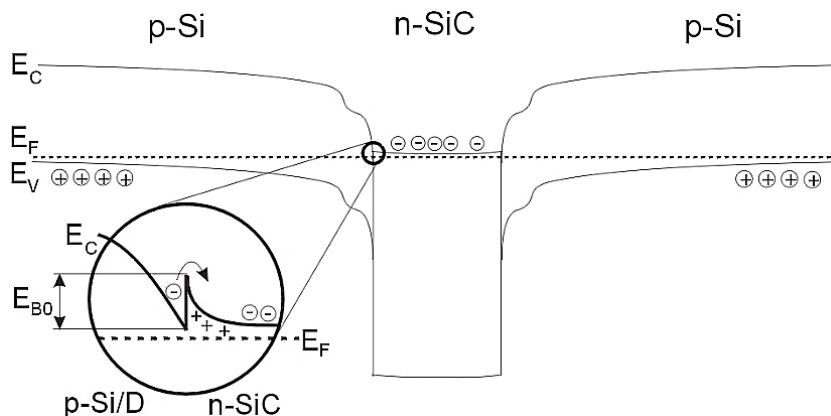


Fig. 7 Model of the band diagram.

6 Summary

Precipitates, which occur in mc-Si for solar cells, were isolated from the solar Si bulk material. SiC and Si₃N₄ particles were found. Electrical measurements were performed on the particles. The Si₃N₄-rods are electrically insulating and the SiC-filaments are highly conductive with a resistivity of $\rho = 0.002 \, \Omega \, \text{cm}$. The result of 4-probe measurements on SiC-filaments was that they are n-type. From the C - V characteristics a diffusion voltage at the heterojunction Si-SiC of 1.1 V was determined. The simulation of the band structure of the heterojunction leads to a low positive conduction band offset with a barrier height of only some ten meV. Hence, obviously the shunt current flows inside of the SiC filaments.

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