# A STUDY OF THE CHARGE TRANSPORT ACROSS GRAIN BOUNDARIES IN POLYCRYSTALLINE SILICON SOLAR CELLS WITH A FRONT CONTACT ALONG THE GRAIN BOUNDARIES

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ABSTRACT: The influence of a front contact applied along grain boundaries in polycrystalline silicon solar cells on the charge transport across grain boundaries was investigated by DC and AC current voltage measurements. The measurements were done on the same samples before and after the grain boundaries were covered by the painted silver contact. A comparison of these measurements shows that the resistance in the highly doped emitter region across grain boundaries can be reduced by about 30 per cent when a metal contact is applied on the grain boundaries.
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## 1. INTRODUCTION

Most of the reduction of the conversion efficiency observed on solar cells made from coarse polycrystalline silicon (poly-Si) or multicrystalline silicon compared to solar cells manufactured from single crystal wafers can be attributed to the presence of grain boundaries [1]. In the past much work was done on the determination of the electronic structure of grain boundaries in silicon [2,3]. A simplified explanation of the influence of grain boundaries on the solar cell output can be given by assuming that the whole solar cell is divided into individual photovoltaic devices as given by the grains. The grain boundaries then can be considered as crystal surfaces. As a consequence dangling bonds and surface defects cause an enhanced recombination of free carriers along the grain boundaries. Therefore grain boundary passivation becomes an important item in non single crystal solar cell preparation [4,5]. Due to the metallisation of the backside and the front side metal grid the individual grains are electrically connected together in a parallel circuit. A geometrical front contact grid usually forces the light generated current to pass through one or more grain boundaries in the emitter region of the photovoltaic cell before it is collected. Assuming a simplified electrical circuit grain boundaries in this case can be considered as regions with an increased resistance thus contributing to the overall series resistance of the multicrystalline solar cell with a geometrical metal grid. The region of the crystal near grain boundaries usually exhibit a lower quantum efficiency due to enhanced recombination of light generated carriers than regions within the grain. Locally at grain boundaries the light generated current density is lower than within the grains. These regions of high quantum yield are shaded by the geometrical front contact grid. In a previous work we suggested to apply the front contact along the grain boundaries instead of the geometrical design of conventionally prcessed front contact grids [6]. The current voltage behaviour of solar cells made with a front contact along the grain boundaries exhibit a significant decrease in the series resistance and as a consequence an increase of the curve fill factor of about 5 per cent compared to reference solar cells with a geometrical front contact grid.

In the present work we present some results obtained from investigations of individual grain boundaries in order to get a more detailed picture how the intentionally metallised grain boundaries influence the solar cell output.

## 2. SAMPLE PREPARATION

From commercially available multicrystalline p-silicon wafers with large grains were selected and about 1 cm wide stripes were sawed attempting to prepare the stripes with a prefered orientation of the grain boundaries perpenticular to the cutting edge. In figure 1 a typical sample is shown. The indicated grain boundaries A and B have been examined in our experiments.
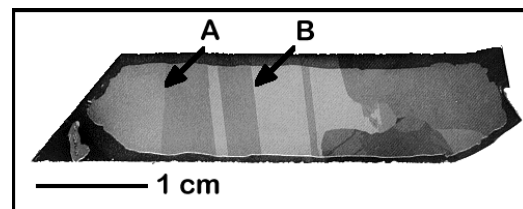


Figure 1: Topview of a typical photovoltaic test device we used in our experiments. Front and backside metallisation and antireflective coating is missing. The grain boundaries marked with A and B have been examined.

On the front side of the samples a pn-junction was applied by a solid state diffusion of phosphorus. At the fromt side the edges were etched in order to avoid any short-circuit of the pn-junction. No passivation of either surface or grain boundaries was done in order to study the influence of a contact along the grain boundaries without taking into account additional effects arising from the grain boundary passivation. The backside was coated with aluminum except along the grain boundaries in order not to electrically short cut the grains on the back side. On the front side silver pads about 1mm in diameter were evaporated within the grains. No antireflective coating was applied which allowed us to further process the device after the first series of measurements without changing optical parameter or surface conditions unintentionally. Electrical

measurements were performed within and across grain boundaries. After these measurements a silver paste was drawn along the investigated grain boundaries and annealed. The same set of electrical measurements within the grains and across grain boundaries were repeated.

## 3. EXPERIMENTAL RESULTS

### 3.1 Spectral response

For every sample the surface reflection losses for wavelengths at 600nm and at 900nm of the incident light along the length of the sample was recorded with a lateral resolution of about 0.5mm. The photocurrent as a function of position was measured at the same two wavelengths. In order to obtain information about the deviation of the minority carrier diffusion length, $L_n$, between the individual grains the ratio of the photocurrent which was corrected for reflection losses was plotted as a function of the position of the incident light. In figure 2 the results obtained for the sample shown in figure 1 is displayed. Two grains were selected where the average minority carrier diffusion length was completely eveluated using the constant photocurrent method in the wavelength range between 800nm and1000nm. A published set of data for the absorption coefficient of single crystalline silicon at room temperature was used to compute the electron diffusion length in the grains [7].
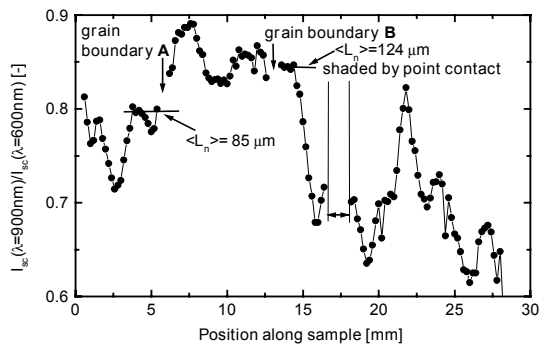


Figure 2: Variation of the ratio of short circuit current generated by incident light at wavelengths of 900nm and 600nm along the midline of the sample shown in fig.1. The ratio is corrected for local variations of the reflectivity and is a measure of the local minority carrier diffusion length, which was evaluated for two grains as indicated.

For further investigations boundaries between grains with small differences of the minority carrier diffusion length (case B in fig. 2) and boundaries which seperate grains with significantly different minority carrier diffusion lengths (case A in fig. 2) were distinguished.

Between one point contact at the front side and the corresponding back contact the diode and solar cell parameter were measured in the dark and under simulated sun light before and after the grain boundaries were covered with the silver paste. Since the diode parameter should not be affected by the procedure a comparison of the two results ensures us that there has not been an unintentionally introduced short circuit across the pn-junction. In some cases however a slight increase of the series resistance has been observed which was attributed to

the ageing of the evaporated silver pads when they were exposed to air during the annealing of the silver paste.

### 3.2 Current voltage measurements

Two terminal current voltage measurements in a frequency range between DC and 1MHz between pairs of evaporated silver pads on the front side of our devices - either within a grain or across a grain boundary - were performed. The experimental setup and the simplified small signal equivalent circuit used for data evaluation is shown in figure 3. The experiments were carried out in the dark at room temperature before the grain boundary under investigation was covered with the silver paste. The same measurements were repeated after a contact was applied along the grain boundary.
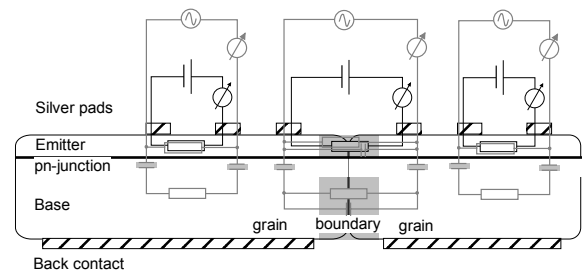


Figure 3: Experimental setup to investigate the increase in the resistance due to grain boundaries. The simplified small signal equivalent circuit for DC conditions (black) and AC conditions (dark gray) is shown.

For the DC measurements a current source was used to introduce a constant current into the sample. The voltage was recorded using the same contacts. Although in this configuration contribution of voltage drops across the metal-semiconductor interface to the measured signal could not be neglected this geometry was used in order to directly compare data with results from AC measurements.

The current was varied between +1mA and -1 mA resulting in voltages of about ±1 V. Since no potential was applied between the front contacts and the back contacts the space charge region of the pn-junction was depleted during the measurements.

For measurements at frequencies up to 100kHz a DC bias voltage - ranging from +2V to -2V - was superimposed by a sinewave - $V_{pp}=40mV$ - and applied to the sample under test. An impedance free 50$\Omega$ resistance was connected in series. Amplitude and phase of the AC voltage drop at the 50$\Omega$ resistance was recorded with an Lock In amplifier and taken as the differential current flow through the sample. The real part of the signal (at phase = 0 deg) was taken to evaluate the sample conductance as a function of bias voltage and frequency. At a frequency of 1Mhz a Hewlett Packard capacitance bridge model 4280A with internal bias voltage source was used. In order to directly compare the data obtained from the different measurements the current voltage dependence was evaluated from the real part of the AC measurements. A typical result for 3 different frequencies obtained from measurements on the sample shown in figure 1 across grain boundary B is shown in figure 4a before the grain boundary was covered with silver paste and in figure 4b after the contact has been applied.
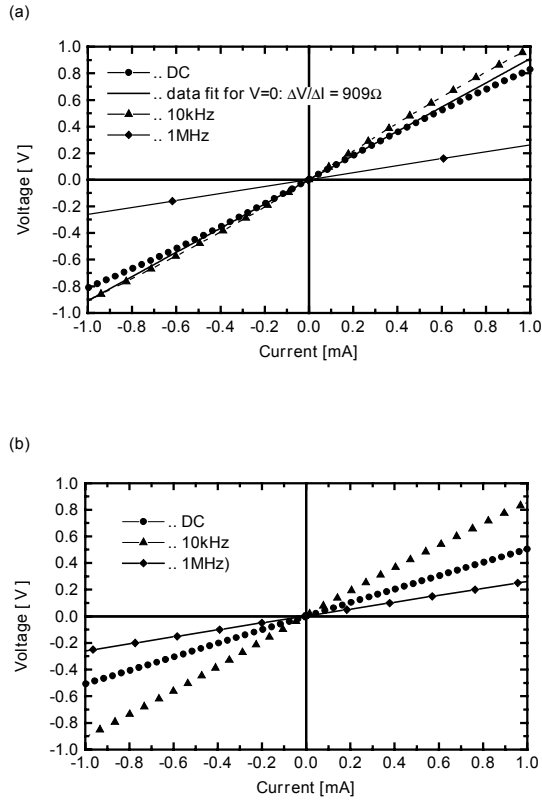
(a)

(b)

Figure 4: Current - voltage dependence measured at three different frequencies across a grain boundary before (a) and after (b) the application of a contact along the grain boundary.

## 4. RESULTS AND DISCUSSION

For a series of grain boundaries the current voltage dependence in the highly doped emitter region on the front side of the photovoltaic device was recorded from DC measurements (i) within the grains forming the boundary and across the grain boundary before the grain boundary was covered by a silver contact. Within the grains little or no deviation from a merely ohmic behaviour was observed. This deviation if any was mainly caused by the semiconductor metal transition region which contributes to the total, measured voltage drop since the measurement was done in a two terminal geometry. As can be seen in figure 4a the DC current voltage dependence across grain boundaries obviously differs from linearity. In order to obtain a value for the ohmic resistance assumed in our small signal equivialent circuit model - see figure 3 - a linear fit for voltages close to zero was carried out which is displayed in figure 4a as a straight line. Since the distance between contact pads was not equal in all cases  the resistance values were evaluated for zero-voltage and divided by the closesd distance between the measurement terminals - i.e. from one contact edge to the other - . This length normalized resistance was used instead of a calculated sheet resistance or the resistivity which implies the junction depth for two reasons: (i) the uncertainity of

the contribution to the resisitance arising from the semiconductor-metal transition and (ii) the pn-junction depth can not be assumed to be equal within grains and across grain boundaries.

The same measurement and data evaluation procedure was done after the grain boundary was painted with a silver paste and annealed. A comparison of the individual normalized values for the resistivity before (further refered to as initial values) and after the application of the grain boundary contact (further refered to as final resistance) indicated that the evaporated silver pads had suffered from the exposition to air during the annealing of the silver paste.

**Table I:** Mean values of the resistance per unit length in the highly doped emitter derived from DC measurements.

| region | $<R/d>(\Omega/mm)$ | | change |
|---|---|---|---|
| | initial | final | (per cent) |
| grain | 268.1 | 273.5 | +2.0 |
| grain boundary | 602.0 | 398.5 | -33.8 |

Averaging of all the samples we have examined results in the values given in Table I for grains and across grain boundaries. The final average resistance within the grains exhibits a slight increase of two per cent due to ageing of the contacts. Although the final average resistance across grain boundaries is significantly reduced as expected it does not approach the value for measurements within a grain. Looking at individual samples an even more complex dependence was observed. In some cases the length reduced final resistance was even greater than the initial value. Furthermore not all measuremens across grain boundaries covered with a contact showed a simple ohmic dependence as might be expected from the simple equivalent circuit model we have assumed. The origin is unclear and needs further investigations. One reason might be that the region which is affected by the grain boundary extends the width of the contact which covers the grain boundary. Surface conductance at the sample edges which have not been passivated may contribute to the overall resistance which is not assumed in our equivalent circuit model. Although diode parameter do not indicate a significant influence of the edges of the diodes surface conductance may have changed during the annealing of the silver paste. As mentioned above two cases of grain boundaries have been distinguished: (i) boundaries between grains with similar electrical properties - minority carrier diffusion length, $L_n$ - and boundaries between grains with significantly different electrical properties. However no resolvable dependence of the initial or final resistance on the kind of grains was found for the resistance within grains and across grain boundaries.

For DC measurements the space charge region of the pn-junction electrically isolates the emitter from the base as long as there is no voltage applied between front contacts and back contacts. For AC measurements the base contributes to the real part of the measured current voltage characteristics due to the capacitive coupling of the signal across the space charge region. The circuit equivalent is shown in dark gray in figure 3. Up to 10 kHz the contribution from the base region to the overall conductance is negligible. At 1MHz however emitter and

base almost equally contribute to the total conductance. In figure 4a and 4b the current voltage curve for the DC measurement and for the AC measurement at 10kHz are almost identical. The results of the AC measurement at 1MHz exhibit merely about half the voltage drop for the same current. The difference between the results measured at 10kHz and the results obtained from the measurements at 1MHz was used to calculate the resistance in the base. The same data evaluation as described above for the DC measurements was applied. The averaged results are given in table II.

**Table II:** Mean values of the resistance per unit length in the base obtained from the difference between AC measurements at 10kHz and at 1MHz.

| region | $<R/d>(\Omega/mm)$ | | change |
| --- | --- | --- | --- |
| | initial | final | (per cent) |
| grain | 479 | 395 | -17.5 |
| grain boundary | 930 | 731 | -21.4 |

For the interpretation of the results given in table II the assumed equivalent circuit from figure 2 appears to be insufficient. As expected the contact along the grain boundary does not have a great effect on the resistance across the grain boundary when compared to the values obtained from measurements within the grain. The ratio remains approximatly 2 for the initial results as well as for the final data. However there is no simple explaination that both the resistance within the grain as well as the resistance across the grain boundary is decreased by about 20 per cent when a silver paste is applied along the grain boundary on top of the emitter region.

## 5. CONCLUSIONS

From our investigations we conclude that a contact along grain boundaries is able to reduce the average sheet resistance across grain boundaries in the highly doped emitter of multicrystalline solar cells by about 30 per cent. Which explains the reduction in series resistance of solar cells with a metal grid along grain boundaries as observed by J. Summhammer [6]. The influence of a metal covered grain boundary on the charge transport in the emitter as well as in the base of the solar cell can not be fully explained by the assumption of the simplified small signal equivalent circuit model we used for data evaluation. Further investigations including the imaginary part of AC measurements will be necessary.

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