Temperature induced Degradation of the Contact Resistance of Ag-screen printed p-type Silicon Solar Cells

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ABSTRACT: This contribution targets on the stability of screen printed silver front contacts on n-type emitters of crystalline silicon solar cells during thermal treatment steps in the range of 200-300°C which could be of importance for e.g. some dielectric layers [1] or Regeneration [2]. As measurements of the contact resistance taken by TLM technique reveal, the contact resistance may seriously increase within the thermal treatment steps giving rise to a significant degradation of the fill factor of the solar cell. Furthermore it is found that the TLM technique itself has an influence on the measurements.

Keywords: FRONT CONTACT, DEGRADATION, THERMAL

1 INTRODUCTION

A high and permanently stable fill factor is essential for high conversion efficiencies especially for industrial type crystalline silicon solar cells. In the cause of several experiments involving elevated temperatures in the range up to 300°C in ambient air it was found that the fill factor of some samples degraded significantly. To clarify the cause of the degraded fill factor, current voltage measurements under various conditions were performed.

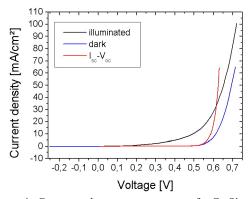


Figure 1: Current-voltage measurements of a Cz Si solar cell suffering from a degraded fill factor. The comparison of the J_{sc} - V_{oc} and the dark J(V)-curve shows a rather high classical series resistance (splitting up around 0.6V). The illuminated J(V)-curve (shifted by J_{sc}) has a completely different shape responsible for the bad fill factor.

It is extremely eye-catching that the J(V)-curves in Fig. 1 measured in the dark and under illumination (shifted by J_{sc}) differ remarkably. Even by taking into account that there seems to be a high series resistance, the illuminated curve cannot be described by a two-diode model excluding distributed resistances. As electroluminescence images have proven the cell suffers strongly from a distributed series resistance although no significant manufacturing errors are visible in the front side contact grid and more important the cell featured a high fill factor before the temperature treatments.

To further identify the problem, the contact resistance was measured by the transfer length method (TLM). TLM measures the resistance between two adjacent front grid fingers that are only contacted by the emitter in between. Therefore slices of a solar cell perpendicular to the fingers are cut. TLM allows for the extraction of the emitter sheet resistance as well as the contact resistance of the fingers. One requirement for unambiguous TLM measurements is that the sheet resistance and contact resistances are isotropic.

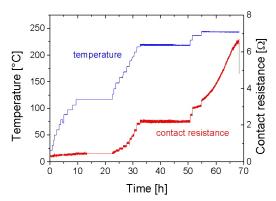
TLM measurements have proven that a strongly degraded contact resistance was responsible for the degraded fill factor of the cell discussed in the beginning. This explains the problem of this specific cell but not the cause of the problem.

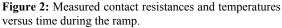
2 EXPERIMENTS

2.1 Technique and Temperature Range Definition

To clarify whether the thermal treatments was responsible for the contact resistance degradation, TLM measurements were performed at elevated temperatures.

In a first approach, the dependence of the contact resistance on temperature was measured in a temperature ramp experiment. Fig. 2 shows the collected data.





The curves in Fig. 2 answer already the question, whether the contact resistance suffers from elevated temperatures. Up to a temperature of about 220°C, the contact resistance shows no significant slope. For a stabilized temperature of around 250°C, the contact resistance increases steadily with time.

For a more systematic analysis, the temporal development of the contact resistance was measured at a stabilized temperature. The results are shown in Fig. 3.

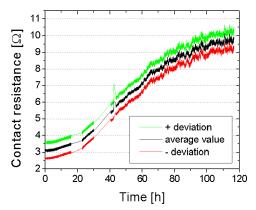


Figure 3: Contact resistance measured in-situ by TLM during a temperature treatment at ~240°C.

As can be seen in Fig. 3, the contact resistance increases in the beginning as expected but seems to saturate for longer times. To make sure that this saturation is not due to the in-situ measurement at around 240°C the experiment was repeated with ex-situ TLM measurements at room temperature. To speed up the experiment the temperature was slightly increased to around 265°C. The results are shown in Fig. 4.

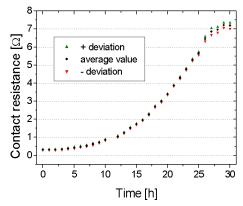


Figure 4: Contact resistance measured ex-situ at room temperature during a temperature treatment at $\sim 265^{\circ}$ C.

Although the absolute values of the contact resistance and the time scale have changed, the principle shape of the curve resembles the one shown in Fig. 3 indicating that the saturation is not an artifact due to measurements at elevated temperatures and that it is a relevant part of the measurement.

Every black data point shown in Fig. 4 represents an average of several measurements. Thus a mean deviation could be defined represented by the data points in green (upper limit) and red (lower limit). It is conspicuous that this mean deviation increases for higher values of the contact resistance. The measurements averaged for each time were closer examined and it was found that they do not feature a normal distribution but rather a slight decay with each subsequent measurement.

2.2 Influence of the measurement technique

To investigate this point further, a strongly degraded samples was used which featured an even worse contact resistance than the cell shown in Fig. 4. The contact resistance was measured over and over again as shown in Fig. 5.

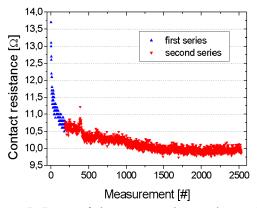


Figure 5: Decay of the contact resistance due to the measurements taken at room temperature.

The contact resistance begins at a very high value and decays with each measurement. To check, if this development is not induced by the room temperature itself, the measurement series was interrupted for several hours (between blue and red data points). As there appears no significant step, it is assumed, that not the temperature is responsible for the recovery of the contact resistance. This means that the measurement itself influences the measurements reducing the averaged contact resistance with each measurement. The saturation observed in Fig. 7 suggests that this influence is probably only of relevance for high contact resistances and leads to the progression as depicted in Fig. 6, showing a close up on the latest data points from Fig. 4.

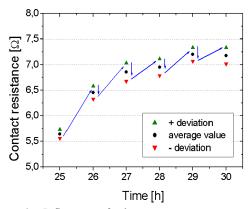


Figure 6: Influence of the measurements on the progression. The blue arrows hint at the sequence of the measurements enforcing a saturation.

The contact resistance increases due to the temperature treatment to a high value and is then decreased due to the influence of the measurement. If the measurements decrease the contact resistance that much as it would increase within the next treatment step, a stagnation is enforced which could explain the saturation observed in Fig. 3 and Fig. 4.

2.3 Temperature dependent measurements

Irrespective of the systematic problem due to the influence of the measurement the temporal development of the contact resistance was monitored for different temperatures to examine the influence of temperature on the degradation of the contact resistance. The results are shown in Fig. 7.

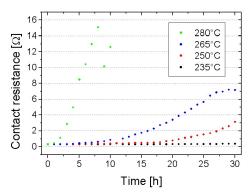


Figure 7: Temporal development of contact resistances at different temperatures for adjacent samples.

For temperatures around 235°C or below, a change is hardly noticeable. As one could expect, the contact degradation speeds up with rising temperature. For 280°C the data could only be taken for 10 hours before the influence of the measurements becomes dramatically important.

2.4 Validity of the TLM model

Furthermore, the results were examined closer in order to check the validity of the TLM method. As mentioned above, the evaluation of TLM measurements emanates from an isotropic emitter sheet resistance as well as isotropic contact resistances of each finger involved in the measurement. Inhomogeneities of the emitter sheet resistance due to the diffusion may be excluded by far. The question is, whether the contact resistance of the contact grid is homogeneous especially when the contact resistance degrades almost an order of magnitude.

According to the TLM model, the resistance R_{ij} between the fingers *i* and *j* is given by the equation

$$R_{ij} = \left(D_i(I) + D_j(-I)\right) + R_{sheet}^{eff} \left|i - j\right| \cdot d$$

wherein $D_x(I)$ represent a Schottky-type diode resistance, R_{sheet}^{eff} the effective emitter resistance and d the finger distance. If all contact resistances are similar and the behavior is ohmic (D(I)=D(-I)), the equation describes a perfect straight line.

Fig. 8 shows a single TLM measurement of a sample after a treatment with a high temperature for quite some time.

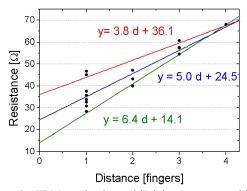


Figure 8: TLM evaluation with inhomogeneous, high contact resistances. The straight lines are a worst case (red), a best case (green) and a simple TLM fit (blue).

As can be seen, the measurements between several fingers do not result any more in a perfect straight line but instead are statistically spread. As the measurement setup used 5 fingers there exist only two measured resistances (back and forth) for four inter-finger distances and coincidentally the values match each other. The spread originates from strongly differing contact resistances of the fingers under investigation. A closer look on the data even shows, that the back and forth measurements do not match each other in each case indicating that the resistance of the metal-semiconductor interface does not follow approximately Ohm's law (at least not for the applied measurement currents) but instead shows rather a Schottky-diode behavior.

The wide spread of the data points raises in any case the question whether the evaluation with a straight line yields in reasonable data. Three cases for an evaluation are shown in Fig. 8 representing a worst case estimation (red line), a best case estimation (green line) and the best fit of a straight line to the data (blue line) resulting in strongly different axis intercepts and different slopes. Assuming that the emitter sheet resistance has not changed, the slope of the straight line after the treatment should not differ from the slope prior to the treatment and thus one variable can be eliminated. Vice versa a measurement yielding approximately the correct emitter resistance can be used to describe a mean contact resistance. As the experience has shown, the spread of the data points increases with high evaluated contact resistances and thus the uncertainty of the TLM model becomes less important for lower contact resistances.

Nevertheless, the standard TLM model based on isotropic resistances shows serious problems, a general trend for the degradation of the contact resistance is indisputable and conclusions drawn so far remain principally valid.

3. CONCLUSIONS

The results of the investigations done so far imply that the contact resistance of solar cells may degrade during temperature treatments at least in ambient air. Experiences show that not every contact degrades identically but a general trend towards a faster degradation with higher temperatures can be assumed. At least for the samples used in these experiments temperature induced degradation of the contact resistance plays a role if temperatures exceed around 235°C and is assumed to become critical if temperatures exceed 280°C for longer times.

The results may vary with the applied manufacturing process of the cell and the used silver paste for screen printing and should be checked if temperature treatments are planned.

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