INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON



# **Experiment Report Form**

# The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

http://193.49.43.2:8080/smis/servlet/UserUtils?start

#### Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

#### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

#### **Published** papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

# **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

#### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	Experiment title:	<b>Experiment</b> <b>number</b> : MA765
Beamline:	Date of experiment:	Date of report:
ID22ni	from: 08.07.09 to: 11.07.09	24.08.09
Shifts:	Local contact(s):	Received at ESRF:
9	Gema Martinez-Criado	
Names and affiliations of applicants (* indicates experimentalists):		
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*Martin C. Schubert		
*Paul Gundel		
*Friedemann Heinz		
*Wolfram Kwapil		

# **Report:**

# Aim of the experiment:

Diode breakdown in multicrystalline (mc) silicon solar cells has become an increasingly important issue in recent years. The development of new feedstock fabrication sources – which provide cheaper but at the same time also dirtier silicon – has forced cell module manufacturers to adapt the module design to inferior breakdown behaviour of the resulting solar cells.

Recently, we have identified at least three different breakdown mechanisms at work in mc-Si solar cells<sup>1,2</sup>. One of them is related to recombination centers in the Si crystal, often related to dislocations and grain boundaries. We found that the breakdown voltage  $V_B$  directly correlates with the impurity concentration of the silicon wafer. The higher the transition metal concentration in the wafer, the lower the breakdown voltage.

The important question is whether the transition metals directly lead to pre-breakdown or whether secondary effects like dislocation multiplication due to strain fields in the Si crystal result in decreased breakdown voltage.  $\mu$ -XRF is the ideal tool to answer this question since no sample preparation (e.g. for TEM-based investigations), which possibly alters the sample properties, is necessary.

# **Experimental results:**

For this investigation, a solar cell from the bottom of the ingot was chosen. The local pre-breakdown behaviour was characterized by bias-dependent electroluminescence (EL) intensity measurements<sup>1,2</sup>. A

sample of  $10 \times 20 \text{ mm}^2$  featuring a high density of pre-breakdown sites which were related to recombination active defects was cut out.

In the next step, microscopic investigations of this sample were carried out with an electro- / photoluminescence-spectroscopy mapping tool with a high resolution in the order of 1  $\mu$ m. The setup comprises a confocal optical microscope and a sample holder attached to a piezo stage. The sample can be connected to a voltage generator which allows to apply a reverse bias to the sample and thus to generate breakdown light emission.

In Figure 1, the SEM image of a small grain is shown which was chosen for the investigation. By applying - 10 V to the sample, breakdown light emission (see insets in Fig. 1) was detected with the EL- / PL-mapping tool at two sites, marked with the white circles. Both spots emit light in an area of approximately 5 to 10  $\mu$ m in diameter and are localized along grain boundaries. The exact position of the pre-breakdown sites was determined by making use of the piezo stage yielding the exact coordinates of both spots. Characteristic features of the wafer surface around these coordinates which were found in the microscopic images (resolution ~1  $\mu$ m) were taken as a marker.

Using the markers determined in the EL maps, the  $\mu$ -XRF mappings were carried out in an area of 20 x 20  $\mu$ m<sup>2</sup> centered at the pre-breakdown spots. The results are shown in Figure 2.

Iron precipitate colonies were detected at both pre-breakdown sites. They are distributed along single lines which correspond to the grain boundaries. In one case, also one copper precipitate was found. The distance between this cluster, however, and the position of the pre-breakdown was determined to be approx. 5  $\mu$ m. The location of the iron precipitate colonies, on the other hand, coincides well with the breakdown spots taking into account the limits of the spatial resolution provided by the EL- / PL-mapping tool (1  $\mu$ m) and the accuracy of the positioning of the X-ray spot on the sample which we estimate to be around 1 to 2  $\mu$ m.

In addition, we performed several  $\mu$ -XRF mappings distant to the pre-breakdown sites along the grain boundary labelled A in Figure 1. However, no other precipitates were detected, underlining the evident concurrence of Fe-containing clusters and pre-breakdown spots.



Figure 1: SEM image of the grain under investigation. Two pre-breakdown sites were found at the grain boundaries marked by the white circles.





# Conclusion

The direct observation of metal precipitates at pre-breakdown sites gives indications about the nature of the breakdown mechanism. Further experiments have to decide between the following three possible scenarios:

I Avalanche<sup>3</sup> or Zener diode breakdown<sup>4</sup> assisted by the presence of impurity cluster defect levels close to the center of the silicon band gap<sup>5</sup>.

II The presence of an electrical charge in the vicinity of the metal precipitates e.g. due to Schottky contacts between the silicon matrix and the metal clusters<sup>6</sup>. The electrical charge in turn may increase the local electric field and lead to pre-breakdown.

III Variation of the phosphorus emitter layer due to the presence of metal precipitates and an increase of the local electric field.

The results summarized above were submitted for publication in Applied Physics Letters.

#### References

- <sup>1</sup> W. Kwapil, M. Kasemann, J. Giesecke et al., presented at the Proceedings of the 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, 2008 (unpublished).
- <sup>2</sup> W. Kwapil, M. Kasemann, P. Gundel et al., Journal of Applied Physics accepted (2009).
- <sup>3</sup> W. Mönch, Phys. stat. sol. **36** (9), 9 (1969).
- <sup>4</sup> A. G. Chynoweth and K. G. McKay, Physical Review **106** (3), 418 (1957).
- <sup>5</sup> O. Breitenstein, J. Bauer, J. M. Wagner et al., presented at the Proceedings of the 34th IEEE Photovoltaic Specialists Conference, Philadelphia, USA, 2009 (unpublished).
- <sup>6</sup> M. D. Negoita, T. Y. Tan, Journal of Applied Physics **94** (8), 5064 (2003)