EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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.

<table>
<tr><td> </td><td>Experiment title:
Precipitation of Metals at Dislocations in Silicon for solar cells</td><td>Experiment number:
MA 765</td></tr>
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from:03.04.2009 to: 06.04.2009</td><td rowspan="2">Date of report:
30.08.2009
Received at ESRF:</td></tr>
<tr><td>Shifts:
9</td><td>Local contact(s):
Juan Angel Sans-Tresserras</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
Eicke R. Weber
Wilhelm Warta
*Martin C. Schubert
*Wolfram Kwapil
*Paul Gundel
All Fraunhofer Institute for Solar Energy Systems
Manfred Reiche (Max-Planck-Institute for Microstructure Physics)</td></tr>
</table>

Report:

In this experiment we investigated the impact of metal precipitates on the photoluminescence. For this direct bonded wafers were intentionally contaminated and the results of XRF maps from the ESRF were compared to the luminescence spectra of the corresponding areas. For the detection of the metal precipitates XRF was absolutely crucial. The results are published in Phsica Status Solidi Rapid Research Letter (DOI: 10.1002/pssr.200903221 published online). The publication is summarized here:

Abstract

Metallic impurities are detrimental to many silicon devices and limit the efficiency of multicrystalline silicon solar cells. Therefore they are a major subject of ongoing research. Photoluminescence spectroscopy is a promising technique for detecting precipitated metals in silicon because of its sensitivity to the minority carrier density and to specific types of defects; however the impact of impurities on the defect luminescence could not be clarified yet. In this paper we examine the role of micron sized iron and copper precipitates in Direct Bonded Wafers by micro-photoluminescence spectroscopy. Both kinds of precipitates are detectable by means of the reduced band-to-band luminescence. An element specific effect on the defect luminescence is observed. The results are confirmed by X-Ray Fluorescence spectroscopy.

Introduction

The performance of many silicon devices heavily depends on the metal contamination. In particular the efficiency of solar cells made of block-cast multicrystalline (mc) silicon with its inevitable high transition metal content is significantly reduced. Two of the most common and at the same time detrimental impurities

are iron and copper. While at least the interstitial iron concentration is detectable with minority carrier lifetime measurement techniques, the detection of single metal precipitates is only possible with technically demanding methods such as X-Ray Fluorescence spectroscopy (XRF) or Transmission Electron Microscopy (TEM), which requires a time-consuming sample preparation and pre-characterisation. The precipitation of metals is relevant for mc silicon solar cells in many ways: Metal precipitation at crystal defects during the crystal growth can clean grains from impurities and thus, improve the performance, or can cause shunts and sites of pre-breakdown and damage the cell or module respectively These effects make the development of an accessible, fast and non-destructive technique for the detection of metal precipitates highly relevant for the further improvement of mc silicon solar cells. A promising approach for the detection of metal precipitates is photoluminescence (PL) spectroscopy with a high spatial resolution. PL spectroscopy provides complementary material parameters in one measurement: The intensity of the band-to-band (BB) peak is a qualitative measure for the recombination activity, the intensity and energy position of the defect PL peaks between 0.8 eV and 0.99 eV at room temperature or below yield additional information about the nature of the defects. The role of impurities in the defect PL has been widely discussed, but is far from being clarified yet. To obtain meaningful experimental results our study is based on well defined samples and maximum spatial resolution. As highly defined samples we choose Direct Bonded Wafers (DBWs), whose clean dislocation networks represent an ideal model system for mc silicon. The DBWs are contaminated with iron or copper, which precipitate at the dislocation network or close to the interface. These defect systems, which consist of the dislocation network and the metal precipitates, are examined with micro-PL spectroscopy at ambient temperature and the results are compared to XRF measurements with similar resolution, which were conducted at ID22 at the European Synchrotron Radiation Facility (ESRF).

Results

In the iron contaminated sample the intensity of the BB PL peak is reduced at the dislocation network (which intersects the surface of the bevelled sample to right side of the blue line in Fig. 1 (a)) due to its recombination activity. At some distinct spots of a size between 1 μm and 4 μm the BB PL peak is particularly low (circles in Fig. 1 (a)). At these spots iron precipitates were detected by XRF (Fig. 1 (b)). Both measurements show a good agreement though the escape depth of the PL is smaller than the information depth of the fluorescence, which demonstrates the potential of micro-PL spectroscopy to detect precipitates due to their increased recombination activity. As expected, XRF did not detect any other impurities other than iron in this sample. The dashed circle shows a limitation of the micro-PL setup. The sensitivity is limited to an area close to the surface because of the short absorption length of the excitation laser (about 1μm). Since the iron precipitate in the dashed circle lays deeper in the sample, it cannot be detected by the current micro-PL setup. This limitation might be overcome by an excitation laser with a longer wavelength and absorption length in silicon.

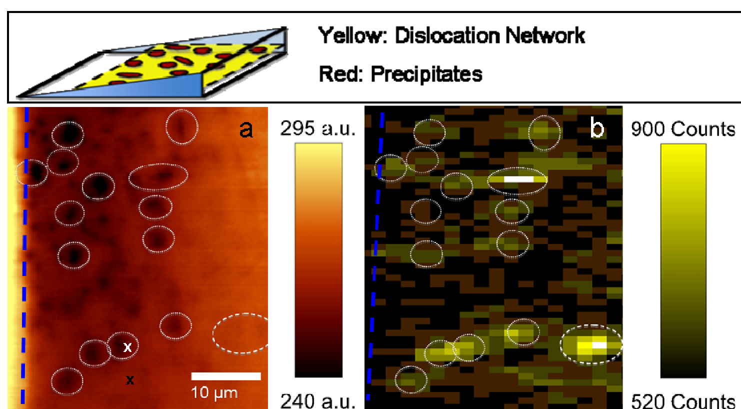

Figure 1: Above a scheme of the sample preparation with the polished angle. Below: Intensity of the BB PL peak at room temperature (a) and of the iron x-ray Kα fluorescence (b). The dislocation network intersects the surface to the right of the dashed blue line. The spots with reduced BB PL intensity (white circles) are caused by recombination active precipitates, which were detected with XRF (b). The PL measurement clearly shows more details than the XRF measurement, which suggests a higher sensitivity.

The iron precipitates alter not only the BB PL but also the defect PL. In Fig. 2 four normalised PL spectra are compared: (1) At an iron precipitate (white x in Fig. 1), (2) at a position without precipitate (black x in Fig. 1), (3) the reference DBW, which was subject to the same temperature steps as the iron contaminated sample, without contamination and (4) at a copper precipitate (white x in Fig. 4).

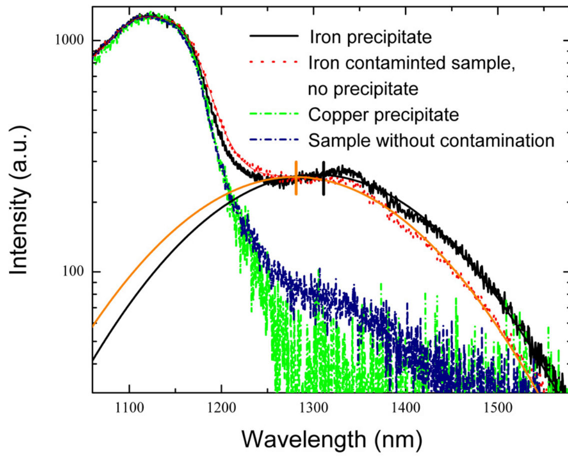

Figure 2: Comparison of the normalised room temperature PL spectra at an iron precipitate (white x in Fig. 1), at a position without precipitate (black x in Fig. 1), the bonded wafer without contamination and at a copper precipitate (white x in Fig. 4). The defect PL at the iron precipitate is shifted to longer wavelengths, which can be seen from the fit of the defect PL (thin orange curve – no precipitate, thin black curve – precipitate) with the thick vertical lines marking the peak positions. The BB peak is also fitted, but the fit function is not shown for the sake of clarity.

The iron contaminated sample shows an enhanced defect PL at 1.3 µm compared to the uncontaminated sample, when the spectra are normalized to the BB PL. The spectra are multiplied by the factors: 1 for the iron precipitate, 0.72 for the iron contaminated sample at no precipitate, 7.8 for the copper precipitate and 0.74 for the uncontaminated sample. In the copper contaminated sample the defect PL is drastically reduced.
At the iron precipitate the broad defect PL band is shifted to longer wavelengths. If this is due to an additional peak with a longer wavelength, which is suggested by the decreased quality of the fit for the defect PL with one Gauss peak (see Fig. 2), or due to an energy shift of the peak cannot be conclusively decided from these data. The defect PL is weaker in the uncontaminated sample.
In a sample with copper and iron contamination where both iron and copper were precipitated at the dislocations, the spectrum is a composition between the pure iron and pure copper spectrum. The effect of the defect PL shift at precipitates is demonstrated for a detail from the lower left side of Fig. 1 with longer integration times in Fig. 3. For this the entire spectrum was fitted at each point with four Gauss peaks (three for the BB peak and one for the defect PL). The shift to higher wavelengths at the iron precipitates can be clearly seen and is higher for comparatively big precipitates.

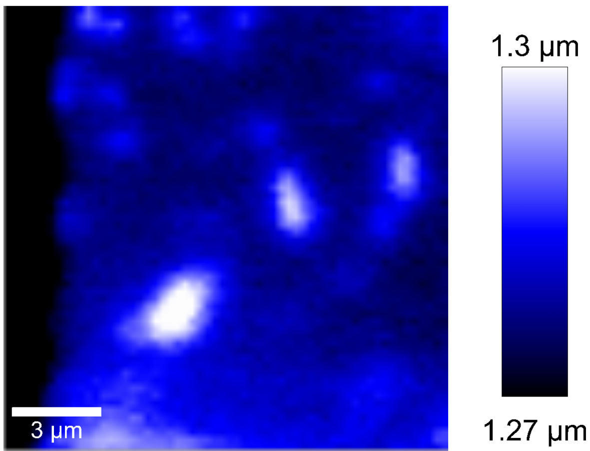

Figure 3: This figure shows the position of the Gauss peak (compare to Fig. 2), which fits the defect PL. A clear shift to longer wavelengths at iron precipitates can be observed. Shown is a detail from the lower left side of Fig. 1. This figure demonstrates the ability of PL spectroscopy to identify precipitates in the size of 1 µm or smaller, since the signal might be broadened.

While the defect PL is almost completely suppressed in all of the sample with only copper, the intensity of the BB PL peak can be used to locate the copper precipitates at the dislocation network, which is demonstrated by the comparison to the intensity of the copper Kα x-ray fluorescence in Fig. 4.

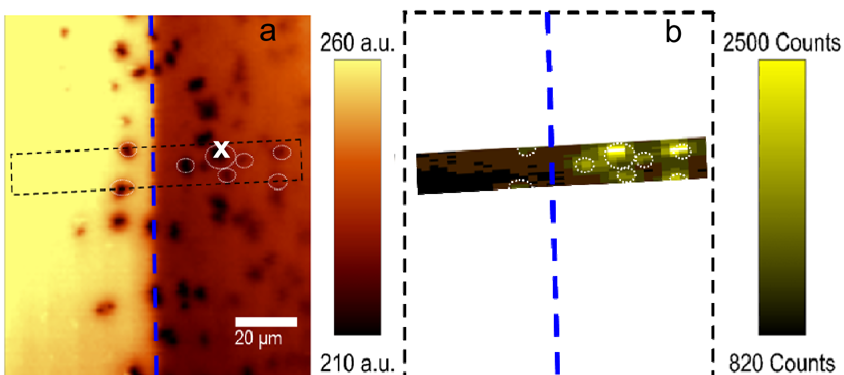

Figure 4: The intensity of the PL BB peak on the left side (a) and the intensity of the copper Kα x-ray fluorescence (b). The dislocations are on the left to the blue dashed line. The spots with decreased PL BB peak intensity (white circles) can be clearly correlated to the copper precipitates, which are identified by XRF (b).

Conclusion

In this paper we showed that micro-photoluminescence is an excellent tool for identifying metal precipitates in silicon. The minimum size for the detection is 1 µm or even smaller, since the PL signal might be broadened. By plotting the intensity of the BB PL peak the position of precipitates correlates to spots of decreased intensity. This was demonstrated for contaminated Direct Bonded Wafers by comparison with XRF. Iron and copper were found to have a different effect on the defect PL around 1.3 µm at room temperature. While the defect PL was increased in the iron contaminated sample and shifted to longer wavelength at iron precipitates, it is suppressed in the copper contaminated sample. This dependence of the defect PL on the contaminant may be utilized in order to identify the chemical composition of precipitates. So far the detection of precipitates is limited to near surface precipitates. This limitation might be overcome by an excitation laser with a longer wavelength and a longer absorption length in silicon.