	Experiment title:	Experiment number:
ESRF	**Experiment title:** High sensitivity, high spatial resolution analysis of metal contamination in silicon materials for solar cells	**Experiment number**: MA-652
Beamline: ID-22 Microprobe	**Date of experiment**: from: 31. Oct. 2008 to: 03. Nov. 2008	**Date of report**: 31 Aug. 2009
Shifts: 9	**Local contact(s)**: Dr. Gema Martinez Criado	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Winfried Seifert, IHP, Frankfurt (Oder), Germany

*Oleg Vyvenko, St. Petersburg State University, St. Petersburg, Russia

Tzanimir Arguirov, BTU Cottbus, Germany

*Maxim Trushin, BTU Cottbus, Germany

Report:

The beamtime at ID-22 was meant to allow detection and analysis of precipitates of precipitates of transition metals heavier than Fe in solar-grade silicon.
To evaluate the status of the beamline and the expected improvement of sensititvity, samples already known from previous experiments (BESSY my-spot beamline, ESRF ID-21) to contain transition metals were investigated first. When studying these samples, no metal precipitates were detected, however. Efforts to optimize the fluorescence detection were undertaken subsequently, but non of the measures was successful.

A second set of samples from intentionally contaminated solar silicon, expected to contain larger Cu and Fe precipitates, was studied afterwards. The synchrotron measurements were performed in regions of enhanced carrier recombination, selected on the basis of EBIC investigations (Fig. 1). Indeed, Cu and Fe precipitates were detected in these regions. The position of the detected Fe and Cu clusters was found to coincide with the position of Si nitride/Si carbide precipitates (Fig. 2), indicating that these precipitates represent effective sites for precipitation of metals. Small Si nitride rods were found to contain moderate, about

equal amounts of Fe and Cu. Very large Cu-rich particles were found at sites of SiC inclusions. The XANES measurements performed at such particles revealed Cu silicide.
In three cases, maps of Cu were obtained that showed a strong Cu signal at the center of the metal cluster, but also very long streaks of enhanced signal in vertical and horizontal direction (Fig.3). Only at the very end of the beamtime it became clear that these streaks are not due to a particular metal distribution, but due to an ill focused beam. The ill focused beam is also the reason that no metals were detected in the reference samples with small- or medium-sized metal clusters.

Summary:

The measurements performed allowed a preliminary insight into the interaction of transition metals and crystal defects in solar grade silicon. It was found that Si carbide and nitride particles represent effective sites for precipitation of Fe and Cu. In particular Si carbide particles seem to strongly facilitate precipitation of metals.
The goal of high sensitivity analysis of metal precipitation in the investigated Si materials could not fully be reached. The ill focused beam resulted in a substantial loss of sensitivity rendering detection of small and medium-sized metall particles impossible.

Publications:

M. Trushin,W.Seifert, O. Vyvenko, J. Bauer, G. Martinez-Criado, M. Salome, M. Kittler
“XBIC/μ-XRF/μ-XAS analysis of metals precipitation in block-cast solar silicon”
Nuclear Instruments and Methods in Physics Research, B, accepted for publication.
Abstract:
The results of the investigations of the interaction between the different impurities in intentionally contaminated block-cast multi-crystalline silicon by means of synchrotron-based microprobe techniques XBIC (X-ray beam induced current), μ-XRF (X-ray fluorescence microscopy) and μ-XAS (X-ray absorption microspectroscopy) recently implemented at beamlines ID-21 and ID-22 of ESRF, Grenoble, are presented. It was found that Si_3N_4/SiC particles frequently observed in the upper part of multi-crystalline Si blocks represent effective sinks for Fe and Cu impurities. The amount of precipitated iron was the same order magnitude both at nitride and carbide particles. The amount of Cu precipitated at the SiC inclusions was significantly larger than that at Si_3N_4 rods. Chemical state of the copper precipitates was identified as copper-rich silicide Cu_3Si. The anneal at 950°C that is known to enhance oxygen precipitation in silicon was found to accompany with the enhanced formation of nanoscale iron dicilicide precipitates both inside the grains and at grain boundaries.

W. Seifert, J. Bauer, A. Erko, M. Holla, B. Gründig-Wendrock, M. Kittler, C. Knopf, G. Martinez-Criado, M. Trushin, O. Vyvenko, I. Zizak
“Fe/Cu precipitation at Si nitride and Si carbide particles in intentionally contaminated block cast silicon”
Extended abstract and talk at 3rd Internat. Workshop on Crystalline Silicon Solar Cells, June 3-5, 2009, Trondheim, Norway
Abstract:
Synchrotron-based X-ray microprobe techniques have been applied to study the interaction of metal impurities with SiC/Si_3N_4 particles in the near-cap part of 3 types of multicrystalline Si blocks: blocks grown from melts intentionally contaminated with either Fe and Cu or only Fe and a block grown from an uncontaminated melt. It was found that SiC/Si_3N_4 particles

represent preferred sites for metal precipitation. Clusters of the following metals were detected in the contaminated as well as in the uncontaminated blocks: Fe, Cu, Ni and Ca. However, large Cu clusters have been only observed in the Fe/Cu contaminated material.
Composition and size of metal clusters vary largely. Sole Si_3N_4 rods seem to cause rather weak metal precipitation, while SiC clusters appear to facilitate stronger precipitation. In the Fe/Cu contaminated material, a small nearly equal amount of precipitated Fe and Cu was found at Si_3N_4 rods. No Ca was detected at the rods. Very large metal clusters have been found at some SiC/Si_3N_4 particles. Those clusters may consist nearly completely of Cu, but may as well contain comparable amounts of both Cu and Fe. A large metal cluster containing mainly Fe was detected in the uncontaminated material. Small SiC filaments in grain boundaries are shown to lead to metal precipitation as well.
Electron beam induced current investigations were applied to assess the electrical activity of the SiC/Si_3N_4 particles. It was also found that large SiC/Si_3N_4 particles often cause generation of dislocations in their vicinity, indicating that substantial stress is generated around the particles.

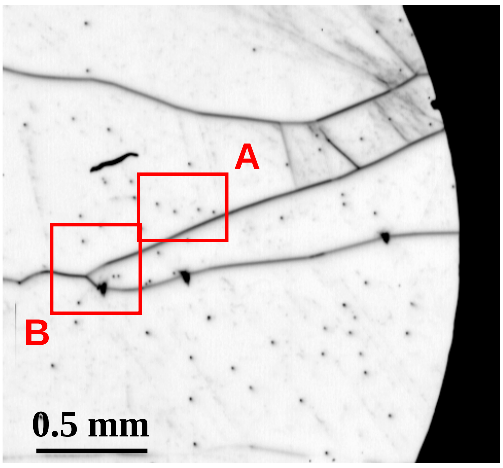

Fig. 1:
Survey EBIC image of a multicrystalline Si sample showing a few grain boundaries, numerous dark dots due to SiN/SiC precipitates and three triangular defects. The regions marked in red were investigated at ID-22.

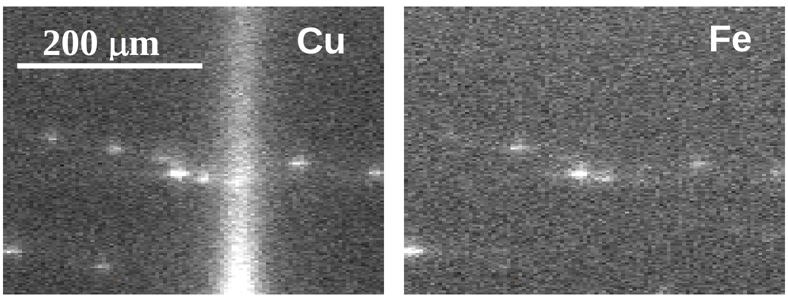

Fig. 2:
XRF maps of Cu and Fe for region A. Both Fe and Cu are seen to precipitate at the SiN/SiC particles. The diffuse vertical streak in the Cu map is caused by a large Cu particle about 200 µm (!) away.

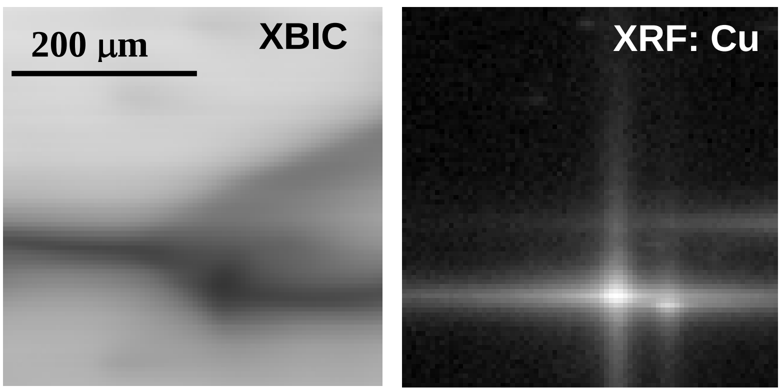

Fig. 3:
XBIC and XRF Cu maps for region B. The triangular defect of strong recombination activity seen in the EBIC map is found to be a large Cu cluster.
The horizontal and vertical streaks in the Cu map are due to an ill focused beam.