Characterization of silicon for photovoltaic applications with INAA and PGAA

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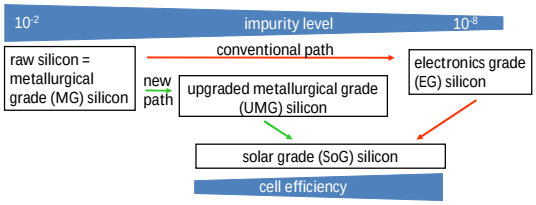
Introduction

In this project processes are investigated to clean the raw silicon to an impurity level just necessary for photovoltaic applications. This silicon is called solar grade (SoG) silicon.

Impurities of interest in silicon:

- boron and phosphorus are dopants and determine the conductivity
- 3d transition metals such as iron form recombination centers for the charge carriers, thus reducing the cell efficiency

Conventional and new path to SoG silicon

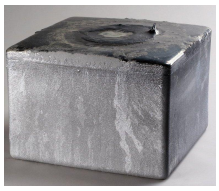


Goal: Improve the quality of SoG silicon made from UMG silicon

Processes investigated

1. Crystallization

A major part of the purification of silicon takes place during directional solidification because most impurities have a segregation coefficient k < 1 [2]. In order to find optimal crystallization parameters, the impurity profile along the crystallization front is determined.

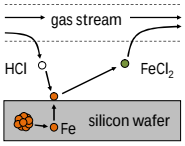


For INAA and PGAA, samples of 1 cm³ were taken along the crystallization front from the bottom to the top of an ingot

Directional solidification from bottom to top results in an ingot of multi-crystalline silicon

2. HCl gettering

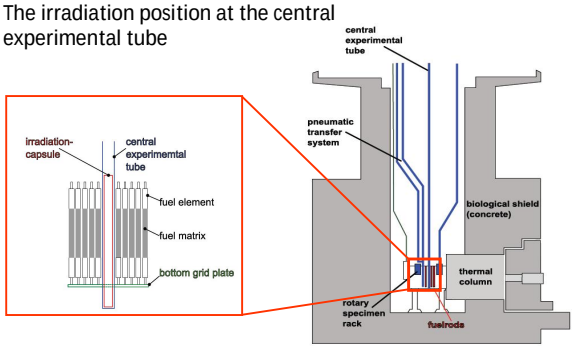
Further cleaning procedures such as HCl gettering [3,6] are applied after cutting the ingots of multi-crystalline silicon into wafers. In this procedure, a wafer is heated to temperatures above 600 °C at which a continuous stream of inert gas (such as N2) or a reducing gas (H2) containing a few percent of HCl interacts with the wafer. Because of the high mobility of 3d metals [5] these metals diffuse to the surface and form volatile chlorides by the reaction with the HCl.

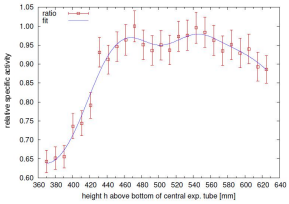


INAA at TRIGA Mainz

For Instrumental Neutron Activation Analysis (INAA), most of the samples were irradiated in the central experimental tube of the TRIGA Mainz at a neutron flux of $4 \cdot 10^{12}$ n/cm²s for up to 30 hours.

The irradiation position at the central experimental tube





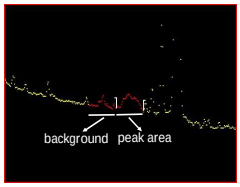
To correct for flux variations, the relative thermal neutron flux along the irradiation capsule was measured with a sample consisting of iron wires at distances of 1 cm [4]. This flux correction was rechecked at some positions by the specific ^{31}Si activity of the Si samples, which should be constant for all samples of the same irradiation.

To calculate the absolute concentration of the elements under consideration, elemental standards are co-irradiated with the samples.

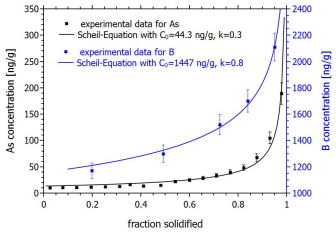
PGAA at HFR Petten

Prompt gamma activation analysis (PGAA) is used to determine the boron concentration. The irradiations were carried out at the beam line HB07 at a thermal neutron flux of 6.6×10^7 n/cm²s.

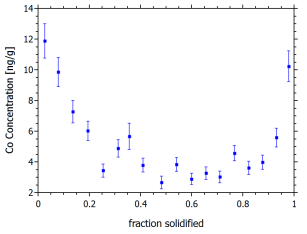
For PGAA of boron, the reaction n + ^{10}B => ^{4}He + ^{7}Li + γ (478keV) is used. Because the γ is emitted during the flight of the ^{7}Li, the γ - line is Doppler broadened. The data evaluation was performed by integrating the peak area between 466.8 keV and 487 keV and subtracting the background between 447 keV and 446.6 keV. As standard, a certified solution of boron acid suspended in powder of pure silicon was used.



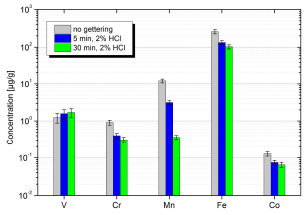
Results



The behavior of the dopants is shown for boron and arsenic. These elements occupy lattice sites in silicon and are therefore almost immobile in solid silicon even at high temperatures. In this case the concentration profile (C) follows the Scheil-equation: $C=C_0k(1-f_s)^{(k-1)}$ with C_0 = starting concentration, k = segregation coefficient and f_s = fraction already solidified, which is equal to the relative height along the crystallization front. Phosphorus, the other important dopant, with k=0.35 should behave similarly to arsenic.



The behavior of the 3d metals is shown for Co. All 3d metals occupy interstitial sites in the silicon lattice and are therefore very mobile at high temperatures in silicon. The segregation coefficients are very low (10^{-5} – 10^{-6}) [5] and therefore, they are enriched in the liquid phase. After crystallization during cooling of the ingot they can diffuse back from the upper part and also from the crucible. This leads to the shown U-shaped concentration profile.



HCl gettering of the 3d metals has been studied in recent years in detail [3,6] for MG and UMG silicon and under different ambient conditions such as temperature, HCl concentration, and time. As shown here for different 3d metals in MG silicon, HCl gettering can reduce the metal content. The gettering efficiency depends on the ambient conditions but also on the diffusivity of the element in the silicon wafer. Vanadium has the lowest diffusion coefficient and cannot be removed by HCl gettering.

Conclusions

- The concentration profile of the dopants boron and arsenic and of the 3d metal Co along the crystallization front of multi-crystalline silicon could be measured by INAA and PGAA.
- The profile of the dopants can be described by the Scheil-equation.
- The 3d metal Co shows a U-shaped concentration profile.
- The efficiency of HCl gettering was investigated for most 3d metals under different ambient conditions in MG and UMG silicon.

Outlook

- The measured concentration profiles of multi-crystalline silicon will be used to optimize the crystallization parameters.
- To optimize the analytical effort for these studies, it has to be tested if the behavior of one element is representative for the whole group, e.g. Co for the 3d metals or As for the n-dopants.
- The study of the HCl gettering will help to develop a simulation model for this process.

Acknowledgement

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References

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