Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 92 (2016) 392 – 398

Energy Procedia

6th International Conference on Silicon Photovoltaics, SiliconPV 2016

Localization of inorganic impurities in silicon samples by sequential etching and ICP-MS detection

Stefanie Wahl*, Sylke Meyer, Christian Hagendorf

Fraunhofer Center for Silicon Photovoltaics CSP, Otto-Eissfeldt-Str. 12, D-06120 Halle (Saale), Germany

Abstract

The investigation of trace elemental contaminations in silicon material is of major interest as it has detrimental impacts for further process steps. Thus, the detection of surface impurities in silicon samples was investigated by sequential etching steps followed by ICP-MS measurements. Due to variations of etching solutions containing HCl, HF and HNO_3 trace element contents could be assigned to different layers of silicon samples, like the outer surface, the silicon oxide and the sub-oxide layer as well as the bulk material. The method is not only suitable for silicon wafers but can also be adapted to powdery samples like etched silicon nanowires and kerf silicon. In this study, we show exemplarily the sequential etching procedure for metallurgical silicon powder samples. This method enables the layer dependent quantification of impurities in silicon samples.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer review by the scientific conference committee of SiliconPV 2016 under responsibility of PSE AG.

Keywords: sequential etching; ICP-MS analysis; localization of inorganic impurities

1. Introduction

Over the past years ICP-MS combined with wet chemical sample preparation has been established as a powerful tool for the quantification of trace elements in silicon [1]. Besides integral bulk analysis, methods were developed for the sensitive determination of surface contaminants [2, 3]. The acceptable contamination levels within silicon materials were investigated [4] and also impurities of feedstock materials before and after crystallization were determined [5]. In many cases however, a more detailed detection of trace elements is essential to explain where contaminations come from and how the material can be purified before introducing it into the process. A new

* Corresponding author. Tel.: +49 345 5589 5122; fax: +49 345 5589 5999
E-mail address: stefanie.wahl@csp.fraunhofer.de

1876-6102 © 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer review by the scientific conference committee of SiliconPV 2016 under responsibility of PSE AG.
doi:10.1016/j.egypro.2016.07.118

method for the layer dependent quantification of impurities in silicon samples was developed, which is suitable for silicon chunks and wafers but also for the localization of contaminations in granulate or powder samples. Basically, sequential etching steps are performed to dissolve a certain layer (outer surface, silicon oxide, sub-oxide layer) and subsequently the etching solutions are analyzed by high resolution ICP-MS. Results show that the sum of all individual etching steps correlates well to the amount of contaminations which are measured after one-step digestion of the complete sample.

2. Material and methods

2.1. Silicon samples

Two batches of metallurgical silicon powder samples (batch A and batch B) were used for the whole procedure of sequential etching and chemical decomposition. The two batches both had a three hour milling procedure. While batch A only had a treatment with H_2SO_4 for cleaning purposes, batch B was additionally etched with HF.

2.2. Surface extraction

For localizing impurities in silicon samples a four-step etching method was developed. Thus the impurities can be allocated to the outer surface, the oxide layer, sub surface layers and the bulk material. All samples were analyzed in three parallel vials to ensure the data and give some statistics of deviations from the analysis and material itself. Four vials without any sample were carried along to determine the background contaminations of the procedure. They were subtracted from the sample results and determined for every etching solution.

First of all the samples were treated by 34 % HCl / 69 % HNO_3 / H_2O (volume ratio 1:1:23) for ten minutes. After centrifugation to separate the silicon powder from the etching solution, the latter was poured into an extra vial for the ICP-MS measurement. The samples were rinsed with water once which was discarded after centrifugation. In the first step only impurities of the outer surface were etched and neither silicon oxide nor silicon itself was dissolved. Two analogue steps with 48 % HF / H_2O (volume ratio 1:24) and 48 % HF / 69 % HNO_3 / H_2O (volume ratio 1:1:23) were carried out subsequently to dissolve the oxide layer and the sub-oxide layer, respectively. After the third etching step the samples were transferred into PFA vials suitable for bulk analysis and dried on a hot plate at 130 °C in order to determine exactly the initial weight of the samples. All solutions from the three previous etching steps were analyzed by ICP-MS. The whole procedure is shown schematically in figure 1.

2.3. Bulk analysis

Samples after the three-step surface extraction as well as samples without any preceding extraction were decomposed by concentrated 69 % HNO_3 / 48 % HF (volume ratio 10:7). The latter was added dropwise to keep the exothermal reaction under control. The acid was evaporated to a small droplet of liquid which was then diluted in 69 % HNO_3 and water (volume ratio 1:75). This solution was analyzed by ICP-MS.

2.4. ICP-MS analysis

For the measurements of 16 elements a high resolution ICP mass spectrometer was used (Element XR, Thermo Scientific, Germany). Calibration was done as standard addition with commercial available multi element standard solutions. Only ultrapure chemicals (element contaminations < 20 ppt) and ultrapure water were used for all procedures.

Results of ICP-MS analysis were received in µg/L and were converted into ng/g by taking the initial sample weight and the volume of used acid for the etching steps into account.

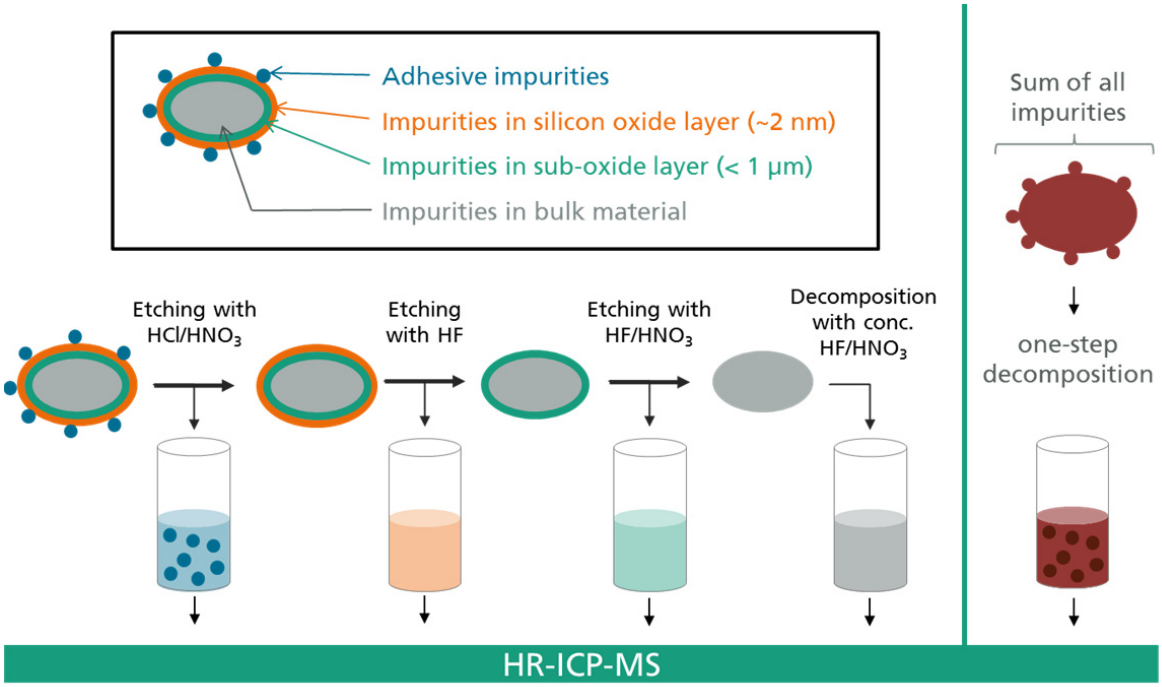

Fig. 1. Schematic workflow of the three-step surface extraction and subsequent bulk analysis as well as complete bulk analysis followed by ICP-MS measurement.

3. Results and discussion

Two different powdery metallurgical silicon samples were analyzed for their inorganic contaminations in different layers. While the first step, etching with HCl/HNO_3, only removes adhesive particles at the outer surface, the next steps with HF and HF/HNO_3 dissolve the silicon oxide layer and the sub-oxide layer, respectively. Afterwards the pre-etched samples were completely digested. In parallel, the whole sample without previous etching steps was decomposed in one single step.

3.1. Limits of detection

The limits of detection (LOD) were determined by the triple of the standard deviation of the four background samples. They can vary due to handling, contaminations in acids and vials as well as daily performance of the mass spectrometer. To keep the limits of detection as low as possible only ultra-pure acids and chemical inert vials were used. The manual handling has the highest impact on the limits of detection, which are shown in figure 2. Over all, they are lower than 53 ng in 1 g sample for all elements and even lower than 3 ng in 1 g sample for most of the elements. Thus they are proved to be low enough for the analysis of the studied samples, so that almost all elements can be determined.

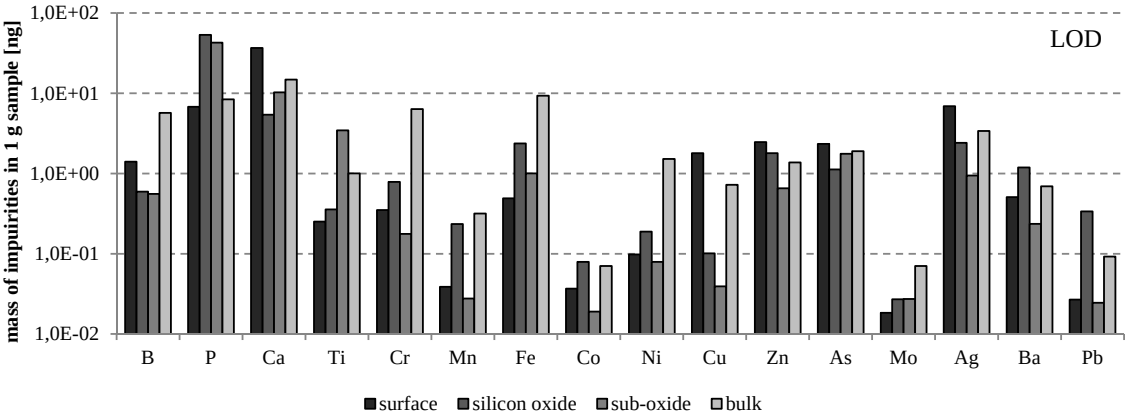

Fig. 2. Limits of detection (LOD) for the three etching steps (dark grey to light grey correspond to etching steps 1 to 3) and the decomposition of the whole sample as determined for each of the investigated elements.

3.2. Results of etching steps

The results of the three single etching steps for the surface contaminations as well as the results of the decomposition of the surface cleaned sample are shown in figure 3 (batch A) and figure 4 (batch B). Standard deviations are referred to a three-fold determination of each sample. Colorless bars show values below the limits of detection.

Results of both batches, A and B, show that some elements like Cu, Ag, Ba and Pb are mainly found on the outer surface while other elements like B, P, Ca and Mo are more present in the bulk of the material. Metals like Cr, Mn, Fe and Ni are found with increasing values from the surface to the bulk material. The contents of impurities of most of the elements of batch A are found to be higher in all three analyzed layers than in batch B. In contrast, the bulk contaminations in both samples were almost within the same order of magnitude except for Ag, which was found more present in batch B. These results show that trace elements can be detected and matched to their origin by step-by-step surface extraction methods followed by ICP-MS measurements.

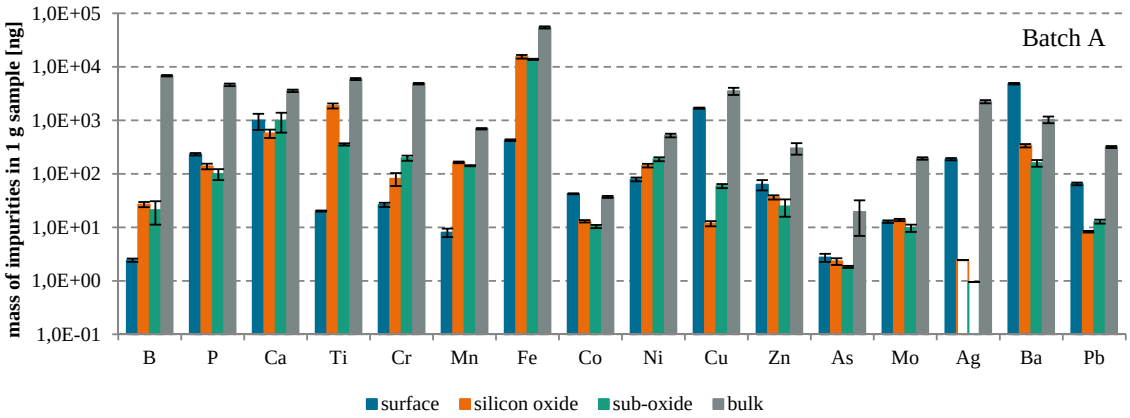

Fig. 3. Elemental contaminations in different layers of metallurgical silicon powder batch A. Standard deviations are refered to multiple measurements.

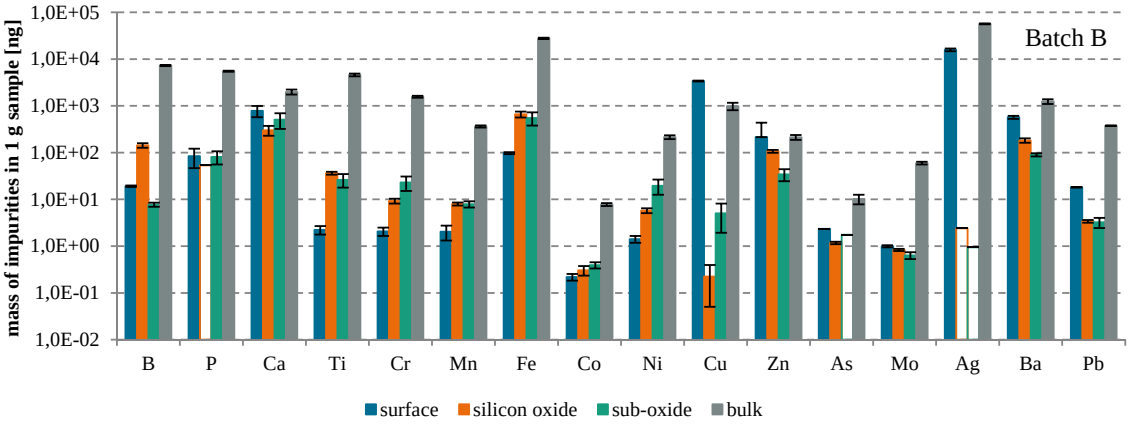

Fig. 4. Elemental contaminations in different layers of metallurgical silicon powder batch B. Standard deviations are refered to multiple measurements.

The sum of the impurities of the single sequential etching steps and the subsequent bulk analysis correlates with the element content of impurities obtained from the one-step decomposition. The results are shown in figure 5 (batch A) and figure 6 (batch B), respectively, where stacked bars show the summed up masses of impurities of the sequential etched samples while dark grey colored bars show the results of the one-step decomposition.

For ten out of 16 elements the compared values correlate very well. For Co, Ni, Cu, Zn, As and Mo the measured impurities of the complete sample differ slightly compared with the sum of impurities of the single etching steps. This may be due to failures of the procedure which occur in the rinsing step when water is discarded after the centrifugation steps. As the sample was not dried between every etching step the initial weight (and therefore the absolute amount of impurities) could be slightly reduced due to particles which are discarded with the water after rinsing.

Nevertheless, a very good correlation of the results was achieved showing the reliability and precision of the newly developed chemical analysis method.

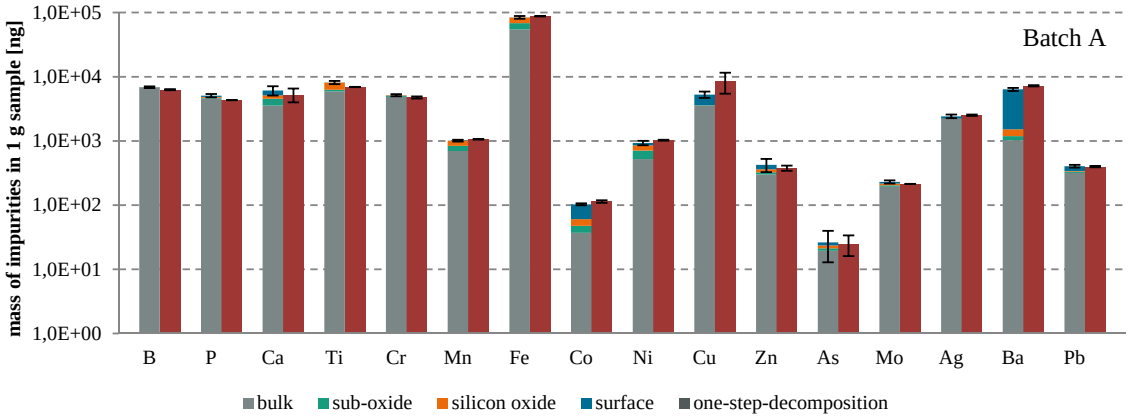

Fig. 5. Summed up masses of impurities of sequential etching steps and final decomposition of the samples (stacked bars) compared to the amount of impurities after one-step decomposition (dark grey bars) for batch A.

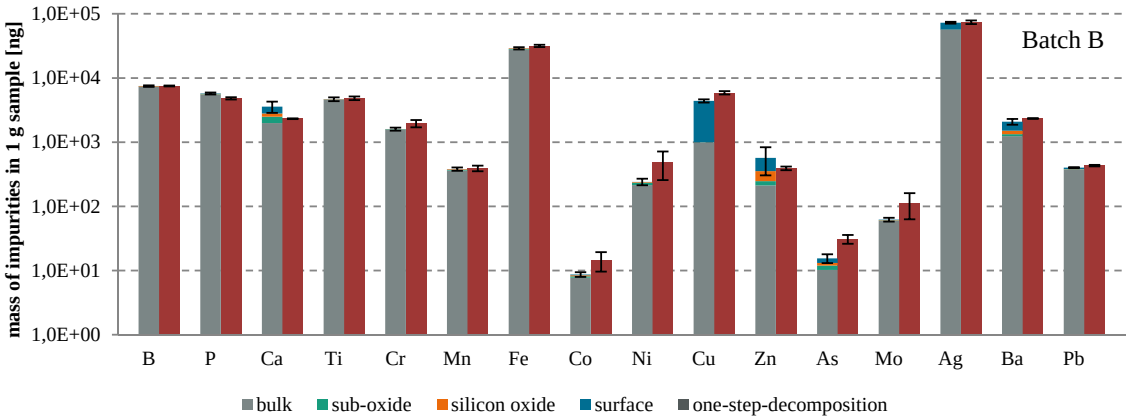

Fig. 6. Summed up masses of impurities of sequential etching steps and final decomposition of the samples (stacked bars) compared to the amount of impurities after one-step decomposition (dark grey bars) for batch B.

3.3. Evaluation of cleaning strategies

The developed chemical analysis method is a powerful tool for the quantitative evaluation of cleaning processes. This can be demonstrated with the two silicon powder batches which were analyzed in this study. Batch A was cleaned with H_2SO_4 while batch B received an additionally cleaning step with HF. This purification results in a higher purity level of the surface layers. Figure 7 shows the localized impurities of both batches exemplarily for the elements Ti, Fe and Ni. While the bulk content is similar in both materials it can be clearly seen that the HF step significantly reduces the impurities of the surface, in the oxide and sub-oxide layer, respectively, by about one to two orders of magnitude.

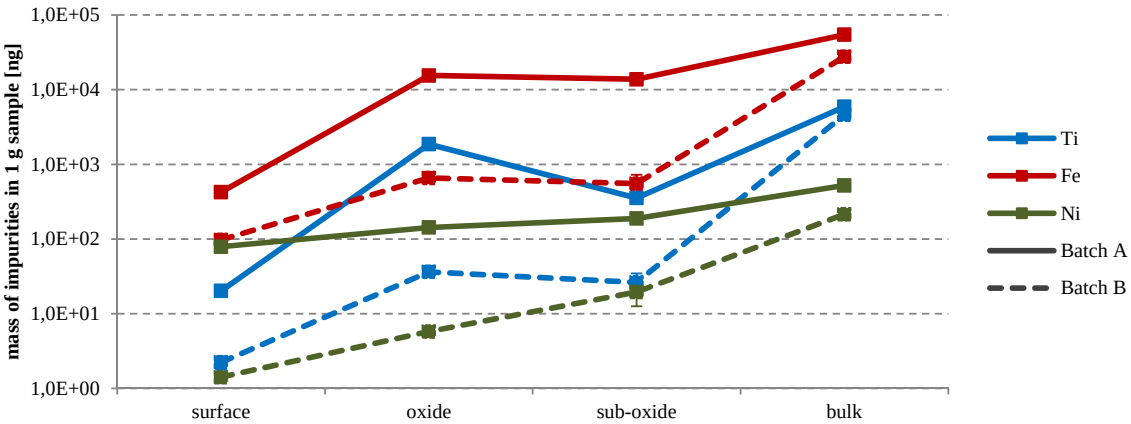

Fig. 7. Layer-specific impurities of batch A (cleaned with H_2SO_4) and batch B (cleaned with H_2SO_4 and HF) silicon powder material.

4. Conclusion

A new method for the quantitative determination and localization of impurities within different layers of silicon samples was developed. As different acid solutions etch only specific regions the impurities in silicon materials can be localized. Thus an HCl/HNO_3 solution is used for adhesive contaminations on the outer surface and neither silicon nor the silicon oxide layer is dissolved. With a HF solution and a HF/HNO_3 solution the impurities in the

silicon oxide layer (~2 nm) and the sub silicon oxide layer (up to 1 µm), respectively, can be dissolved. In general the last etching step, containing HF/HNO_3, can be performed repeatedly to get a depth profile of the contamination.

For the bulk analysis a subsequent complete digestion with concentrated acids can be performed. All etching solutions were then analyzed by HR-ICP-MS for their element concentrations with low limits of detection. It was shown that the summed up masses of impurities of different etching steps equals the mass of impurities in a sample which was digested without preceding etching steps. The limits of detection are not only sufficient for the analysis of metallurgical silicon but also for kerf samples, feedstock chunks and wafers as well as for nanostructured silicon surfaces.

It was shown that the developed method is a useful tool to analyze contaminations on silicon powdery samples with regard to their presence in individual surface layers. This is of further interest to explain in which surface layers contaminations are localized as well as how the material can be purified before introducing it into further process steps.

Acknowledgement

This work was financially supported by the German Federal Ministry for Economic Affairs and Energy within the research project »HELENE« (contract no. 0325777E).

References

[1] Balski, M., Kipphardt, H., Berger, A., Meyer, S., Panne, U., "Determination of impurities in solar grade silicon by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) subsequent to matrix evaporation", RSC Anal. Methods 6, 77-85 (2013).

[2] Meißner, D., Meyer, S., Anspach, O., "Enrichment of metal ions in virgin Si-surfaces", Energy Procedia 27, 27 – 32 (2012).

[3] Buchholz, F., Wefringhaus, E., Eisert, S., Egenolf, H. and Groß, A., "Measurement and Impact of Surface Transition Metal Contamination of Textured Multicrystalline Silicon Wafers", in: Proceedings of the 26th European Photovoltaic Solar Energy Conference and Exhibition, 1187–1190 (2011).

[4] Hofstetter, J., Lelièvre, J. F., Del Cañizo, C., & Luque, A. D., “Acceptable contamination levels in solar grade silicon: From feedstock to solar cell”. Materials Science and Engineering: B, 159, 299-304 (2009).

[5] Meyer, S., Wahl, S., Molchanov, A., Neckermann, K., Möller, C., Lauer, K., Hagendorf, C., "Influence of the feedstock purity on the solar cell efficiency", in: Solar Energy Materials and Solar Cells 130, 668-672 (2014).