Trace element analysis in crystalline silicon

Sylke Meyer[1], **Susanne Richter**[1], **Matthias Balski**[2] & **Christian Hagendorf**[1]
[1]Fraunhofer Center for Silicon Photovoltaics CSP, Halle; [2]BAM Federal Institute for Materials Research and Testing, Berlin, Germany

ABSTRACT

The reliable analysis of trace elements in silicon is of fundamental importance for the understanding of material properties and quality control of solar cells. This paper presents a demonstration of the power of two analytical techniques for the determination of trace elements in solar silicon: inductively coupled plasma mass spectrometry (ICP-MS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These techniques are among the few that achieve sufficiently low detection limits and they may complement each other because of their specific performance. Examples are given of the quantitative chemical analysis of boron, phosphorus and iron in different types of solar silicon, as well as of the enrichment of metals and alkali metals in Si_3N_4 precipitates.

Introduction

The impurities and contaminants in feedstock material and crystallized silicon blocks are a major source of defects and electrical losses in the later solar cells. Starting with the as-cut raw wafer, all subsequent solar cell processing steps rely on the prerequisites defined at the very beginning of the production chain.

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Figure 1. ICP-MS facility at Fraunhofer CSP.

It is known that the majority of contaminants found in ingots and wafers migrate into the silicon material from the crucible and the surrounding gas atmosphere during the crystallization process. Moreover, the distribution of the contaminating elements is not homogeneous, because of segregation between solid and liquid phases during crystallization, diffusion processes in the crystal, and local enrichment at grain boundaries and other defective structures. Therefore, a reliable analysis of trace elements in silicon is very important for understanding silicon material properties and quality control. This analysis includes analytical methods that can be applied for a local analysis in the volume and at the surfaces. However, only a few analytical techniques achieve the very low limits of detection and local resolution necessary for this task. Among these are the mass spectrometry techniques ICP-MS, GD-MS and ToF-SIMS, which may complement each other due to their specific performance.

Inductively coupled plasma mass spectrometry (ICP-MS) is currently the most powerful and useful trace-analysis tool capable of quantitatively measuring the total elemental impurity concentrations in solar silicon down to ppbw level. The advantages of ICP-MS analyses, besides the high sensitivity, are flexibility and relatively low costs per sample. A limitation compared to GD-MS or neutron activation analysis (NAA) is the need for chemical decomposition of the samples, which can be a source of external contamination. However, coupling of ICP-MS with laser ablation (LA-ICPMS) can be used for direct sampling of solid silicon and avoids the contamination-prone decomposition procedure [1,2]. But there are drawbacks with LA-ICPMS: it has lower sensitivity and requires a matrix-matched reference material for quantification.

High-resolution glow discharge mass spectrometry (GD-MS) is used more and more in the photovoltaic and semiconductor industry as a technique for surveying most elements in the periodic table with detection limits in the ppbw range. The measurement is independent of chemistry and electronic state, and requires minimal (only mechanical) sample preparation. A broad variety of sample shapes – such as chunks, granules, wafers and even powders – are suitable. An international standard test method (SEMI PV1-0309) for the determination of boron and phosphorus in solar silicon using GD-MS was approved in 2008.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is an analytical method suitable for investigating surface contamination since the technique is quasi non-destructive and has a local resolution in the low µm range [3]. Additionally, ToF-SIMS has a detection limit in the ppm range for many elements and a high mass resolution that also permits the detection of whole molecules and molecule fragments. The yield of measured ions and molecules can be increased by applying secondary sputter guns. The secondary sputter sources Cs^+ and O_2^+ are used for negative and positive ion polarity, respectively, and accelerated with 2keV each time, with a sputter target of 300×300µm up to 500×500µm, depending on the analysis area. To eliminate remaining surface contaminants, the Bi-cluster liquid metal ion gun (Bi_1^+, 25keV) is used while observing the decrease in the intensity of typical contaminants.

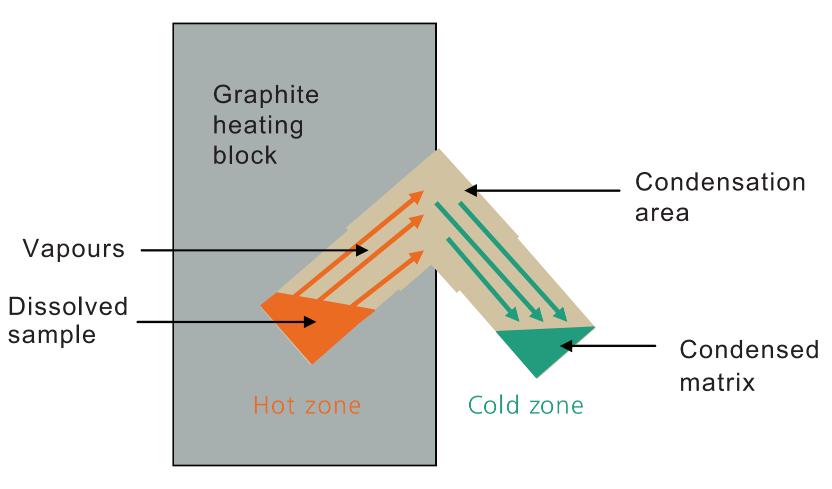


Figure 2. Schematic of the evaporation apparatus.

Results

Chemical decomposition and ICP-MS analysis of silicon

Sample preparation has to be thoroughly optimized because of the relatively high risk of contamination during the procedure. Ultrapure reagents and water, vessels made of material of the highest quality (perfluoroalkoxy – a type of fluoropolymer, otherwise known as PFA) and at least a partial clean-room environment are essential. Surface contaminants must be removed by acid etching prior to the decomposition reaction. The silicon is completely dissolved during an exothermic reaction with HF and HNO_3. Finally, the reaction mixture has to be evaporated until almost dry in order to remove acids and the matrix. Best results were obtained using the Evapoclean apparatus, which operates in a closed system with low risk of external contamination.

Following this optimized protocol for sample preparation, ICP-MS can be successfully used for trace element analysis with detection limits down to the ppbw level. Limits of detection between 0.05ppbw (Ga) and 30ppbw (Ca) were achieved, depending on the particular element (see Table 1). For iron, which is one of the most critical contaminants in solar silicon, concentrations down to 2ppbw (5×10^{13} atoms/cm^3) could be measured with ICP-MS.

A feedstock material with lower purity (upgraded metallurgical grade) was used to perform comparative trace

Element		B	Na	Al	P	Ca	Ti	Cr	Mn	Fe	Ni
LOD	[ng/g]	10	15	40	10	30	5	1	0.1	2	1
LOD	[atoms/cm^3]	1×10^{15}	9×10^{14}	2×10^{15}	5×10^{14}	1×10^{15}	1×10^{14}	2×10^{13}	2×10^{12}	5×10^{13}	2×10^{13}
Element		Co	Cu	Zn	Ga	Sr	Mo	Pb	K	As	Ge
LOD	[ng/g]	0.2	1	1	0.05	1	1	0.1	15	0.3	0.04
LOD	[atoms/cm^3]	4×10^{12}	2×10^{13}	1×10^{13}	1×10^{12}	2×10^{13}	1×10^{13}	6×10^{11}	5×10^{14}	5×10^{12}	7×10^{11}

Table 1. Limits of detection (LOD) for the most important contaminating elements in solar silicon as measured with ICP-MS.

element analyses using ICP-MS, NAA and GD-MS. As seen in Fig. 3, there is a very good correlation between the results of all three techniques. Bearing in mind that NAA is time consuming and cost intensive, and requires larger samples of silicon, it is clear that mass spectrometry techniques are preferable. Although ICP-MS is the more flexible method and can be easily calibrated by using single-element standard solutions, GD-MS is less labour intensive and contamination prone, but its accuracy is tied to reference materials.

> "ICP-MS is a rapid and reliable tool for the quantitative determination of the total boron and phosphorus content in a silicon material."

Boron and phosphorus profiles

The concentration and distribution of the dopant elements boron and phosphorus has a significant effect on the efficiency of the solar cell. It is shown here that ICP-MS is a rapid and reliable tool for the quantitative determination of the total boron and phosphorus content in a silicon material. It is possible to obtain elemental profiles by taking samples from different positions of an ingot. Fig. 4(a) shows a vertical cut from a silicon ingot (compensated material) that was analyzed by chemical decomposition and ICP-MS; the positions of the samples are indicated in the drawing. The resulting concentrations shown in Fig. 4(b) correlated well with a theoretical profile calculated from Scheil's equation using the added dopant concentration C_0 and the segregation coefficients $k_{boron} = 0.8$ and $k_{phosphorus} = 0.35$. Similar results can be obtained by using GD-MS and have been reported elsewhere [1].

Determination of the total iron content

As mentioned earlier, the sensitivity of both of the mass spectrometry methods (ICP-MS and GD-MS) is too low to measure iron concentrations lower than 10^{13} atoms/cm^3. However, crystalline silicon is expected to have iron concentration below this value. Nevertheless, ICP-MS can be used to characterize crystallization processes, that is ascertain the influence of different crucibles or coatings. Fig. 5(a) shows mechanically prepared samples from the lateral edge of a typical ingot; typically, this area of the ingot is called the 'bad region' based on measurements of carrier lifetimes. After chemical decomposition the total iron concentration was determined in these samples. Decreasing concentrations in the range 10^{13} to 10^{15} atoms/cm^3 show the influence of the

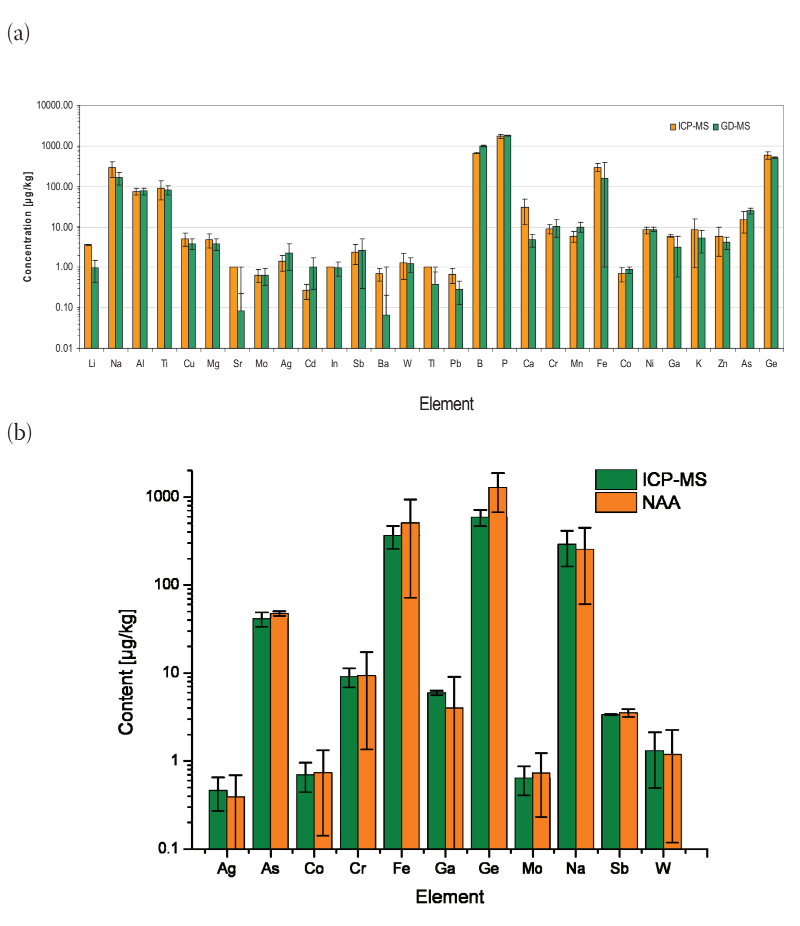


Figure 3. (a) Comparison of trace element and dopant concentrations measured with ICP-MS and GD-MS. (b) Comparison of trace element concentrations measured with ICP-MS and NAA.

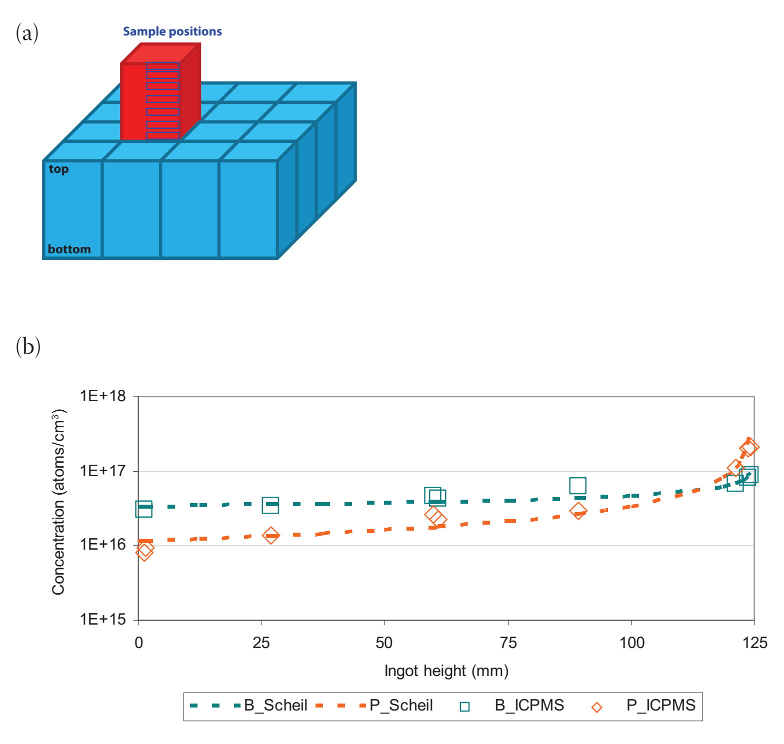


Figure 4. (a) Positions of the samples in the ingot. (b) B and P concentrations determined by ICP-MS and calculated from Scheil's equation.

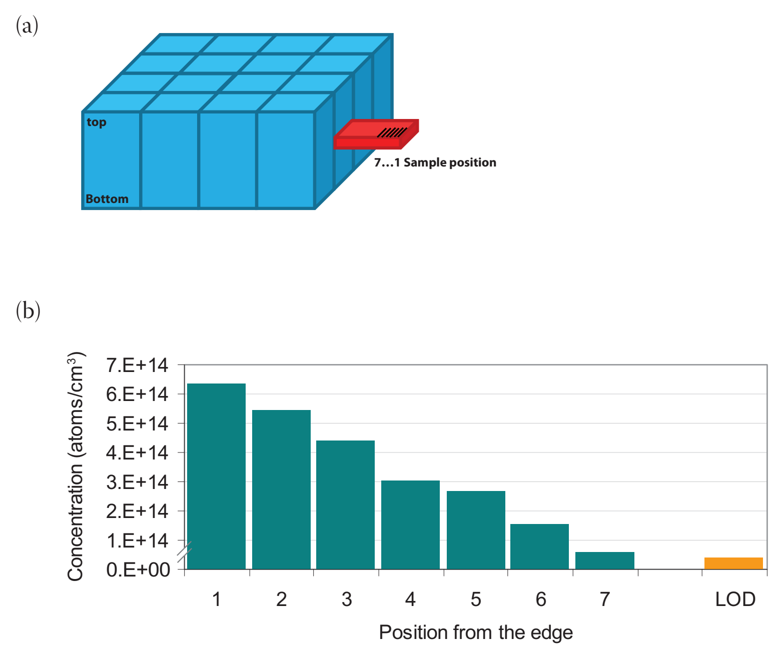


Figure 5. (a) Positions of the samples in the ingot. (b) Iron concentrations in samples from the electrical 'bad region' of the lateral edge of a multicrystalline ingot, determined by ICP-MS.

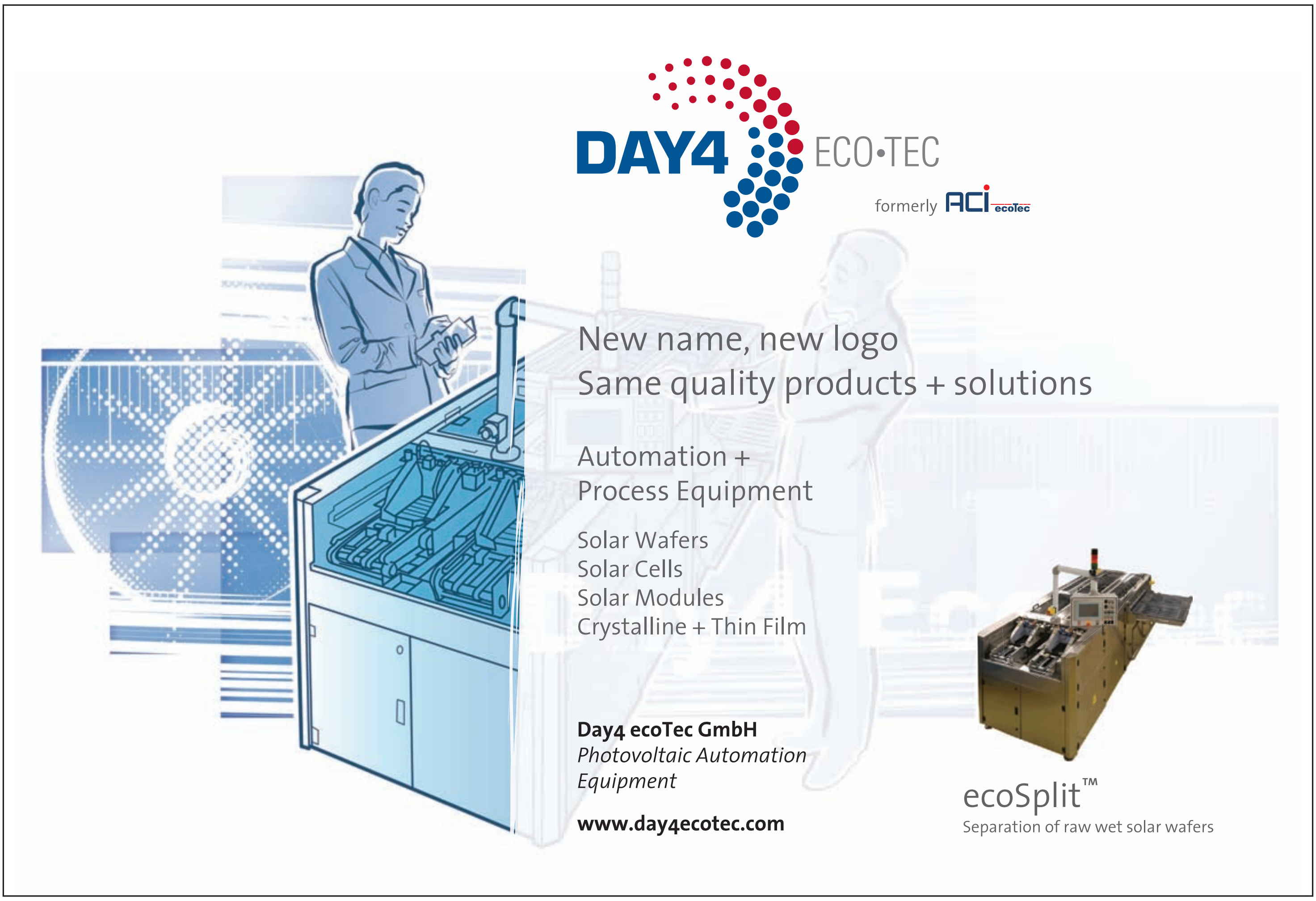
crucible during crystallization (Fig. 5b). As expected, the iron concentrations in the central part of the ingot are below the detection limit of the ICP-MS method.

Trace element analysis of precipitates

ToF-SIMS was performed with an Iontof TOF.SIMS V apparatus for the investigation of the trace element composition of characteristic precipitate clusters down to the ppm range. For this purpose, the dual-beam interlaced mode was used with Bi^+ (25keV) as the primary ion gun working as the analysis beam, and, optionally (for better yield of the analyzed ions), the different Cs^+ or O_2^+ secondary ion guns were used for negative or positive secondary ion sputtering, respectively. An acceleration voltage of 2keV was chosen for the sputter sources.

ToF-SIMS is a suitable analytical method for determining the chemical composition of microscopic structures because of its high mass and high lateral resolution down to 60–100nm, depending on the measurement mode. In accordance with the size of the investigated precipitate, the sputter target (up to 400×400μm²) was selected to be larger than the analysis target (up to 250×250μm²). Prior to data acquisition, surface contaminants were removed by low-energy sputtering.

In this study, precipitates were investigated in the dual-beam and Bi^+ bunched mode (with a pulsed Bi^+ gun) for high mass resolution and low detection limit. A surface preparation of precipitates by means of transmission infrared microscopy was performed before the localized ToF-SIMS analysis. Fig. 6 depicts the investigated precipitation types containing a SiC particle with a Si_3N_4 rod, Si_3N_4 fibres and a Si_3N_4 net. The identification of the structures was



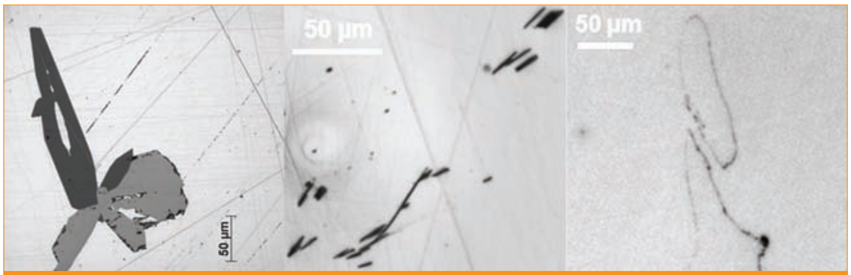


Figure 6. Reflected light images of a SiC particle with a Si_3N_4 rod (left), Si_3N_4 fibres (centre) and a Si_3N_4 net (right).

supported by determining the elemental composition using nanospot EDS.

To obtain a detailed chemical characterization with high local resolution, ToF-SIMS was performed on each structure. Ion images were obtained using the O_2^+ sputter source for enhanced positive ion yield. It was observed that Si_3N_4-like precipitation types contain the alkali metals Li, Mg and Ca. In addition, metals such as Al can be found at the interface position of the SiC and Si matrix as well as at the position of the Si_3N_4 nets (Fig. 7). The alkali metals probably only have a small influence on the electrical properties of the precipitates, as previously shown by Richter et al. [2,3]. The main influence can be explained by the n-doping. Nevertheless, recombination effects and breakdown mechanisms due to the trace elements cannot be excluded.

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Conclusion

It has been shown that ICP-MS and ToF-SIMS are suitable techniques for

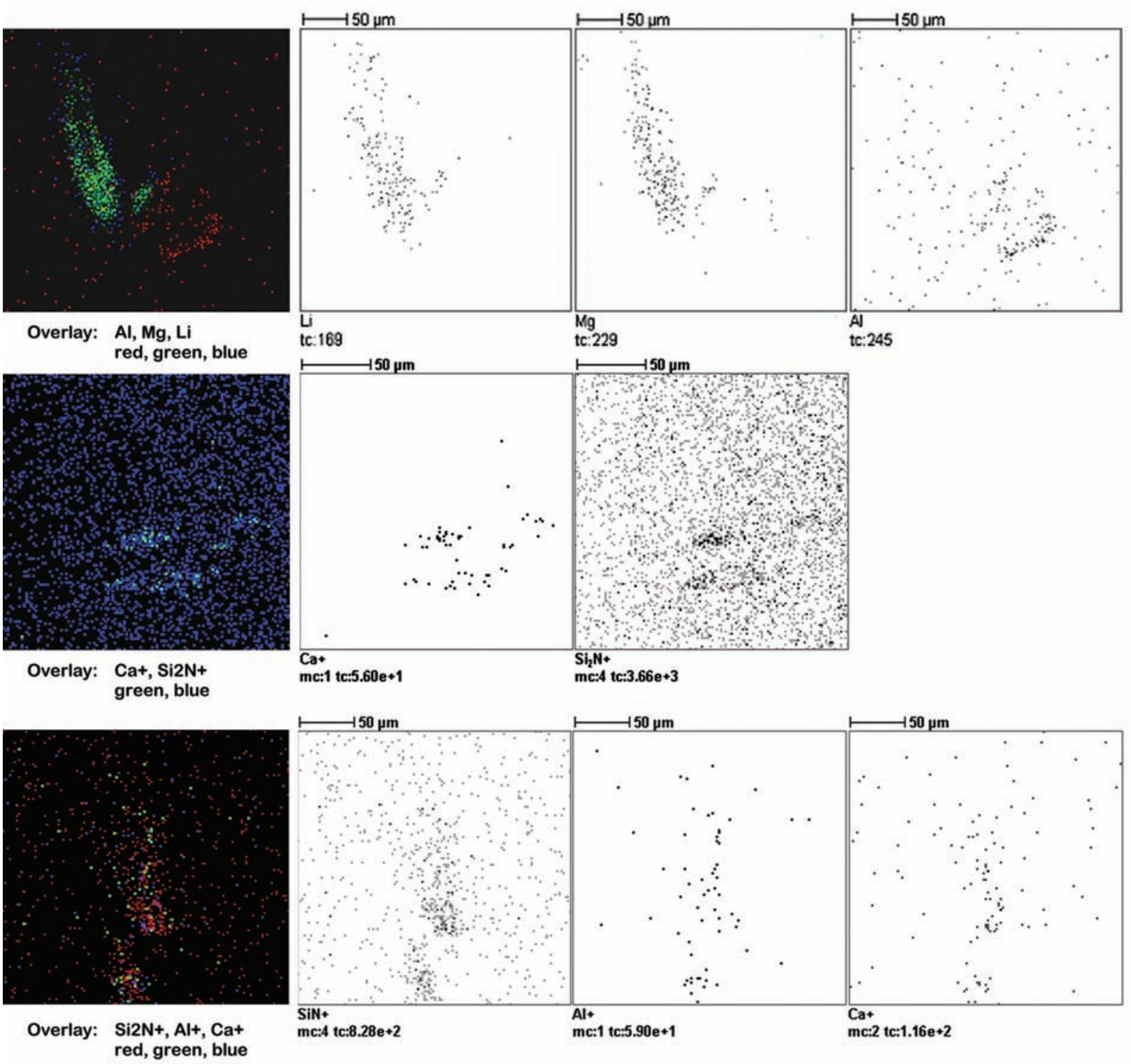

Figure 7. Positive ToF-SIMS ion images of trace metals and alkali metals of a SiC particle with a Si_3N_4 rod (top), Si_3N_4 fibres (centre) and a Si_3N_4 net (bottom). The overlay is shown in the first column.

analyzing trace elements in silicon material. ICP-MS may be used for quantitative determination of total metal and dopant concentrations because of its high sensitivity, whereas the power of ToF-SIMS is its high local resolution. Therefore, both techniques may complement each other in studying the material properties of solar silicon.

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About the Authors

Sylke Meyer studied biochemistry and received her Ph.D. in the field of structural analytics from the Martin Luther University in Halle-Wittenberg. She now leads the chemical analytics team in Fraunhofer CSP's solar cell diagnostics group. Sylke's research focus is trace element analytics of all solar cell materials.

Susanne Richter is currently working on her Ph.D. thesis on elemental and structural analysis of defects in multicrystalline silicon at Fraunhofer CSP, where her daily scientific activities are based on ToF-SIMS. Susanne studied physics at the University of Leipzig and wrote her diploma thesis in the area of solid-state physics.

Matthias Balski studied chemistry at the Humboldt University in Berlin. Since 2009 he has been working on his Ph.D. thesis at the Federal Institute for Materials Research and Testing. Matthias' work covers the comparison of different methods and strategies for the determination of trace impurities in solar-grade silicon.

Christian Hagendorf is the head of the solar cell diagnostics group at Fraunhofer CSP, where he works on material characterization and defect diagnostics in solar cells. Christian studied physics at the Goethe University in Frankfurt, before receiving his Ph.D. in surface physics from the Martin Luther University in Halle-Wittenberg.

Enquiries

Fraunhofer Center for Silicon Photovoltaics CSP
Walter-Huelse-Str. 1
06120 Halle (Saale)
Germany

BAM Federal Institute for Materials Research and Testing
Unter den Eichen 87
12205 Berlin
Germany