Analysis of impurities with inhomogeneous distribution in multicrystalline solar cell silicon by glow discharge mass spectrometry

C. Modanese *, L. Arnberg, M. Di Sabatino

Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Alfred Getz vei 2B, N-7491 Trondheim, Norway

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ABSTRACT

Multicrystalline silicon for solar cells presents material inhomogeneities related to the presence of extended defects such as grain boundaries or dislocations. These defects are possible sources for nucleation of precipitates, which generally show a highly inhomogeneous distribution in the crystal structure. The use of direct current (dc), continuous operation glow discharge mass spectrometry (GDMS) as an analytical technique to study these distributions is presented in this article, with focus on ultra-trace elements such as Fe and Cu. In order to evaluate the impact of the analytical parameters, a doping element (B) is also analyzed, since it generally shows a more homogeneous distribution in the crystal structure. The results suggest that, for commonly used mc-Si for solar cells, due to the size of the precipitates and the high degree of inhomogeneity in the bulk, single precipitates cannot be detected during common bulk analysis by dc GDMS.

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1. Introduction

The performance of multicrystalline silicon solar cells is ultimately limited by carrier recombination in the substrate, which is dominated in practice by recombination related to impurities, decorated dislocations and grain boundaries [1]. Average metals concentrations of 1 ppma (5×10^{16} cm^{-3}) have been shown to lead to nanometer-scale precipitates/agglomerates, which are present on μm-scale areas, especially at dislocations, and at a lower extent at grain boundaries and microdefects [2]. Metal silicide precipitates have been observed in TEM studies on as-grown mc-Si, with sizes from tens of nanometers to several hundreds of nanometers in large multi-metal clusters [3,4]. In those studies, Fe, Ni and Cu were found to be present; and many of the precipitates were nucleated around dislocations or grain boundaries. Stokkan *et al.* [5] modeled and evaluated experimentally the combined effect of grain boundaries and dislocations on minority carrier lifetime, showing that recombination activity of grain boundaries can be related to their misorientation. Since the concentration of metal impurities in the silicon substrate [1] and their spatial distribution (*i.e.*, precipitated at grain boundaries or dislocations, or dissolved into the Si lattice) plays a major role on the performance of the solar cell device, studying the distribution of impurities in the bulk of mc-Si materials is the aim of the present work.

In the last decades, glow discharge mass spectrometry (GDMS) has become a well-established technique for multi-element investigation of trace- and ultra-trace impurities in highly pure metals and semiconductors [6]. Details on the technique can be found in Ref. [7]. With focus on PV materials, GDMS is widely used in the industry for the chemical analysis of upgraded metallurgical grade and solar grade silicon feedstock thanks to the low detection limits achievable (potentially down to pptw) [8]. Moreover, contrarily to most of the other techniques employed to measure the chemical composition of Si feedstock, sample preparation for GDMS does not require any sample dissolution, which in itself can introduce external contamination [9]. A further advantage of GDMS is the possibility for depth profiling of multi-layered structures over a relatively large bulk area [9]. GDMS analyses are carried out on areas typically 50 mm^2, which can provide a rather representative value of the bulk concentration/distribution of the impurities. Since the calibration for each element has a weak dependence on the sputtering rate of the matrix composition, quantitative multi-elemental analysis can be carried out directly [10]. The precision of the quantitative measurements of Si feedstock had been quantified to be ±10–25%, increasing with decreasing concentration of the impurity [8]. Note that, since materials with high enough conductivity are needed in order to establish a stable glow discharge, analyses on electronic grade materials are extremely challenging, particularly at low doping levels.

* Corresponding author. Tel.: +47 41520593.
  E-mail address: chiara@material.ntnu.no (C. Modanese).

Depth profiling by GDMS is usually performed using standard bulk methods to determine the analytical concentration [11]. A few studies of depth profiling of crystalline Si are available in the literature, and they have been performed by radio frequency GDMS [9], or by direct current (dc) GDMS [10]. Both studies used pulsed sources, whose advantage over continuous operation is related to an enhanced sputter atom yield (*i.e.*, ionization rate/count rate), and to an increased signal-to-noise ratio due to greater excitation and ionization [12]. However, continuous, dc-powered GDMS sources are currently more widely used and well-established quantification procedures are readily available. Moreover, Schmitt *et al.* [10] observed a rather high detection limit of 100 ppbw for P due to a loss in sensitivity in the pulsed-operated dc-GDMS. Those studies focused on B and P, elements that are most likely neither segregating at grain boundaries nor precipitating in mc-Si materials. It is worth noting that, in order to obtain a low detection limit and hence a high sensitivity in the analysis, GDMS calibration should aim for a high sputtering rate, possibly coupled with high integration times. However, this affects in turn the depth resolution of the analyses since the mass spectrometer operates in scanning mode [10]. In addition, the impact on depth resolution becomes more relevant in the case of a multi-elemental analysis.

Dc high resolution (HR) GDMS analyses were tuned in the present study with the aim of investigating the extent of impurities inhomogeneity in mc-Si materials for PV applications, *e.g.*, the presence of precipitates. Two types of impurities are analyzed, namely i) metal impurities (Fe and Cu) and ii) doping element (B). The impurities are selected with the twofold aim of being representative of elements usually present in the Si for solar cells, and providing an understanding of the spatial distribution of elements that are likely precipitating (metal impurities), and elements that are generally homogeneously distributed into the Si matrix (doping elements). Depth profiles of the impurities concentrations are taken for this purpose, with focus on the relation to crystal structure on one side, and to the homogeneity of the distribution on the other side. The number of analyzed impurities is limited in order to obtain a high depth resolution. Both the expected concentration of impurities and the expected size of precipitates are used to tune the analysis parameters.

2. Experimental

In this work, samples from two directionally solidified mc-Si ingots are analyzed by a HR-GDMS, Element GD instrument from Thermo Scientific. A first ingot, named S2, was selected in order to investigate the presence of precipitates and the homogeneity of the spatial distribution of impurities, with particular focus on the effect of (random) grain boundaries. Ingot S2 is a representative of solar grade silicon materials for solar cells. The samples are taken high in the ingot, *i.e.*, close to the end of the solidification, where a higher concentration of impurities is expected due to segregation during solidification. A second ingot, named D6, was selected to focus on the distribution and segregation of Fe. Ingot D6 is a standard p-type mc-Si material, but with 50 ppmw Fe added to the melt. The samples are reported according to their height along the ingot (solid fraction). All samples are cut perpendicularly to the ingot growth direction, *i.e.*, the sputtering direction is parallel to the growth direction. The samples are ground on SiC papers. The sputtered area is about 8 mm in diameter. Electron backscatter diffraction (EBSD) maps are taken for the samples from ingot S2 in order to confirm the grain orientations of the spots analyzed by GDMS. In particular, twin boundaries $\Sigma3$, $\Sigma9$ and $\Sigma27$ are highlighted.

The dc-GDMS parameters are kept as similar as possible between the various samples. The discharge current is similar for all the samples, whereas the discharge Ar gas flow is 300 ml/min

Table 1
Parameters of the methods used for the analyses. Total time includes the processing time required by the software.

Ingot	Method	Analysis time (s)				
		^{11}B	^{56}Fe	^{63}Cu	^{28}Si	Total
S2	–	20	20	20	5	66
D6	#1	–	25	–	6	33
D6	#2	25	–	–	6	33
D6	#3	25	25	–	6	58

and 400 ml/min for samples from ingot S2 and D6, respectively. GDMS is a comparative technique [13], where quantification of the impurities is performed through internal standards, considering the total ion current and the impurity ion current. In the present work, the quantification is performed manually, integrating the peak intensity and subtracting the background intensity for each isotope. This allows having better control over the background noise on the observed peaks, particularly relevant for analyses with very low counts. The quantification of the impurity concentration is obtained from the ion beam ratio (IBR) and the relative sensitivity factor (RSF):

$$C_x = IBR_x \cdot x \cdot RSF_x = (I_x/Ab_x)/(I_m/Ab_m) \cdot x \cdot RSF_x \quad (1)$$

where I is the intensity [counts per second (CPS)] and Ab is the abundance of the (impurity) isotope x and the matrix isotope m. The RSF takes into account the analytical sensitivity for different elements; consequently, it is matrix- and element specific. The formula is valid for low concentrations, characteristic of impurities in silicon for solar cells. The procedure followed to calculate the RSFs can be found in Ref. [14]. Two different sets of RSFs are used for the ingots S2 and D6, since the discharge gas has a strong influence on the factor. For the analyses reported in this work, the detection limit is ~1.5 ppbw for both Fe and Cu.

The analysis times for each isotope are reported in Table 1. The time for each isotope is set considering the expected concentration and the targeted depth resolution in the analysis. The total time is the time for one repetition, *i.e.*, a complete analysis of the isotopes included in the list. The sputtering rate for the analysis parameters used here is approximately 1 μm/min, which corresponds to ~0.1 mg Si/μm sputtered. The analyses are carried out in a sequential order on the same crater, i.e., the depth of the sputtered material increases with increasing the repetition number.

3. Results

Three different areas, namely i) single grain, ii) with random grain boundaries, and iii) with twin boundaries, were visually selected on a slice from ingot S2. These are named SG1, GB1 and TW1, respectively. EBSD maps were collected on the three spots after GDMS analysis (Fig. 1). The inverse pole figure shows the color code for the grain orientations, where the z-direction is the ingot growth direction. The white dots in the maps are non-indexed points. The highlighted grain boundaries are $\Sigma3$, $\Sigma9$ and $\Sigma27$, and the non-colored grain boundaries in GB1 map are random grain boundaries. It can be observed that SG1 does not have any grain boundaries. GB1 presents some twin boundaries (of these, most are $\Sigma3$), together with other random grain boundaries; whereas TW1 has only twin boundaries, the vast majority being $\Sigma3$.

The concentrations of B, Fe and Cu in samples from ingot S2 are reported in Fig. 2. 'Repetition #' in the x-axis refers to a complete analysis, *i.e.*, B, Fe and Cu measured in sequence. The spots labeled 're-ground' are on the same position as before grinding, *e.g.*, SG1 re-ground is taken right below the SG1 spot. The re-grinding was aimed at studying possible macrosegregation in the samples. Only three repetitions are taken for SG1, GB1 and TW1 spots; and they are reported as repetitions #16–18 to take into account the