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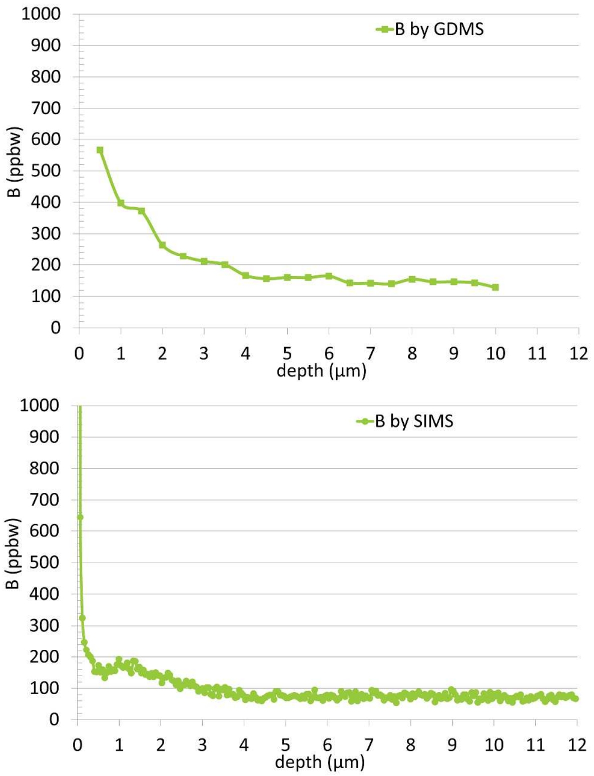

Comparison of the SIMS (top) and GD-MS (bottom) analysis on sample R6-2b (implanted B).

-dc HR-GD-MS can be used for depth profile analysis of impurities in PV Si with good sensitivity and a depth resolution of 0.5µm.

-Concentration profiles of the samples contaminated with B, P and Ti agreed well with the implanted levels.

-For fast diffusing transition elements, e.g. Fe and Cu, different impurity distribution mechanisms are occurring. This should be taken into account when analysing these impurities and their depth profiles.

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Depth profile analysis of solar cell silicon by glow discharge mass spectrometry

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In this work we have assessed the capability of depth profile analysis by glow discharge mass spectrometry (GD-MS) for several impurities relevant for solar cell silicon. A fast-flow direct-current high resolution GD-MS has been used. Six multicrystalline p-type silicon samples with contamination of B, P, Ti, Fe and Cu have been investigated. Ion implantation has been used for impurity contamination with a target depth of 3 µm. The acquisition time was approximately 30 seconds, giving a depth resolution of approximately 0.5 µm. The GD-MS concentration profiles of the samples contaminated with B, P and Ti agreed well with the levels implanted. Because Fe and Cu are fast diffusers, their distribution deviates from the target implantation. This indicates that for fast diffusing transition metallic impurities, such as Fe and Cu, different impurity distribution mechanisms are occurring and should be taken into account when analysing their depth profiles.

A Introduction

Analytical methods based on glow discharge (GD) as ion source have been investigated for decades[1] and currently are receiving increasing attention for the analyses of materials for photovoltaic (PV) applications.[2] These materials are sensitive to impurity concentration and levels as low as few parts per million- (ppm`s) in the silicon feedstock and even parts per billion- (ppb`s) in the silicon wafer dramatically affect the electrical properties of the final solar cell. Several analytical methods are available for these impurity measurements in silicon materials.

Inductively coupled mass spectrometry (ICP-MS) has been extensively used for analysis of silicon feedstock and ingots for the PV industry. However, the technique requires a sophisticated sample preparation, which includes sample dissolution, and is a source of contamination. Laser ablation coupled plasma mass spectrometry (LA-ICP-MS) has been used for the analysis of spatial distribution of impurities in metallurgical grade silicon samples[3] with limits of detection (LoD) in the ppm level and spatial resolution in the 100 µm level.

Fast throughput methods with wide dynamic range and good sensitivity (hence low LoD`s) are necessary for PV since few ppb`s can significantly decrease the solar cell energy conversion efficiency. [3] Fe, Cu and Ti are among the most detrimental metallic impurities for solar cells. Coletti *et al.*[3] reported that Fe, Cu and Ti in concentrations below 10 ppbw in the ingot were significantly detrimental for the solar cell performance. Measuring such low levels with high precision and accuracy is not straightforward. Recently, it has been demonstrated that direct current (dc) glow discharge mass spectrometry (GD-MS) is a powerful technique for bulk analysis of a wide range of impurities in PV silicon[4] and with LoD (ppb or sub-ppb level).[5] However, no generally accepted method of quantification of depth profiles has emerged for this technique.[6] Furthermore, the atomization and ionization processes in the plasma are temporally and spatially separated, reducing the matrix effects, contrary to secondary ion mass spectrometry (SIMS). This technique is widely used for the analysis of PV materials due to its low LoD (ppb) and good spatial resolution (< 1 µm).[7] However, SIMS requires ultra-high vacuum conditions and is matrix dependent, which means that good standards and calibration are necessary.

Pisonero *et al.*[8] reported on quantitative depth profile analysis of B implanted Si samples by pulsed radiofrequency (RF) GD time-of-flight (TOF) mass spectrometry. They showed the potential of the pulsed system, compared to SIMS and dc GD-MS, for fast, sensitive and high depth-resolution analyses. Despite its potential, most of the PV industries worldwide do not have access to a pulsed RF TOF-GD-MS facility. Thus, dc GD-MS still remains a simple, fast and sensitive technique for a wide range of impurities in PV silicon. The capabilities for depth profiling by dc GD-MS have been recently reported.[9] In that work, B and Fe concentration profiles of as-cast multicrystalline Si materials were studied, *i.e.* there was no control over the homogeneity and depth distribution of the impurities. In the work presented here, dc GD-MS is used for depth profile analysis of several impurities of interest for the PV industry, namely B, P, Ti, Fe and Cu. The samples were implanted with these impurities up to a depth of 3 µm, analysed by GD-MS and the results compared with SIMS. Hence, the present work is a twofold development of the previous study. On one side, the ion implantation provides control over the depth at which impurities are present, and on the other side the results are compared with another analytical technique.

B Experimental

Six multicrystalline silicon samples grown by directional solidification were investigated. They were all p-type with addition of B to achieve an electrical resistivity of 1 Ωcm, which corresponds to bulk B concentration of 114 ppbw, calculated according to the SEMI MF723 standard.[10] The samples were 20x30x5 mm, ground with SiC papers (500 grit size) and washed with water and ethanol. The samples were implanted with B, P, Ti, Fe and Cu. These impurities were chosen because i) B and P are the most used doping elements for p- and n-type silicon solar cells, respectively; ii) Ti, Fe and Cu are common metallic impurities in silicon and are detrimental for the final electrical properties of the silicon solar cell. Ti typically occupies substitutional sites in the Si crystal lattice (similarly to the doping elements) and is a slow diffuser, while Fe and Cu are interstitial impurities and fast diffusers. An overview of the samples with the implanted impurity and target concentrations and depth is given in Table 1. Note that in sample R6-2b, since the material already contains 114 ppbw of B, the total concentration after implantation will be approximately 200 ppbw. Table 2 shows some properties of the impurities selected (*i.e.* equilibrium segregation coefficient and diffusion coefficient in solid silicon). The diffusion coefficient of the selected impurities is reported at the silicon melting temperature, *i.e.* 1683 K.[11] The sample temperature during GD-MS (same instrument used in this study) analysis has been recently measured to be 373 K.[12] However, data at this temperature were not available for all impurities investigated. Thus, the diffusion coefficient of the impurities selected can be used to compare their different diffusivities. It is clear that Fe and Cu have a diffusion coefficient that is orders of magnitude higher than Ti, P and B; hence they diffuse faster in solid silicon.

Table 1 Overview of the samples investigated, implanted impurity, target concentration and depth of the ion implantation

Sample name	Impurity implanted	Implanted concentration, ppbw	Depth, distance from the sample surface
R6-2a	Fe	400	1-3 µm
R6-3a	Fe and Cu	400 and 450	Fe: 0-1 µm, Cu: 1-3 µm
R6-4a	Cu	450	1-3 µm
R6-2b	B	80 (total 200)	1-3 µm
R6-3b	P	220	1-3 µm
R6-4b	Ti and Fe	343 and 400	Ti: 0-1 µm, Fe: 1-3 µm

Ion implantation was carried out at the University of Oslo with a National Electrostatic Corporation (NEC) instrument, using ions at single charging state. The implanted ions may contribute to the base conductivity; however they will not significantly alter the conductivity of the bulk sample. This was confirmed by the discharge voltage measured during sputtering. The range and profile shape depend on the ion energy for a particular ion/substrate combination and the concentration deviation is within 10%. The ion implantation energies varied between 0.3-1.2 MeV for B, 1.5-4.4 MeV for P, 0.7-2.3 for both Ti and Fe, 1.5-4.5 MeV for Cu, according to the concentration and target depth. Beam transport simulation was performed by SRIM/TRIM,[13] based on Gaussian approximation of one dimensional implant depth profile. For example, for the energies used for ^{11}B^{+} implantation (*i.e.* 0.3, 0.7 and 1.2 MeV), the projected range will be 0.8, 1.4 and 2.0 µm, respectively. Figure 1 shows the results of the simulations for two of the investigated samples. The implantation level was set to 10^{16} cm^{-3} for all impurities and the respective concentrations in ppbw are given in Table 1. This concentration for implantation is representative of silicon materials for photovoltaics, which is the target application for this study. The implanted depth was set to the maximum achievable with the NEC instrument used here, for depths between 1 and 3 µm (that could be analysed by GD-MS). There were two implantation series: the first one with Fe and Cu, and the second series with B, P, Ti and Fe, which was carried out a few months later. The GD-MS and SIMS analyses were performed approximately 8 months and 1 month after the ion implantation of the first and second series, respectively.

Table 2 Equilibrium segregation coefficient and diffusion coefficient in the solid silicon for the five impurities investigated at 1683 K[11]

Impurity	Segregation coefficient	Diffusion coefficient (at 1673K), cm^2/s
B	0.8	1x10^{-11}
P	0.35	1x10^{-6}
Ti	3.6x10^{-6}	1x10^{-7}
Fe	6.0x10^{-5}	5x10^{-5}
Cu	1.5x10^{-5}	1x10^{-4}

A fast-flow direct current (dc) high resolution (HR) Thermo Element GD was used for the depth profile analysis. All samples were analysed under the same conditions, namely a discharge current of 56.7 mA, discharge voltage of approximately 800V and Ar flow of 400 ml/min. The general principle of the technique and the method used to calibrate the relative sensitivity factors (RSF`s) are given elsewhere.[4] For each sample, 12 to 20 repeated analyses (on the same crater) were made. The acquisition time for each repetition was approximately 30 seconds, giving a depth resolution of approximately 0.5 µm.

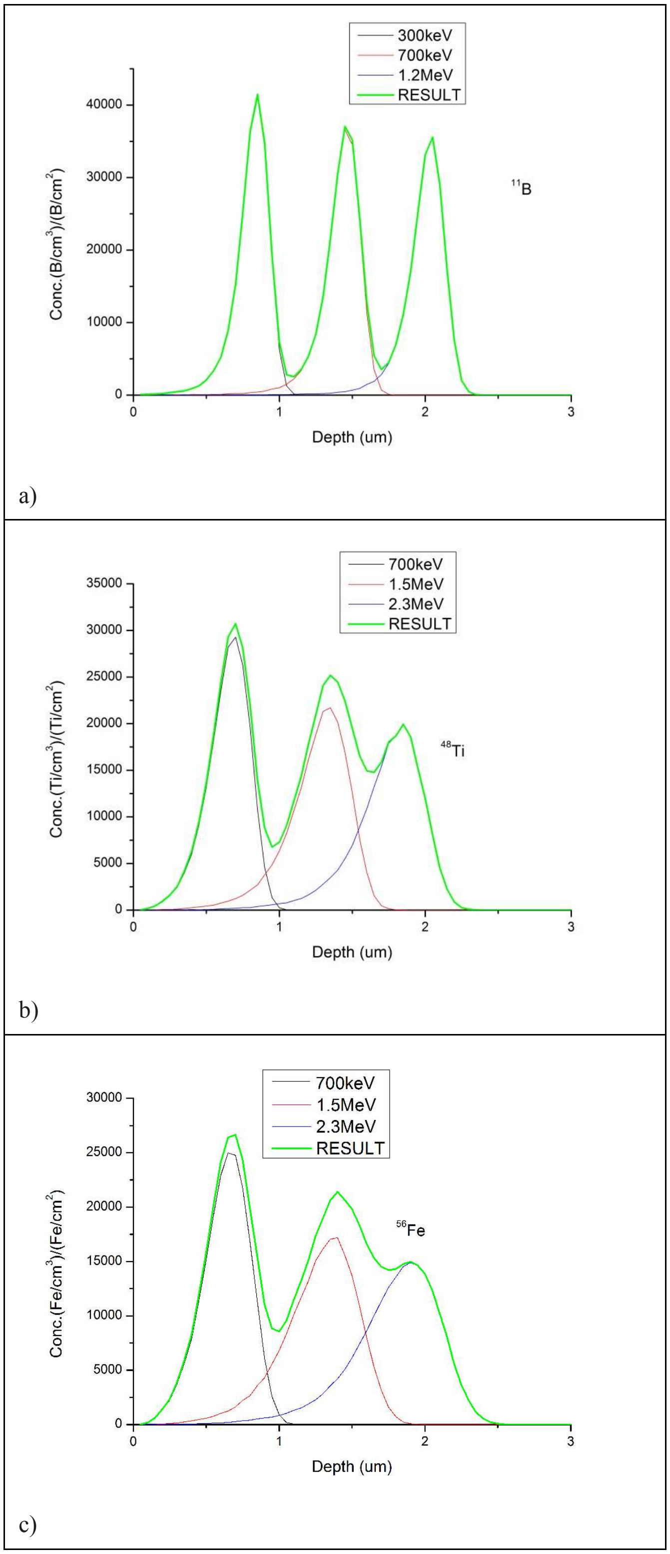

Fig. 1 Simulations of the ion implantation of a) B in sample R6-2b, and b) Ti and c) Fe in sample R6-4b.

The crater depth and shape of the analysed samples were measured by a Mahr`s profilometer in order to check the sputtering rate of the GD-MS analysis.

The GD-MS results were compared with analyses made in a Cameca IMS 7f magnetic sector secondary ion mass spectrometer (SIMS) at the University of Oslo, operated at standard conditions with 10 keV O_2^+ (for B, Ti and Fe) and C_s^+ (for P and Cu) as primary ions, respectively.

C Results and Discussion

Figure 2 shows the crater shape and depth of sample R6-4b after the GD-MS analysis. The shape of the crater for all analysed samples is quite regular, indicating a stable and homogeneous glow discharge. For sample R6-4b, the measured depth is 15 µm and confirms a sputtering rate of approximately 1 µm/min. Thus, the implanted interval, corresponding to approximately 1 µm, would therefore allow obtaining two measurements by GD-MS.

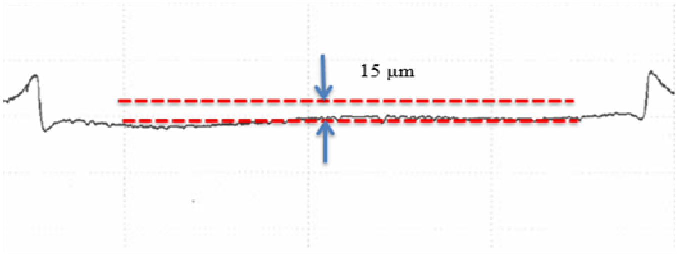

Fig. 2 Crater profile of sample R6-4b (implanted with Fe and Ti).

The results of both GD-MS and SIMS for the first series with implantation of i) Fe, ii) Fe and Cu, and iii) Cu are shown in Figures 3-5, respectively. Note that the Cu concentration by GD-MS is given as ion beam ratio (IBR), thus it is only semi-quantitative. In fact, no RSF value was used for Cu since, as recently reported,[12] the procedure previously developed for the calculation of RSF values in Si matrix[4] may not be straightforward to apply to elements with high solid diffusivity, *e.g.* Cu. Furthermore, the comparison between the SIMS and GD-MS analysis for Fe concentrations (in both series) is difficult since the Fe measurements by SIMS have a high background noise.

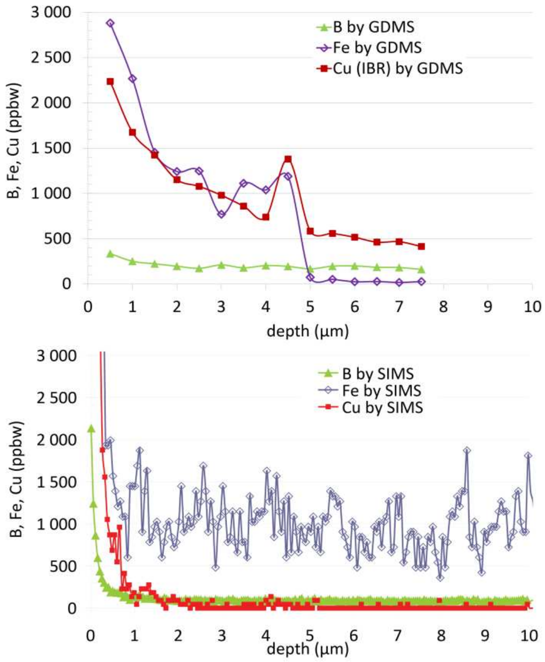

Fig. 3 B, Fe and Cu concentration along the sputtered depth of sample R6-2a (implanted Fe), measured by GD-MS (top) and SIMS (bottom). Note that Cu concentration by GD-MS is reported as IBR.

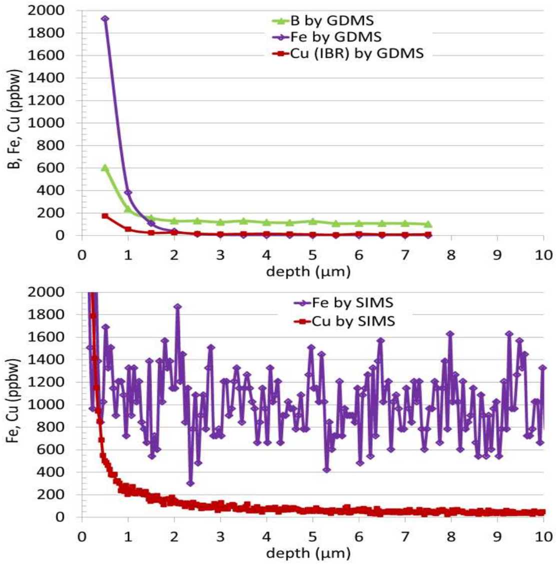

Fig. 4 B, Fe and Cu concentration along the sputtered depth of sample R6-3a (implanted Fe up to 1 µm and Cu from 1 to 3 µm), measured by GD-MS (top) and SIMS (bottom). Note that Cu concentration by GD-MS is reported as IBR.

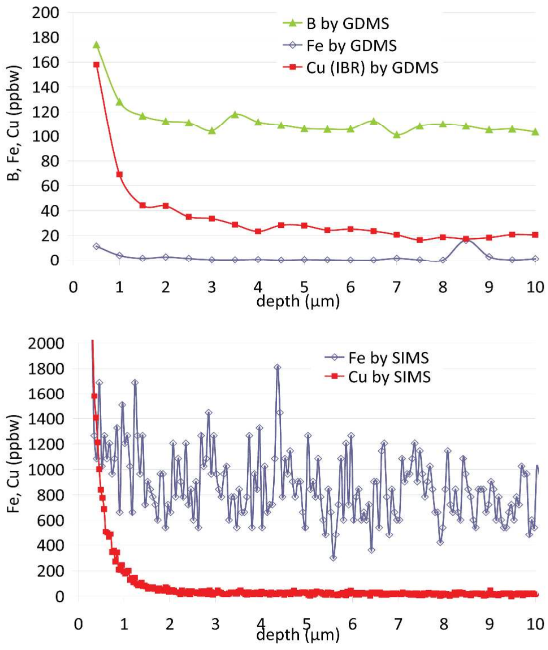

Fig. 5 B, Fe and Cu concentration along the sputtered depth of sample R6-4a (implanted Cu), measured by GD-MS (top) and SIMS (bottom). Note that Cu concentration by GD-MS is reported as IBR. Note also that the scale of the y-axis is different in these two graphs.

Figure 3 shows the B, Fe and Cu concentrations in the sample R6-2a. Both GD-MS and SIMS indicate that B is homogeneously distributed along the sample depth and the concentration is approximately 120 ppbw as one would expect from the material` s electrical resistivity. The GD-MS analysis of Fe shows that this impurity has high concentration at the sample surface, it reaches a plateau between 2 and 5 µm depth, then it rapidly decreases below the LoD of GD-MS. This result agrees fairly well with the implantation range of 1-3 µm for Fe.

Figure 4 reports the analysis of sample R6-3a, which was contaminated with both Fe and Cu at different depths (0-1 µm and 1-3 µm, respectively). Similarly to the previous sample, Fe concentration is very high close to the surface (approximately 1.9 ppmw), then it rapidly decreases below its LoD. Cu content is also higher at the sample surface, and then it decreases below the LoD already in the region where it was implanted (*i.e.* 1-3 µm). This seems to indicate that it has out-diffused towards the sample surface. Both Fe and Cu are fast diffusers in solid silicon (as indicated by their diffusion coefficient reported in Table 2). During the time between the ion implantation and analysis by GD-MS and SIMS (approximately 8 months), these impurities could have out-diffused from the implanted depth, and thus being measured mainly close to the surface. Considering the room temperature diffusivity calculated from Nakashima et al.,[14] the predicted diffusion length of Fe is higher than 7 µm in 8 months, *a*lthough these calculations were made for monocrystalline materials, [14] and consequently the grain boundaries in the materials presented here could have an effect on the solid state diffusion. It is also calculated that in 8 months Cu would diffuse more than 9 mm, *i.e.* higher than the sample thickness. This clearly indicates the difficulty of measuring the depth profile of this type of impurities.

Figure 5 shows the results of sample R6-4a, which was implanted with Cu only. The Cu concentration is higher close to the sample surface (approximately 160 ppbw) and it rapidly decreases. The Cu concentration profile by GD-MS and SIMS is very similar. The B and Fe concentration profiles by GD-MS indicate that they are both as one would expect, *i.e.* a flat profile in the order to 100 ppbw for B and low Fe concentration (below LoD). Again no comparison between GD-MS and SIMS can be made for Fe.

The comparison of the GD-MS and SIMS analyses of the second series with implantation of i) B, ii) P, iii) Ti and Fe are shown in Figures 6-8, respectively. The concentration profile of B in sample R6-2b (given in Fig.6) is flat above 4 µm and approximately 120 ppbw as measured by GD-MS and approximately 100 ppbw as measured by SIMS. Both techniques reveal that there are two B concentration plateaux, one between 1-2 µm and the other between 2.5-3.5 µm. However, the GD-MS results are slightly higher that the SIMS measurements which are indeed closer to the expected concentration (200 ppbw considering the bulk and implanted levels). The reason for this is not clear yet.

The concentration profile of P in sample R6-3b (Figure 7) by GD-MS varies between 200 and 300 ppbw up to the depth of 4 µm. This is very close to both the implanted concentration and the targeted depth (see Table 1). Above 4 µm depth, the P concentration drastically decreases below 20 ppbw. Since these materials are only B-doped, this confirms no contamination during the GD-MS measurements. The SIMS results are very scattered and show an extremely high P concentration towards the surface (up to 3 µm). This may be due to an unexpected contamination before or during the SIMS analysis. However, the P profile between 3 and 5 µm is similar to the one shown by GD-MS. Both techniques indicate that between 3 and 5 µm the P concentration decreases from approximately 300 ppbw down to 100 ppbw.

Figure 8 shows the concentration of Ti and Fe in sample R6-4b. GD-MS and SIMS profiles agree well, even though no quantitative SIMS data could be given for the Ti implanted sample due to technical problems with the instrument used in Oslo. Nevertheless, the depth profile corresponds very well with that measured by GD-MS. Ti is approximately 300 ppbw up to 1µm and then it sharply decreases below the detection limits, as expected from the implantation. Differently from both Cu and Fe, Ti follows the expected concentration and depth owing to its low diffusivity in solid silicon. The GD-MS results of the Fe concentration in the same sample show a high Fe peak close to the surface and then it decreases to a plateau at about 500 ppbw between 1 and 2 µm depth, close to both the expected concentration and the targeted depth of the implantation. Similarly to the previous samples, the higher Fe concentration close to the surface is likely due to its fast solid diffusion.

No statistical data are presented here since this is beyond the scope of this work. However, it is known from a previous study[4] that the reproducibility of the GD-MS used here varies between 5% and 12 %. Moreover, the RSF values that have been used to calculate the GD-MS concentration of B, P, Ti and Fe may have en error between 10% and 20%.[4] The reproducibility and errors associated with the SIMS measurements are not known.

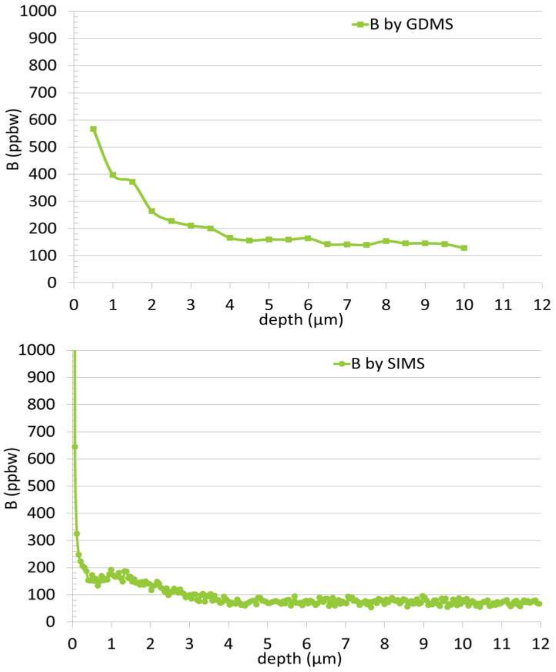

Fig. 6 B concentration along the sputtered depth of sample R6-2b (implanted B), measured by GD-MS (top) and SIMS (bottom).

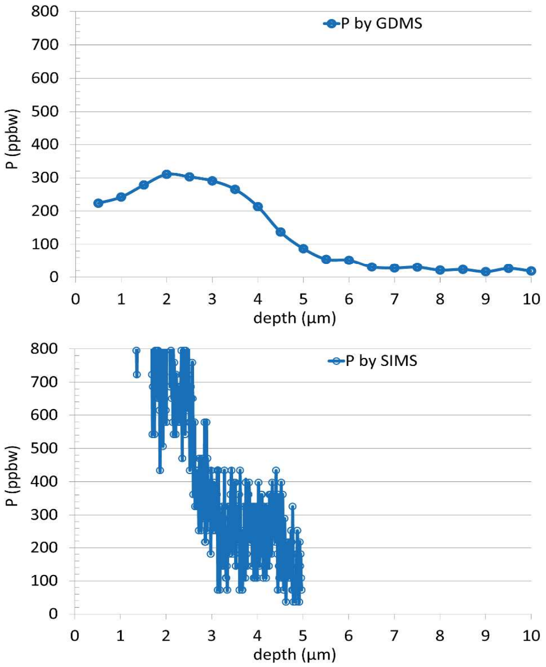

Fig. 7 P concentration along sputtered depth of sample R6-3b (implanted P), measured by GD-MS (top) and SIMS (bottom).

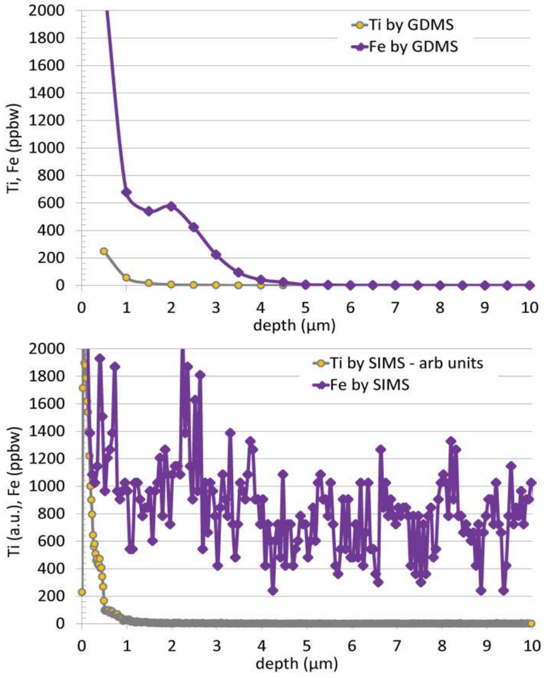

Fig. 8 Fe and Ti concentration of sample R6-4b (implanted Ti up to 1 µm and Fe from 1 to 3 µm), measured by GD-MS (top) and SIMS (bottom).

Conclusions

In this work we have assessed the capability of depth profile analysis by dc HR-GD-MS for several impurities relevant for solar cell silicon. This technique can be used for depth profile analysis with good sensitivity and a depth resolution of 0.5 µm. The latter might be further improved (decreased). The results of this work show that the concentration profiles of the samples contaminated with B, P and Ti agreed well with the implanted levels, while Fe and Cu concentrate towards the surface. This indicates that for fast diffusing transition elements different impurity distribution mechanisms (e.g. solid state diffusion) are occurring. This should be taken into account when analysing these impurities and their depth profiles.

Thus, this study proves that it is possible to analyse depth profiles by dc GD-MS. The depth resolution may be inferior to the one by SIMS; however, the sensitivity of the analysis (*i.e.* detection limit) is better than SIMS. Generally when analyzing impurity depth profiles one should take into account the type of impurity and distribution mechanisms occurring.

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Notes and references

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