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# Quantitative depth profile analysis of boron implanted silicon by pulsed radiofrequency glow discharge time-of-flight mass spectrometry

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ABSTRACT

The analytical potential of pulsed radiofrequency glow discharge time-of-flight mass spectrometry (pulsed-rf-GD-TOFMS) is investigated for fast quantitative analysis of major and dopant elements in bulk and thin film layers. This technique does not require sampling at ultra-high vacuum conditions and so it facilitates high sample throughput compared to reference techniques as secondary ionization mass spectrometry (SIMS). In this paper, bulk and boron implanted silicon samples are analyzed. Boron concentration in Si samples is calculated from calibration curves obtained using solar grade silicon and B doped silicon wafers as calibrating materials, and using $^{29}Si^+$ ion signal as internal standard. Qualitative depth profiles of $^{10}B$ implanted silicon are determined in a few seconds using the low-pressure pulsed-rf-GD-TOFMS system. Additionally, quantitative depth profiles are easily determined making use of the calibration curves. A good agreement with the depth profiles measured using SIMS was obtained, demonstrating the analytical potential of the pulsed-GD-TOFMS system for fast, sensitive and high depth resolution analysis of implanted silicon samples.

## 1. Introduction

Nowadays there is a great demand for silicon (Si) for the solar cell industry. New methodologies to purify large quantities of metallurgical grade Si (MG-Si) to obtain solar grade Si (SoG-Si) are being developed. As a result, analysis techniques with high sensitivity, depth and elemental resolution, dynamic range and that are low cost and high throughput are critically needed.

In the raw silicon industry, most of the routine analyses used to determine the chemical composition (minors and traces) are carried out using techniques that require sample dissolution. Therefore, the sample preparation is a source of contamination due to the presence of impurities in the reactive source chemicals and in the surface of the silicon samples. Moreover, not all elements contained in the bulk silicon can be dissolved using these same dissolution methods, increasing the analysis time and decreasing the sample throughput and the efficiency of the quality controls.

Fast throughput nm depth resolution techniques with isotopic and wide dynamic range are highly required for solid-state physics, materials science and electronic devices understanding (interface chemistry, diffusion issues, dopants and major elements quantification) [1]. Secondary ionization mass spectrometry (SIMS) is widely used in the direct analysis of semiconducting materials, due to its low limits of detection ($<$ng/g) and high spatial resolution ($<\mu$m). It requires, however, ultra-high vacuum conditions and suffers from high matrix effects [2]. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been also employed to investigate the spatial distribution of impurities in metallurgical grade silicon samples [3] with limits of detection in the µg/g level and high spatial resolution (120 µm).

Glow discharge mass spectrometry (GD-MS) provides an alternative technique for fast direct solid analysis with high depth resolution of comparatively large sample areas ($\sim$mm$^2$) [4]. While more work might be necessary to diminish the sample probe size, large area depth profiling is a significant advantage in analysis of heterogeneous bulk and thin film samples, such as polycrystalline Si. When using highly focused probes, scanning mode analysis is required, further lowering throughput. Glow discharges (GD) operate at low pressure conditions ($\sim$torr), eliminating costly and time consuming ultra-high vacuum requirements. Moreover, the atomization and ionization processes in GD plasmas are temporally and spatially separated, reducing the matrix effects.

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Among the different mass analyzers, GD-sector field (SF)MS systems have shown to provide high sensitivity for bulk elemental analysis of solid materials (in the ng/g range) [5]. These instruments are only commercially available with direct current powered GDs, therefore bulk analysis of conductive and semi-conductive materials is their major application. For instance, GD-SFMS (Thermo Fisher Scientific, Model Element GD) has been recently employed for quantification of boron and phosphorous in solar grade silicon, based on relative sensitive factors calculations [6]. This instrumentation affords good spectral resolution (up to$\sim$10,000); however, their scanning nature in the detection mode is not suitable for the analysis of thin films.

On the other hand, radiofrequency (rf)-GD time-of-flight mass spectrometry (TOFMS) uniquely provides fast, sensitive and high depth resolution analysis of bulk and nanostructured thin film samples [7,8]. Pulsed-rf-GD mode combined with the orthogonal extraction TOFMS permits quasi-simultaneous detection of ions along the GD pulse period, and thus, the observation of the different time domains as result of the different ionization/excitation mechanisms in the plasma. This allows for selecting the integration time detection window that provides the highest analyte signal with minimum interference [9].

Here we illustrate the use of pulsed-rf-GD-TOFMS for the quality control of Solar grade Si in photo-voltaic (PV) applications. A major effort today is to obtain solar grade silicon from metallurgical grade Si, instead of electronic grade Si. This would provide large-scale supplies at lower cost of production. However, the mass content of trace elements in this kind of solar grade Si is higher and should be carefully determined and appropriately controlled for such industrial applications. In this sense, an innovative analytical method based on pulsed-rf-GD-TOFMS is investigated here for fast and sensitive direct determination of B impurities in mono- and poly-crystalline solar grade silicon, and for fast and high depth resolution analysis of boron ($^{10}$B) implanted silicon.

## 2. Experimental

The rf-GD-TOFMS consists of a rf-GD bay unit (rf-generator, matching box, rf-connector, refrigerator disc and sample mounting system with a pneumatic piston to press the sample against the GD) from Horiba Jobin Yvon (Longjumeau, France), coupled to a fast orthogonal time-of-flight mass spectrometer (TOFWERK, Switzerland) with a microchannel plate detector, and has been described in more details elsewhere [10].

The GD anode is a copper-based modified Grimm-type chamber (EMPA, Switzerland) with a 4 mm diameter anode and a 2.5 mm inner diameter flow tube. The GD ion source is designed in such a way that the sample does not need to be inserted into a vacuum chamber. Moreover, a refrigerating disc, placed behind the sample, is used to keep the sample at low temperature ($<5\,^{\circ}$C) and ensures application of rf power. A pneumatic holder presses the sample against the GD ion source [11].

The GD-TOFMS instrument can record a complete mass spectrum with a frequency of up to 100 kHz. It also provides an average mass resolving power of 3000, which is adequate to resolve most of the polyatomic interferences from hydrocarbons and matrix ions.

The rf generator can be run in continuous and pulsed modes, but in this work only the pulsed mode is considered. GD pulse width can be selected from less than 50 $\mu$s up to several ms, and duty cycles (relationship between pulse width and pulse period) can be optimized for the desired application. The maximum forward power provided by the rf-generator is about 150 W, defining the forward power as the average power along the GD pulse duration. The operation mode “constant pressure–constant forward power” was used in all the experiments.

High-purity argon (99.999% minimum purity) from Air Liquide (Oviedo, Spain) was employed as discharge gas for the measurements using pulsed-rf-GD-TOFMS.

Boron doped monocrystalline Silicon samples from Q-Cells-AG (Bitterfeld-Wolfen, Germany) and polycrystalline solar grade Si from Ferroatlántica S.L. (La Coruña, Spain) were used as calibration samples. These bulk samples have a relative homogenous distribution of B. The boron concentration in these samples ranged from 23 ng/g up to 33 $\mu$g/g (see Table 1). Moreover, single crystal Si (1 0 0) 2 in wafers were implanted with a dose of $10^{14}$ atom/cm$^2$, 100 keV $^{10}$B$^+$ (Innovion Corp., San Jose, CA, USA). In this case, B distribution is inhomogeneous and reaches a maximum value at a certain depth from the surface of the Si substrate.

Secondary ion mass spectrometry (SIMS) depth profiles of the $^{10}$B implanted Si samples have been obtained for comparison, using a Cameca SIMS instrument (Probion Analysis, Bagneux, France). Primary ions were 3 keV $O_2^+$, the sputtered area was 150 $\mu$m × 150 $\mu$m, and the analysis area was a spot of 30 $\mu$m diameter. Positive $^{10}$B, $^{11}$B, $^{29}$Si and $^{30}$Si ions were detected.

Crater shapes produced in the homogenous Si samples after sputtering in the GD source were measured with a mechanical stylus profilometer (Perth-o-meter S6P, Mahr Perthen, Göttingen, Germany).

## 3. Results and discussion

### 3.1. GD source pre-cleaning

Source contamination leads to a poor start of the discharge (e.g. instabilities during the plasma ignition process), affecting the quality of the measurements. For instance, analytical information from the surface or from the first atomic layers of a thin coated/implanted material could be disturbed or lost. Additionally, the presence of elements such as O, C and N not only affects the plasma stability but also produces polyatomic interferences with the analyte signals (e.g. $^{28}$Si$^+$ is interfered by $^{14}N_2^+$ and $^{12}$C$^{16}$O$^+$). To obtain a faster stabilisation of the GD plasma after the ignition process, pre-cleaning of the inner surface of the GD anode was performed at the beginning of each analysis session (e.g. 1 or 2 times per day), making use of 6 min of non-doped Si wafer sputtering at 500 Pa and 30 W (continuous rf mode)) [12]. Moreover, during each sample interchange an Ar overpressure is used to avoid the entrance of air contaminants into the GD source. In addition, a 5 min Ar flushing previous to the analysis is used to reduce the contaminant species adsorbed on the surface of the sample. Analysis after the GD source pre-cleaning shows stable ion signals from the beginning of the analysis.

### 3.2. Optimization of the operating conditions

GD operating parameters were investigated to obtain high sensitivity in the analysis of the homogeneous Si samples. In particular, ion signals from B and Si were evaluated at applied

**Table 1**
Boron mass content (ng/g) in the monocrystal Si samples.

| Company | Silicon | Sample | Boron |
|---|---|---|---|
| **Producer** | **Type** | **Thickness** | **Mass content (ng/g)** |
| **Ferroatlantica** | **Polycrystalline** | **2–3 mm** | **32,950** |
| **Ferroatlantica** | **Polycrystalline** | **2–3 mm** | **11,980** |
| **Ferroatlantica** | **Polycrystalline** | **2–3 mm** | **1800** |
| **Q-Cells** | **Monocrystalline** | **200 µm** | **577** |
| **Q-Cells** | **Monocrystalline** | **200 µm** | **385** |
| **Q-Cells** | **Monocrystalline** | **200 µm** | **135** |
| **Q-Cells** | **Monocrystalline** | **200 µm** | **23** |

powers between 60 and 135 W, at pressures between 300 and 1000 Pa, at GD pulse widths between 0.5 and 2 ms and at duty cycles between 0.3 and 0.6. Optimum selected operating conditions are shown in Table 2. Using the pulsed-rf-GD-TOFMS system, it is possible to collect and monitor ion signals along the GD source pulsing period, that is, in the pre-peak, the plateau and the afterglow [13]. Fig. 1 shows the pulse profiles observed for $^{36}Ar^+$, $^{11}B^+$ and $^{29}Si^+$ measured in a homogeneous SoG-Si. It is observed that the $^{36}Ar^+$ ion signal showed its maximum just after the end of the GD pulse ( $<100$ μs after rf is turned off) [14]. On the other hand, analyte ion signals (e.g. $^{11}B^+$ and $^{29}Si^+$) exhibit two maxima in the afterglow region (150–250 μs after the end of the GD pulse). At the first maximum of the analytes, the mass spectrum showed less contribution from polyatomic compounds (e.g. Fig. 1(inset) (dark-grey) shows that $^{14}N^{14}N^{1}H^+$ ion signal is negligible versus $^{29}Si^+$). However, at the second maximum of the analytes (e.g. $^{11}B^+$ and $^{29}Si^+$), the mass spectrum showed that plasma recombination processes start to be dominant [7] (e.g. Fig. 1(inset) (light-grey) shows that $^{29}Si^+$ ion signal is interfered with $^{14}N^{14}N^{1}H^+$ ion signal). Thus, analytical ion signals were only evaluated using their first maximum of the afterglow.

### 3.3. Calibration curves

Ion signals from $^{10}B^+$ and $^{11}B^+$ were then measured for the different homogenous Si samples, using the pulsed-rf-GD-TOFMS system. A calibration curve was obtained plotting the total $B^+$ ion signal ($I_B$) versus the mass content of B in the homogenous Si samples ([B]). It was observed that this direct calibration curve presents an adequate linear relationship ($[B]=0.013I_B$; $R^2=0.997$). The average sensitivity, obtained as the inverse of this slope, is about 100 cps/(μg/g) (cps=counts per second); however, the achieved sensitivity increases to 170 cps/(μg/g) when only low B mass-content samples ( $<1$ μg/g) are considered.

To alleviate day to day variations, an internal standard (relative ion signals, calculated as the ratio between $B^+$ and $^{29}Si^+$ ion signals) is used. Previous studies in our laboratory using the pulsed-rf-GD-TOFMS system for the analysis of metal samples have shown that the day-to-day reproducibility is around 20–30%; however, it is further improved (5–20%) when an internal standard is used [9]. Fig. 2(a) shows the calibration curve obtained plotting the relative ion signals versus the mass content of B in the homogenous Si samples. This further improves linearity of the calibration curve, which is observed across three orders of magnitude in both cases. This fact allows a high dynamic analysis range of B mass content distributions within Si samples. In some cases, it could be of interest to restrict the calibration curve to samples with low B mass-content in order to improve the fitting parameters at this working range. Fig. 2(b) shows the calibration curve restricted to samples with a B mass content below 2 μg/g. In this case, a linear relationship is also observed but with a slightly different slope.

**Table 2**
Pulsed-rf-GD operating conditions for high sensitive analysis of Si samples.

| Operating parameter | Value |
|---|---|
| **Applied power** | 135 W |
| **Pressure** | 950 Pa |
| **Pulsed width** | 2 ms |
| **Pulsed period** | 4 ms |
| **Duty cycle** | 50% |
| **Module** | 5.6 V |
| **Phase** | 2.9 V |

### 3.4. Qualitative depth profiles

The pulsed-rf-GD-TOFMS system was evaluated for the depth profile analysis of real $^{10}B$ implanted Si samples. An average mass spectrum was obtained every ~700 ms. Furthermore, optimization of the rf matching parameters (module and phase) was performed prior to the analysis of the implanted Si samples using a Si wafer with similar dimensions. This optimization avoids instabilities of the plasma at the beginning of the depth profile analysis. Selected values of module and phase are shown in Table 2. Fig. 3(a) shows the qualitative depth profiles (ion signal intensity versus sputtering time) obtained for $^{10}B^+$ using the pulsed-rf-GD-TOFMS system. It is observed that $^{10}B^+$ ion signal peaks after 8 s of analysis, indicating that the distribution of $^{10}B$ atoms within the Si substrate has its maximum at a certain depth from the Si surface.

Moreover, previous studies carried out in our laboratory [15] using rf-GD plasmas, have shown that silicon samples in contact

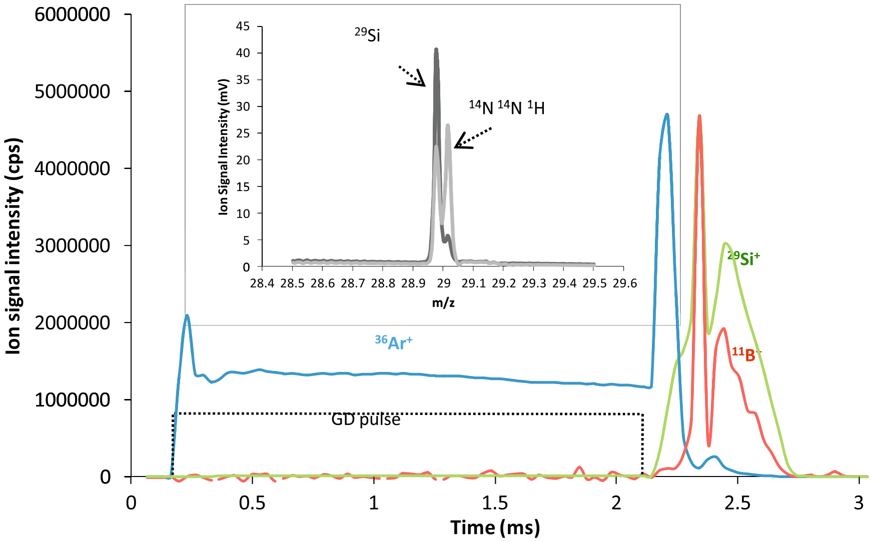

**Fig. 1.** Pulse profile of $^{36}Ar^+$ (blue), $^{11}B^+$ (red) and $^{29}Si^+$ (green) measured in a homogenous SoG-Si using pulsed-rf-GD-TOFMS. The inset shows a section of the mass spectrum around mass 29: (dark-grey) mass spectrum at the first maximum of $Si^+$ in the pulse profile; (light-grey) mass spectrum at the second maximum of $Si^+$ in the pulse profile. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

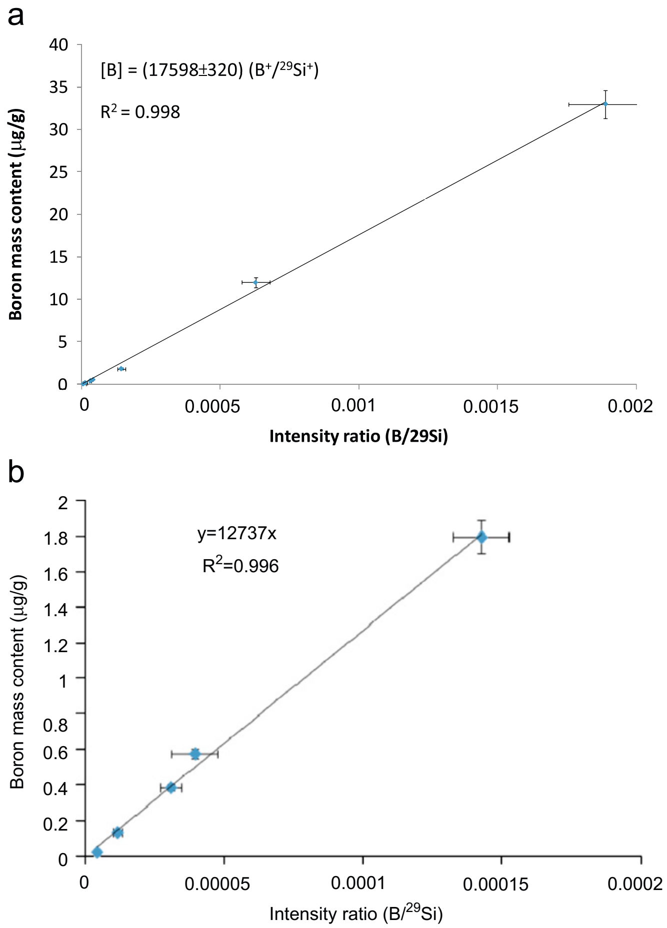

**Fig. 2.** (a) Calibration curve obtained plotting the relative ion signals ($B^+/^{29}Si^+$) versus the mass content of B in the homogenous Si samples. (b) Calibration curve restricted to samples with a B mass content below 2 µg/g.

with air atmosphere suffer from a fast oxidation of the surface. In this sense, native silicon oxide layer ($SiO_2^+$ and $SiO^+$ signals) are detected at the surface of the sample. Additionally, Fig. 3(b) shows the qualitative depth profile of $^{28}Si^{14}N$ and $^{28}Si^{16}O$ in the same sample, where it is possible to observe that $^{28}Si^{14}N^+$ ion signal is much lower than that from $^{28}Si^{16}O^+$ (which has a pronounced maximum during the first seconds of analysis and then decays), indicating that air leaks are negligible during the analysis, and thus, not responsible of the oxide layer formation.

### 3.5. *Quantitative depth profiles*

Quantitative depth profiles can be obtained from the qualitative depth profiles by making use of the calibration curves. This allows conversion of the ion signals into mass contents. Measured relative ion signals ($B^+/^{29}Si^+$) were used to calculate the B mass content ([B]) at each position of the depth profile, by making use of the calibration equation (see Fig. 2) ($[B]=17{,}598\ (B^+/^{29}Si^+)$). The relative error associated to the B mass content ($\delta[B]$) is estimated as $\delta(\text{calibration slope})+\delta(B^+/^{29}Si^+)$. Moreover, calculation of the average sputtering rate allows conversion of the analysis time into depth. An average sputtering rate of ~49 ± 4 nm/s was calculated for the Si samples used for calibration, after measuring the average depth of the produced craters and dividing it by the total sputtering time.

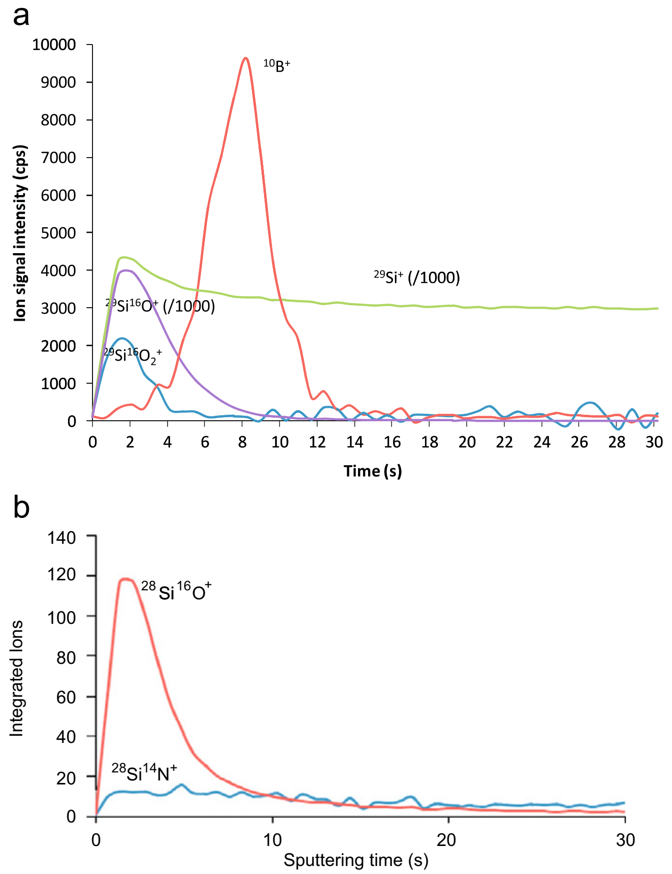

**Fig. 3.** (a) Qualitative depth profiles (ion signal intensity versus sputtering time) of the $^{10}B$ implanted Si sample (single crystal Si (1 0 0) 2 in wafers, which was implanted with a dose of $10^{14}$ atom/cm$^2$ ($^{10}B^+$)), obtained using the pulsed-rf-GD-TOFMS system. (b) Qualitative depth profile of $^{28}Si^{14}N$ and $^{28}Si^{16}O$ in the same sample.

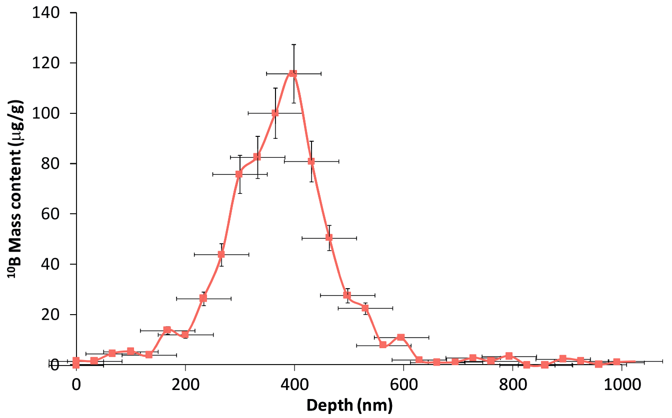

**Fig. 4.** Quantitative depth profiles of the $^{10}B$ doped Si sample (mass content of $^{10}B$ versus depth), obtained using the pulsed-rf-GD-TOFMS system.

Fig. 4 shows the quantitative depth profiles (mass content of $^{10}B$ versus depth), obtained using our pulsed-rf-GD-TOFMS system. The maximum mass content of $^{10}B$ is found to be about 115 µg/g ± 10% at a depth of about 400 ± 50 nm. Final comparative studies, to validate the results obtained with the pulsed-rf-GD-TOFMS system, were carried out using a SIMS instrument. In this case, the sputtering rate was estimated through the measurement of SIMS crater depths in homogenously doped Si standard sample, using a stylus profilometer. Fig. 5 shows the quantitative depth profile of the $^{10}B$ doped Si sample obtained with SIMS. Calculated $^{10}B$ mass content values have an associated relative error of 20%, while for the calculated depth it

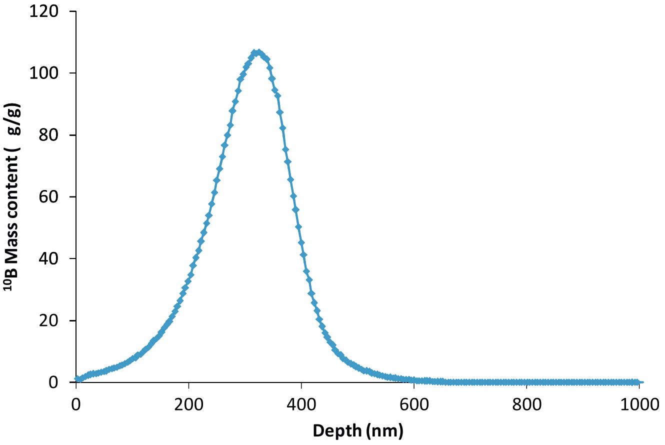

**Fig. 5.** Quantitative depth profiles of the $^{10}$B doped Si sample (mass content of $^{10}$B versus depth), obtained using SIMS. Calculated $^{10}$B mass content values have an associated relative error of 20%, while for the calculated depth it was of 10%.

was of 10%. Thus, it is observed that $^{10}$B mass content shows a distribution with a maximum concentration of about 100 $\mu$g/g $\pm$ 20%, which corresponds to about $5\times10^{18}$ atoms/cm$^3$. The maximum $^{10}$B mass content is observed at a depth of about $330\pm33$ nm.

These results are in agreement (within the uncertainty value) with those obtained using pulsed-rf-GD-TOFMS. Moreover, depth calibration in pulsed-rf-GD-TOFMS analysis was performed using an average sputtering rate calculated from bulk homogenous Si samples. In this case, the influence of the first silicon oxide layers, where the sputtering rate is reduced using pulsed-rf-GD-TOFMS, was not considered; thus, slightly affecting (increasing) the estimated depth. In future studies a quantification algorithm will be developed to consider the presence of the silicon oxide layers.

## 4. Conclusions

In conclusion, an innovative pulsed-rf-GD-TOFMS has been evaluated for fast throughput nm depth resolution direct analysis of homogenous and doped Si wafers. In particular, a linear calibration curve has been obtained for the direct quantification of B mass content in Si wafers (B concentration between tens of ng/g and tens of $\mu$g/g). Moreover, fast qualitative depth profiles were obtained for $^{10}$B implanted Si wafers, showing the $^{10}$B distribution within the Si and a clear detection of the native silicon oxide layers at the surface. Additionally, quantitative depth profiles were achieved by converting the ion signals into mass contents (through a calibration curve), and the sputtering time into depth (through the measurement of the sputtering rate). Good agreement is observed between the quantitative depth profiles obtained using pulsed-rf-GD-TOFMS and SIMS.

The described technique and associated results are extremely relevant to Si PV technology. The ability to rapidly assess both majority and dopant level elements with near SIMS sensitivity and depth resolution, will be critical in the development of the more complex material systems (GaN, GaAs, CuISe, organic, etc.), being explored for next generation devices and systems. From the active device point of view, and unlike traditional chip-based technologies where sub-mm dye areas are utilized, PV devices are generally cm or larger. This poses a challenge insofar materials and dopant control (uniformity and composition) for the growers. From the processed device point of view, a PV device often necessitates integration of various material systems: from the active device, to the contacts, anti reflection coating, intra cell connections, etc. This is a tremendous quality control challenge which is compounded by post-installation issues related to environmental (temperature, humidity, salinity, etc.) factors. The large lateral profile area for the current rf-GD-TOFMS instrument might be an advantage in this application as it permits a better statistical sampling of the multilayered materials under test. Majority and dopant elemental variation at the microscale in a material system are usually driven by intrinsic material chemistry (dictated by the growth technology and surface chemistry) while macroscale variations are often related to engineering issues and instrumentation degradation and failure (non-uniform heater, clogged gas nozzles, pump malfunction, etc.), which need to be calibrated/tested on a regular basis. In light of the above, characterization of large area samples, often, with great sensitivity, depth resolution and low cost will be a necessary requirement in the PV industry. Therefore, the rf-GD-TOFMS technique described in this paper is the ideal tool to address this challenge.

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