

# CALIBRATION OF SIMS MEASUREMENTS BY ION IMPLANTATION<sup>+</sup>

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## Abstract

The paper reviews some joint results of the above institutions in quantitative SIMS (Secondary Ion Mass Spectrometry) analysis of implanted dopants. Quantification of the SIMS was achieved by implanting marker ions as standards prior to analysis. Feasibility of this technique was first demonstrated by Giber et al. (1982). Further considerations will be presented.

## Introduction

It is the sensitivity in atomic concentration that makes SIMS technique outstanding among methods for composition analysis of thin film structures. Though a better understanding of sputtering and ionization phenomena led to better equipment and clearer interpretation of SIMS data, the method still cannot be called as quantitative.

Problems of sputtering are mostly overcome by the so-called Static SIMS, where argumentation follows from the fact that any material, i.e. any composition can be sputtered off fully provided enough sputtering dose is given. If, the sputtering coefficients are  $S_a < S_b < S_c < \dots$  for components  $a, b, c, \dots$ , the given element with smaller  $S$ , say  $S_a$ , will be enriched to a point, where its surface density will compensate for its smaller  $S_a$ . In a sputtering process under equilibrium conditions this should result to a stoichiometric flux of material away from the surface. However, if the moving front for sputtering intersects any inhomogeneity or regions, where any built-in potential is changed, both the sputtering conditions and the amount of ionized species may change. A certain time is then needed to reach equilibrium again.

Thus, elaborate work is necessary to reach "quantitative" analysis with SIMS.

In this paper we review a part of our joint activity, namely, results when implantation was used to add calibration markers to the species to be analyzed. To our knowledge, Giber et al. (1982) were the first to publish this technique.

<sup>+</sup> Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

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## 2. Experimental and discussion

The calibration technique was first demonstrated on silicon implanted with boron. The boron dose was  $1 \times 10^{16}$  ions/cm<sup>2</sup> implanted at an energy of 80 keV. Into one of the samples, an additional implantation was made with 25 keV, dose  $1 \times 10^{15}$  ions/cm<sup>2</sup> for calibration purposes. Following this calibration implantation, both samples were subjected to depth analysis by SIMS. SIMS analyses were made on a Balzers SIMS equipment using the following experimental parameters:

Primary ion:	Ar <sup>+</sup>
Primary energy:	3 keV
Primary current:	1 $\mu$ A
Beam diameter:	1.8 mm
O <sub>2</sub> partial pressure:	3— $3.6 \times 10^{-4}$ Pa
Background pressure	$1.0 \times 10^{-6}$ Pa

The result is shown in Fig. 1, where the reliability of the technique can also be judged. Analysis in quoted paper (Giber *et al.*, 1982) showed that relative errors of concentration scale should not exceed 20%. Oxygen pressure during profiling was set to have the same SiO<sup>+</sup>/Si<sup>+</sup> ratio for both kind of samples. This could have been done with an accuracy of 40%. These

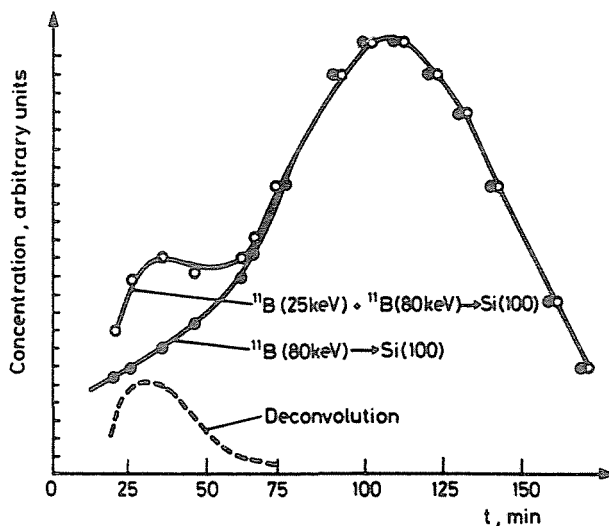


Fig. 1. Concentration vs sputtering time SIMS profiles of boron in silicon, with and without a calibration marker (boron). The  $^{11}\text{B}^+$  implanted profile to be measured is the one implanted with 80 keV,  $1 \times 10^{16}$  ions/cm<sup>2</sup> dose. Added to this, a boron marker for calibration was implanted at 25 keV, with a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. Deconvoluted marker profile is also given (after Giber *et al.*, 1982)

experiments led to a conclusion that implanted standards can be reliably used. Needless to say that the species used for calibration is identical with the one to be profiled.

There are chances, however, that the technique would exhibit certain artefacts. First, ion implantation will introduce damage into the sample. Normal techniques to eliminate it are not applicable, as any thermal treatment would change the distribution to be analyzed. The damage itself will also influence the sputtering rate and, possibly, ionization state. Therefore, low concentrations of calibrating implants are advisable. Needless to say, that to avoid any annealing caused by the implantation beam itself, low dose-rates are mandatory.

The use of minimum doses, however, will cause another problem. The concentrations, where calibration is made will then be quite different from the one of interest. This will bring in some relative error to the analysis. In less "sensitive" cases, however, as will be shown in an example to be cited below, no difficulty was observed, when the marker was introduced with a comparable concentration as the distribution itself. The technique was used in our further research work involving SIMS profiling.

As an example, its use will be presented in evaluating concentration profiles of boron in  $\text{SiO}_2$  and in silicon implanted with a Repetitive Mode Pulsed Ion Beam equipment [2]. Pulsed Ion Beams (PIB) produce pulses of ions typically 50 ns duration. Accelerating voltages can be set in a broad range. In our case 250 kV was used. Density of ions in a single pulse (per  $\text{cm}^2$  of the target) is kept around some  $10^{13}$  ions/ $\text{cm}^2$ , which, at that energy is equivalent to about 1 to 2 Joule/ $\text{cm}^2$ . This limit is kept, because the melting limit for silicon is about 1 Joule/ $\text{cm}^2$ . Further increase in energy will just evaporate surface atoms. This limit is lower for materials with poorer heat conduction.

In experiments reviewed here, the PIB equipment was used in a repetitive mode, i.e. charging and discharging/implanting was conducted automatically with a frequency about 1/3 Hz, till the desired dose was reached. In this case, density of ions in a single pulse was kept low, about an order of magnitude below the above values. At these doses the surface stays solid, and PIB can be treated as a self-annealing implantation. In these cases, few thousand pulses were needed to reach a doping level in the  $10^{15}$  ions/ $\text{cm}^2$  region.

There is a limitation on ion species when using this technique. In a so-called Marx bank operated, magnetically insulated diode system (e.g. Humphries et al., 1974), ions come from the dielectric covering the anode. During discharge, dielectric breakdown occurs and species of the dielectric will be ionized then accelerated. Ion paths follow openings of the cathode then reach the target. These studies were first made by Neri et al., 1980, finding numerous source materials.

In our experiments on doping n-type silicon, it was boron nitride (BN) the compound, which was used as a source for boron. Though ionization rates differ for boron and nitrogen, it cannot be excluded that reasonable amount of nitrogen also reached the silicon and was embedded.

In doping experiments three different implantations were compared (Krafcsik et al., 1987). The first sample received 4000 pulses of boron from BN at 250 kV accelerating voltage through 500 nm thermal SiO<sub>2</sub>. The second sample was bare silicon and received first the same treatment as the previous one, but, in order to get quantitative SIMS results, a <sup>11</sup>B<sup>+</sup> calibration marker was implanted additionally into the sample with 20 keV energy and with a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. A third sample was bare silicon again and received only the calibration implant.

All three were subjected to SIMS measurements with similar parameters as described above. Fig. 2 displays the results. Solid curve is the calibration implant profile alone. The dashed-dot curve shows boron distribution in SiO<sub>2</sub> and in the underlying silicon (dotted line). The latter was measured after oxide removal. The dashed curve shows combined effects of PIB and additional regular implantation (boron marker).

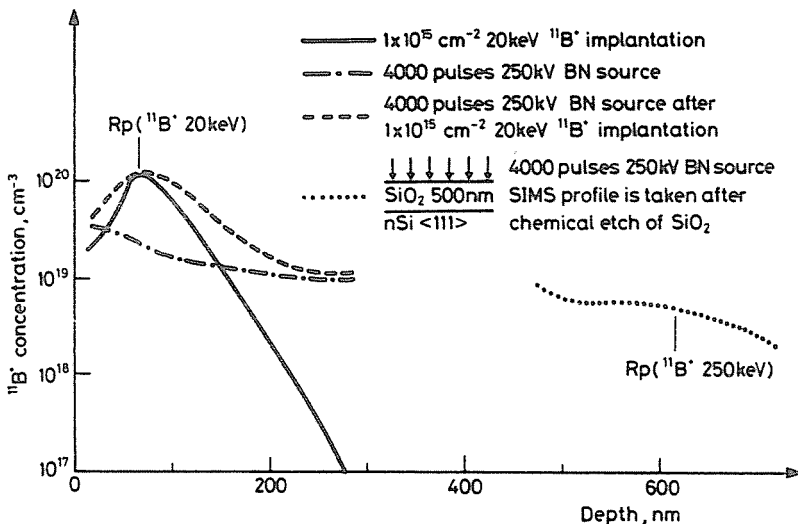


Fig. 2. Quantitative SIMS profiles of boron for a repetitive mode Pulsed Ion Implantation (PIB). Curves are: 1) Boron marker (20 keV,  $1 \times 10^{15}$  ions/cm<sup>2</sup>) alone in silicon (full line), 2) 250 kV PIB implanted boron into SiO<sub>2</sub> (500 nm)— $\langle 111 \rangle$ Si + marker (profile from surface to a depth of 300 nm, dashed line), 3) same, without marker (dash-dot line), 4) PIB boron reaching underlying silicon (SiO<sub>2</sub> etched, dotted line). Note that area (dose) between curves in SiO<sub>2</sub> with and without marker equals the area (dose) underlying the marker profile (after Krafcsik et al., 1987)

Integral value of the boron concentration shows that by 4000 pulses almost exactly  $1 \times 10^{15}$  ions/cm<sup>2</sup> boron dose was implanted into the SiO<sub>2</sub>—Si system. The calculated difference between curves with and without marker yields exactly  $1 \times 10^{15}$  boron/cm<sup>2</sup>, as the top 300 nm part of the distributions was compared. It can be seen that the marker has appreciably raised the nearsurface concentration of the boron. As it was mentioned before, the method will not lose its potential even for a case, where the peak concentration of the marker exceeds that of the dopant.

The SIMS profiles reveal some features of the Pulsed PIB doping, too. 250 keV boron in silicon has a penetration depth of 0.61  $\mu\text{m}$ . PIB results in an extremely flat boron profile, starting from the very surface. Stopping of boron in SiO<sub>2</sub> differs somewhat from that of silicon, being 0.66  $\mu\text{m}$  for 250 keV. Thus, in a first approximation, 250 keV boron penetrating 500 nm SiO<sub>2</sub> still has some 75 keV energy to penetrate somewhat into silicon (over 0.2  $\mu\text{m}$ ). This is clearly shown in Fig. 2 (SIMS profile on etched portion, dotted line).

At present, the PIB equipment produces electrical pulses, which are not fully rectangular. Thus, the distribution of ions in energy is far from being monenergetic. The flat distribution allows an estimate of the broad energy distribution of the boron ions. The self-annealing nature of PIB is an additional factor to contribute to a more-or-less constant doping profile. The small peak in the boron distribution at the SiO<sub>2</sub>/Si interface may also be real, i.e. the consequence of the difference in stopping powers. It may, however, be a SIMS transient. Thus, no conclusions will be drawn on that. A local maximum at 0.59  $\mu\text{m}$  shows that an appreciable portion of the boron ions are really accelerated to maximum energies. For a review of the work on PIB, we refer to Gyulai and Krafcsik (1989).

### 3. Conclusions

The use of calibration markers in quantitative SIMS was shown. Added to early results, some recent work on the field was reviewed. As a conclusion, marker technique to calibrate SIMS is reliable and a good tool to arrive to quantitative results. An example shown has proved that peak concentrations of the marker are not necessarily lower compared to that of the dopant. Measurements yielded reliable results for this case, too.

#### 4. References

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