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Quantitative analysis of boron in wafers and MG silicon using laser induced breakdown spectroscopy

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Laser Induced Breakdown Spectroscopy, LIBS, is an analytical method which allows very fast measurement of the composition of any material by atomic emission spectroscopy, without sampling. LIBS is a promising tool for the analysis of metallurgical and photovoltaic grade silicon. The high sensitivity of the technique (10^{-7}g/g) permits characterization of the purity of silicon which has been treated by various processes. Technical aspects of LIBS will be presented with regard to the optimization of the method for the analysis of silicon, notably for boron quantification. These include the use of sample chamber purge gas and the temporal gating of laser pulse and emissions measurement.

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique for the characterization of the composition of almost any material [1-5] without the need for sampling. LIBS uses a high irradiance pulse emitted by a short duration laser to ablate and vaporize a material and then to heat and excite the atoms and molecules released by the initial surface bombardment, thus forming a transient plasma [6-9]. The optical emission from the relaxation of excited species within the plasma can provide information regarding the elemental composition of the bulk material.

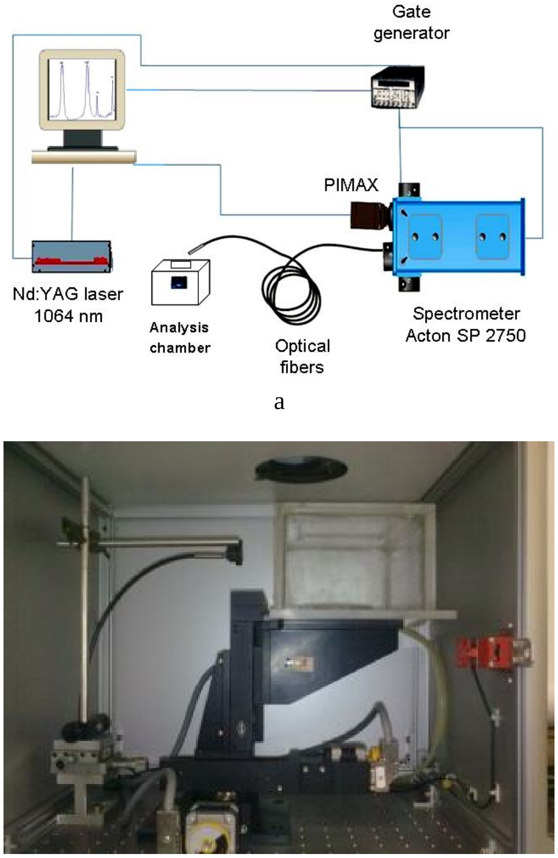
This technique has been used for different silicon materials to measure metals and carbon [10-12], however at this point, boron impurities in silicon have not been measured using LIBS but with glow discharge mass spectrometry (GDMS) and inductively coupled plasma (ICP).

In this work, LIBS was used to analyze boron in various grades of silicon (metallurgical grade silicon, certified silicon standards and photovoltaic grade silicon), at any desired location on the surface of a given sample. The effect of several experimental parameters on the signal-to-background ratio (SBR) was studied including the addition of helium, delay time, and gate width. The temporal evolution of the SBR of the silicon and boron plasma emissions as a function of these parameters was investigated. A calibration curve for boron concentration in silicon was obtained when using the parameters determined during the initial investigations. Boron measurement results using LIBS on unknown silicon samples are compared to other techniques.

2. Experimental setup

A schematic of the experimental setup is shown in Figure 1. The laser used was a Nd:YAG (Brio type, Quantel) at 1064 nm and with a repetition rate of 20 Hz and pulse duration about 4 ns FWHM [13]. All experiments were performed with constant laser energy of 95 mJ per pulse (shot to shot stability about 0.6% RMS). The laser was focused on the sample through a UV-Fused silica (Spectrosil 2000) window. The emitted light was transmitted to the spectrograph via a 19-fiber optical cable (each one having a 200µm core, numerical aperture 0.22) which collected the plasma emission at 90° to the direction of laser beam, through a second quartz window in the chamber wall. The plasma emission was imaged onto the entrance slit of a Czerny-Turner spectrograph with 750 mm focal length (Acton SpectraPro 2750) equipped with three gratings (1200 grooves.mm^{-1}, 300 nm blaze, 2400 and 3600 grooves.mm^{-1}, 240 nm blaze), with a reciprocal linear dispersion of 1.02 nm.mm^{-1} with a 1200 groove grating. The detector was a CCD camera (1024×1024 pixels) with an intensifier system (Princeton instruments PIMAX). The software WinSpec was used for parameter control and spectra were processed using the software Analibs (IVEA SAS).

A 3000 cm^3 analysis chamber with quartz windows was used in order to be able to change the nature of the gas surrounding the samples (air, argon, helium). All experiments were performed at atmospheric pressure and room temperature. Samples were placed on a motorized X-Y-Z table to facilitate surface cartography. For boron analysis in silicon, certified standard samples (Siltronix SAS) were used in order to build a calibration curve.



a

b

Fig. 1a. Experimental setup for laser induced breakdown spectroscopy (LIBS). b. Photograph of the sample analysis chamber.

3. Results

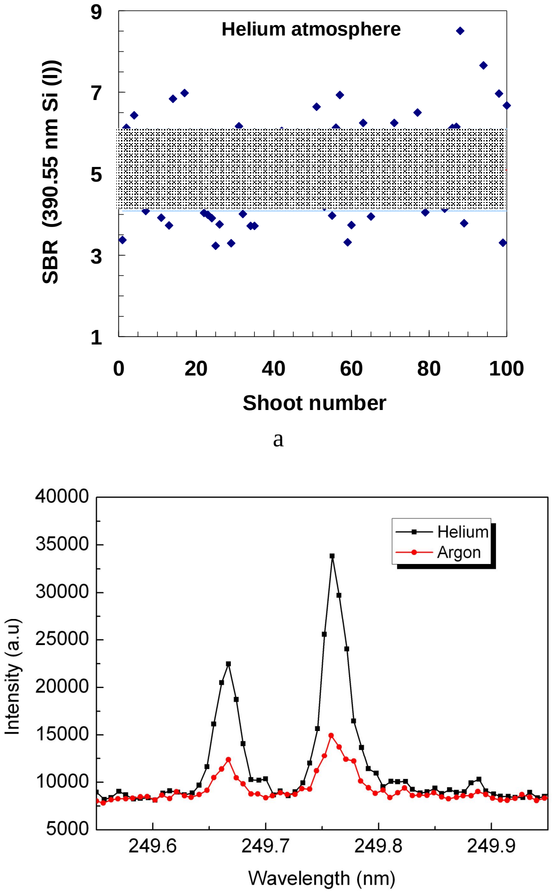
3.1 Effect of ambient gas:

In order to measure low concentrations of boron in samples of silicon, calibrations were made using certified silicon standards. It was noticed that the spectra obtained when not controlling the atmosphere in the sample chamber were of relatively poor quality compared to expectations. It has been previously shown that the use of ambient helium can improve spectral quality [14-15].

The parameter to be used here to quantify the spectral quality will be the signal-to-background ratio (SBR) for either silicon at 390.5 nm or boron at 249.7 nm. The 390.5 nm silicon line was chosen to avoid problems of self-absorption, while the 249.7 nm boron line was chosen for its high intensity to maximize boron detection sensitivity. Preferably, a line intensity ratio between the boron and silicon emissions would have been used in order to have an internal standard. However, in the spectral window used for boron detection (243-250 nm), the three available silicon lines are saturated under most conditions, meaning this type of data treatment was not possible.

Fig. 2.a shows the SBR for the 390.5 nm line of silicon for one hundred single shots in an atmosphere of helium; the average value is shown as a horizontal line with the shaded area representing one standard deviation. As can be seen in the figure, the average value was around 5. When the same experiments were carried out in atmospheres of air and argon, the average SBR value was around 2, meaning that the peak height for this silicon emission was only double the background signal. This positive effect of helium on the line emissions is a complex phenomenon involving changes in plume development and the suppression of chemical reactions caused by the use of helium.

Fig. 2.b shows a comparison of the spectrum for the boron doublet 249,6 and 249,7 nm for both argon and helium purge gas when using the gating parameters which had been determined to be optimum for each gas. The improvement in spectral quality when using helium as purge gas is evident. Helium was therefore chosen to be used as a purge gas for the rest of the results to be presented here.



a

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Fig. 2.a. Distribution of 100 single shots in helium atmosphere. b. Comparison between argon and helium atmosphere on the 249.6 and 249.7 nm boron line intensities with gating parameters having been determined separately for each gas. Delay time = 400 ns (He) and 1300 ns (Ar), gate width = 7000 ns (He) and 8000 ns (Ar), Gain = 190, slit width = 50 μm, helium flow = 5.6 L.min^{-1}.

3.2 Temporal study: determination of gating parameters

The quality of emission lines of both silicon and boron depends strongly on the choice of experimental conditions. The main parameters affecting the analytical performance are delay time and gate width.

Fig. 3 shows the temporal evolution of the silicon 390.5 nm emission line SBR under helium. Experiments were carried out on photovoltaic grade silicon. Fast gating is important because it allows of the high intensity background continuum emission present in the early moments of plasma development to be avoided. The delay time was therefore varied from 200 to 12000 ns, with a gate width fixed at 200 ns and an intensifier gain fixed at 230. Each data point was the accumulation of ten spectra. The SBR was observed to increase sharply at small delay times up to a maximum of about 3.25 at a delay time of about 1000 ns after the laser pulse. After this maximum, the SBR decreases for longer delay times as might be expected. The SBR reached a maximum value at around 1000 ns.

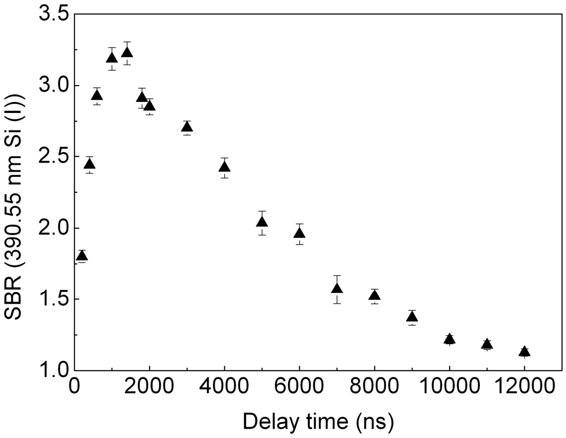

Fig. 3. Effect of the delay time on the SBR for the 390.5 nm silicon line. Gate width = 200 ns, slit width = 10 µm, Gain = 230.

A similar set of experiments was done to study the temporal evolution of the 249.7 nm emission line of boron; the sample was certified silicon containing boron at a concentration of 678 ppmw. The delay time was varied from 500 to 5000 ns in 500 ns increments, with the gate width fixed at 500 ns to avoid overlapping and with a constant intensifier gain of 230. No boron emission was observed below 500 ns. The maximum boron emission was obtained at 1000 ns (figure 4).

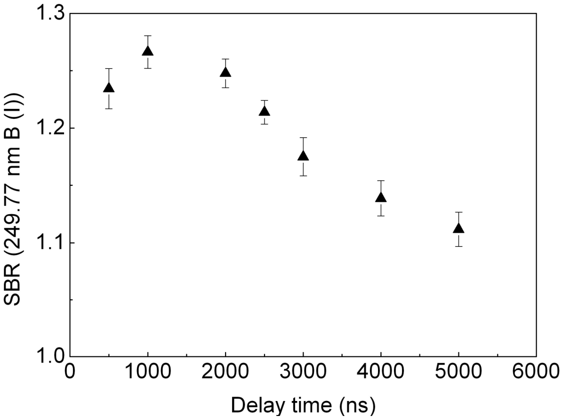

Fig. 4. Effect of delay time on the signal to background ratio for the 249.7 nm Boron line. Gate width = 500 ns, slit width = 15 µm, Gain = 230.

The effect of the gate width on the signal quality was then studied using a constant delay time of 1000 ns. The SBR for boron was observed to increase at low gate widths and then remained stable for gate widths greater than 7000 ns (figure 5). The value of 7000 ns was therefore used since it gives a maximized SBR.

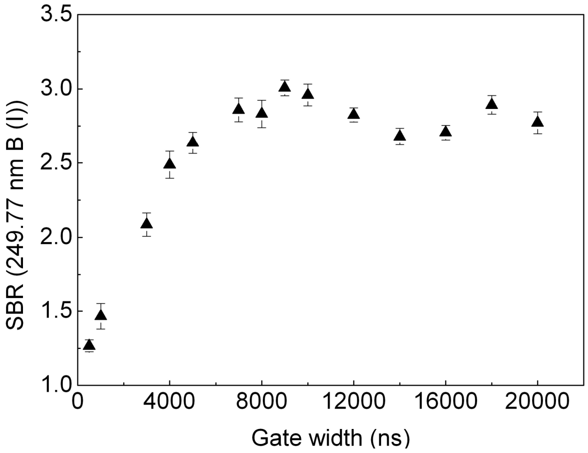

Fig. 5. Effect of the gate width on the SBR for the 249.7 nm boron emission line. Delay time = 1000 ns, slit width = 10 µm, Gain = 230.

3.3 Effect of intensifier gain

Fig. 6 presents the effect of the intensifier gain on the silicon line intensity and SBR for the 249.7 nm boron line respectively. It can be observed that the signal increases exponentially with gain. For a gain value less than 140, a poor SBR for the 249.7 nm boron line was obtained. The best SBR was observed using a gain of 250.

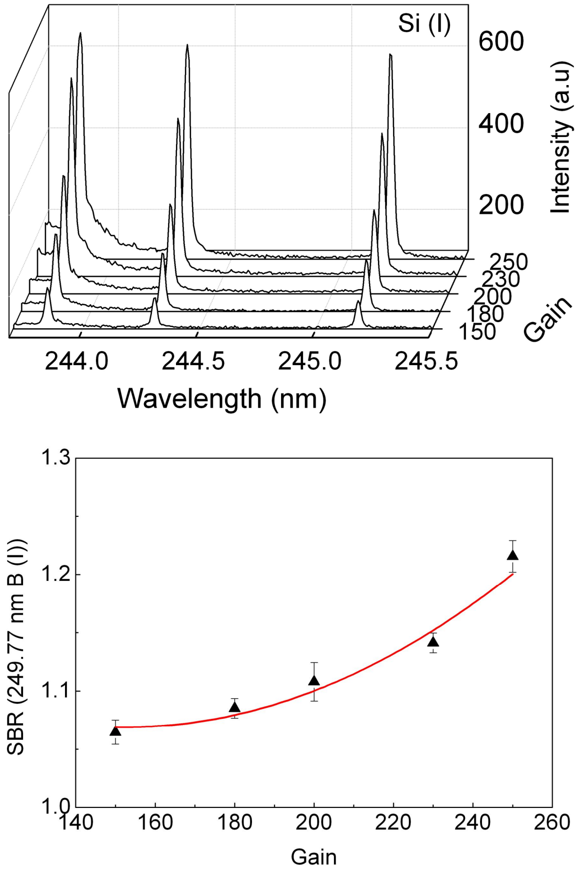

Fig. 6. Influence of intensifier gain. Delay time = 1000 ns, gate width = 7000 ns, slit width = 10 µm.

3.4 Calibration curve for boron in silicon

Fig. 7 presents the calibration curve obtained for boron in silicon samples. Each data point is the average of 150 shots made on different locations on the surface. It has been reported that the LIBS signal emitted by the same element depends on the matrix in which it is incorporated [16,17]. For this reason, certified silicon standard samples were used to build the calibration curve required for the measurements. All of these samples are monocrystalline silicon which were produced using the Czochralski process (Siltronix SAS) and boron-doped in the range 1 to 100 pmmw (resistivity between 0.009 and 0.238 Ω.cm). It should be emphasized that the certification applies to the sample resistivity and not directly to the boron concentration, which was calculated from tables found in the literature [18,19].

The calibration curve presented in Figure 7 should of course have an intercept value of exactly 1; indeed, analyses of silicon samples with zero boron do not exhibit peaks at this wavelength and therefore technically a data point could be placed at (0;1). Two possibilities exist to explain why the calibration curve as presented deviates strongly from this expectation. The first is that at very low boron concentration (i.e. less than the smallest value of 1 ppmw), boron emission exhibits strong non-linearity. As a matter of fact, at much higher concentrations (678 and 924 ppmw, not appearing in the figure), the boron emission intensity falls below what would be expected from extrapolation of the linear relation shown in the figure, thereby demonstrating a saturation phenomena at higher concentration.

The second, less likely, possible explanation involves the certified silicon samples which were used for the calibration. Technically, these samples are certified for their resistivity, and not for an exact concentration of boron. The boron concentrations used in Figure 7 were taken from tables relating boron concentration and resistivity. However, many other factors can affect the resistivity, including the presence of oxygen by the Czochralski process used to create the samples. If, as advertised, the certified silicon standards have the correct resistivity and contain only boron additive, then the calculated boron concentrations must be correct and the first explanation of strong non-linearity of boron emission at low concentration must be correct.

Assuming that the first explanation is correct, (i.e. boron emission is highly non-linear for very low boron concentration), the limit of detection of boron in silicon may be very low, but may not be reasonably calculated from the present data. If, for example the boron emission is linear from zero to one ppmw, a limit of detection of about 200 ppbw can be calculated, but this would be highly speculative considering that the functionality of boron emission at these low concentrations is not known.

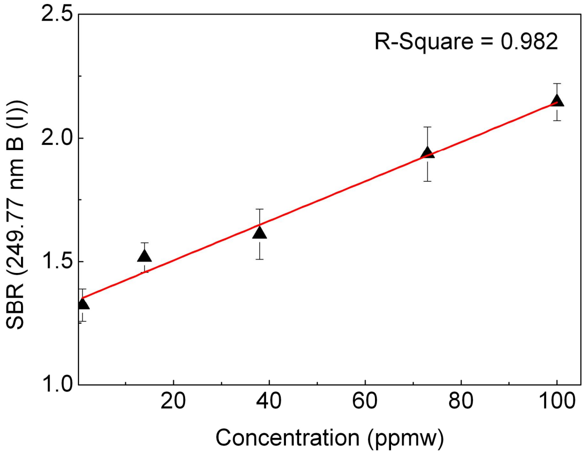

Fig. 7. Calibration curve for boron in certified standard silicon. Delay time = 1000 ns, gate width = 7000 ns, slit width = 50 µm, Gain = 250.

In order to compare the boron measurement results with other techniques, boron concentration in unknown samples was calculated using the calibration curve shown in Figure 7 and the results were compared with those which had been obtained by GDMS. The results of both techniques are shown in Table I. The concentration was obtained from the average of one hundred single shots at different locations on the sample surface. As seen in the table, for the same samples, the measurement of boron in silicon by LIBS gave comparable results to the GDMS method.

Table 1. Comparison between GDMS and LIBS boron concentration. Delay time = 1000 ns, gate width = 7000 ns, slit width = 50 µm, Gain = 250.

Concentration / Samples	GDMS (ppmw)	**LIBS (ppmw)**
1	5.0	**4.1 ± 0.3**
2	8.8	**5.4 ± 0.4**
3	10	**9.3 ± 0.5**
4	**49**	**51.1 ± 5.0**

4. Conclusions

In summary, the present work has investigated the effect of several experimental parameters on the signal-to-background ratio (SBR) for both silicon and boron emissions in laser induced breakdown spectroscopy (LIBS). The use of ambient helium as a purge gas was shown to lead to an improvement in the SBR. Gating parameters such as the delay between the laser pulse and the spectrum measurement and the spectrum accumulation time (gate width) were also optimized to maximize the sensitivity of the method for the measurement of boron in both metallurgical and photovoltaic grade silicon. A calibration curve for boron was obtained using standard silicon samples in the range 1 to 100 ppmw. Boron concentration obtained by LIBS was comparable to GDMS values. This curve will be used to quantify the purity of several silicon samples, in particular, those treated by thermal plasma process [20].

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