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Accuracy of secondary ion mass spectrometry in determining ion implanted B doses as confirmed by nuclear reaction analysis

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(Received 28 March 1999; accepted 18 October 1999)

The recent need for measuring depth profiles for ultralow-energy B ion implants in Si has pushed the technique of secondary ion mass spectrometry (SIMS) into unprecedented degrees of high depth resolution. For such shallow implant distributions, it remained to be seen if the quantification procedures which have been used for determining deeper B in-depth distributions are accurate for these very shallow profiles. What is more, the B concentrations at the surface can be in the percentage range for implants of 1E15/cm^2 at energies below 1 keV. It has not been demonstrated that SIMS can be accurate in this high-concentration regime. In this article, we use the nuclear reaction ^{11}B$(p,\alpha)^8$Be to confirm the accuracy of the implanted doses in low-energy B implants in Si. Our results indicate that the doses measured by SIMS are within 5% of those measured using nuclear reaction analysis. © *2000 American Vacuum Society.* [S0734-211X(00)05601-8]

I. INTRODUCTION

The recent need for measuring depth profiles for ultralow-energy ion implants in Si (Ref. 1) has pushed the technique of secondary ion mass spectrometry (SIMS) into unprecedented degrees of high depth resolution and depth accuracy. This application requires accurate analyses within the top 1–10 nm of the sample surface where the "surface transient" affects secondary ion yields. Flooding the Si surface with oxygen during analysis is an accepted method for reducing the magnitude of the surface transient effect.[2] However, equally important is the need to determine implanted doses accurately in the topmost 1–2 nm region of the Si. With more moderate-energy implants, the accuracy of a SIMS analysis within this depth region of the Si is not so important because only a very small fraction of the implanted dose comes to rest within this very near-surface depth interval. However, when ultralow-energy implants are made into Si, a majority of the dopant can come to rest within this very near-surface region. It has not yet been shown that SIMS can make measurements of total dose within this region, even when using an oxygen leak to stabilize ion yields. What is more, the B concentrations at the surface can be in the percent range for implants of 1E15/cm^2 at energies below 1 keV. It has also not been demonstrated that SIMS can be accurate in this high concentration regime. The question about the accuracy of SIMS in determining boron doses in the very near-surface region is critically important because of the need to evaluate the effectiveness of various anneal treatments at maximizing the fraction of implanted B atoms which become incorporated into the Si.[3]

In order to assess the accuracy of SIMS in determining implanted B doses in the topmost 1–2 nm of the Si, we have used the nuclear reaction ^{11}B$(p,\alpha)^8$Be to measure the total dose of ^{11}B implanted into five Si samples. This technique does not suffer from any matrix effects, and it is considered an "absolute" technique when calibrated with an appropriate standard.

II. EXPERIMENT

Five Si samples were implanted with ^{11}B. The energies and doses were chosen to span a range of depths and surface concentrations which would be encountered in the analysis of ultralow-energy B implants. The energies were 0.25, 0.5, 1.0, and 1.5 keV. Doses for the implants made at these four energies were 5E14/cm^2. One additional sample was implanted with an energy of 0.5 keV but to a dose of 1.0E15/cm^2.

The SIMS analyses were performed on a Physical Electronics model 6600 secondary ion mass spectrometer modified for routine use with an oxygen leak. The sputtering conditions were: 1.5 keV O_2^+ bombardment at 60° with respect to the surface normal. An oxygen leak was directed onto the sample surface during the analyses. The pressure measured in the analysis chamber during the analyses was approximately 2E-6 Torr. Sputtering rates were approximately 1 Å/s. The detected secondary ion species were ^{11}B$^+$and ^{30}Si$^+$.

Quantification of the B profiles was accomplished by analyzing, along with the analytical samples, a boron-doped Si wafer, the B concentration of which was determined by analyzing the sample versus a Standard Reference Material (No. 2137) from the National Institute for Standards and Technology. The dose of this implant of ^{10}B in Si is known to an absolute accuracy of ±3%. We thus estimate the accuracy of the B concentration of our bulk-doped standard to be ±5%.

The sputtering rates were determined from the time needed to sputter to the peak of a buried Ge spike in epitaxially grown Si. The spike is known to be located 312 Å beneath the Si surface of this standard. The primary ion beam

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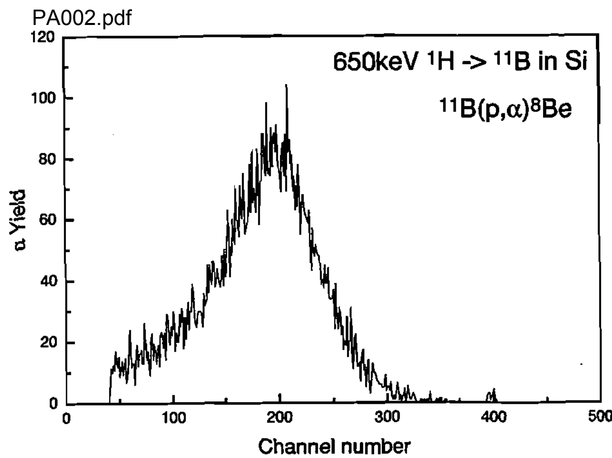

FIG. 1. α-particle energy spectrum from the $^{11}B(p,\alpha)^8Be$ nuclear analysis of the standard of ^{11}B implanted in Si standard.

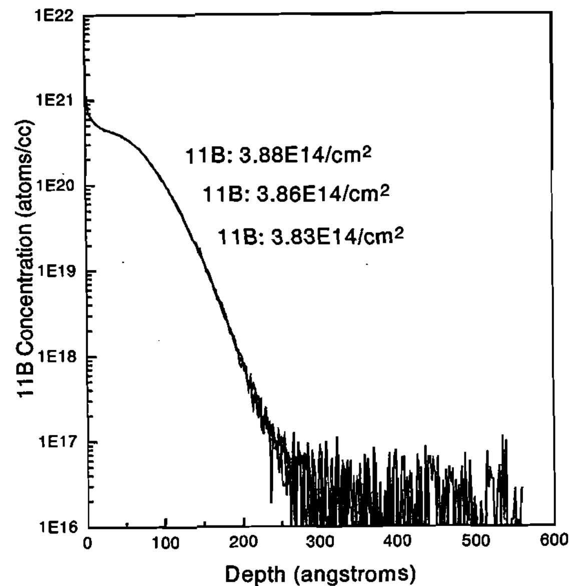

FIG. 2. SIMS profiles of three analyses of sample L-76, a reaction implant of 1 keV ^{11}B in Si. The doses as measured by SIMS are shown on the plot. The dose determined from $^{11}B(p,\alpha)^8Be$ nuclear reaction analysis was 3.86E14/cm^2.

current was checked before and after each analysis and was kept constant to within $\pm 1\%$. Thus, the sputtering rate determined from the sputter rate standard could be used for *all* of the analyses.

The nuclear reaction analyses were performed using a National Electrostatics Model 5SDH-4 accelerator. A 650 keV, 400 nA proton beam was used for analysis. 200 μC of charge were accumulated per analysis. The particle detected was the 5.57 MeV α particle which resulted from the $^{11}B(p,\alpha)^8Be$ nuclear reaction.[4,5] The standard used for the nuclear reaction analysis was a 30 keV implant of ^{11}B in Si with a dose of 8.76±0.60E15/cm^2. The standard is one which has been used at Bell Laboratories for more than six years for these measurements.

III. RESULTS

Figure 1 shows the α-particle spectrum taken when bombarding the standard ^{11}B in Si with 650 keV protons. The dose of 8.76E15/cm^2 gives a total α-particle yield of 9600 counts. Since there are no matrix effects in the $^{11}B(p,\alpha)^8Be$ nuclear reaction, the dose of the analytical samples is simply the ratio of the number of α-particles detected from the samples relative to that detected from the standard. The only assumptions made are: (1) all of the ^{11}B resides within the sampling depth (>8 μm) for the 650 keV proton beam. Since we are dealing with ultralow-energy implants, this is a valid assumption. The second assumption is that all of the boron present in the samples is ^{11}B. The $^{11}B(p,\alpha)^8Be$ nuclear reaction is specific for ^{11}B only. The validity of this assumption was confirmed during the SIMS analysis during which both ^{10}B and ^{11}B were monitored.

Figures 2–4 show the three replicate ^{11}B profiles measured by SIMS on representative samples L-76, L-80, and L-82, respectively. The integrated doses for each SIMS analysis are noted on each figure. These were used to determine the average SIMS doses and relative standard deviations shown in Table I. As shown in the table, the precision of the SIMS measurements is of the order of 1%.

IV. DISCUSSION

The data in Table I illustrate that with proper sensitivity calibration and sputter rate calibration, SIMS can measure implanted doses of ultralow-energy B implants to within 5% of the actual doses. Some features of the $^{11}B(p,\alpha)^8Be$ nuclear reaction analyses and the SIMS analyses need to be elaborated upon, however. The relative standard deviation of the counting statistics for the nuclear reaction analyses is approximately 5%. This is for a ^{11}B dose of 5E14/cm^2 and a

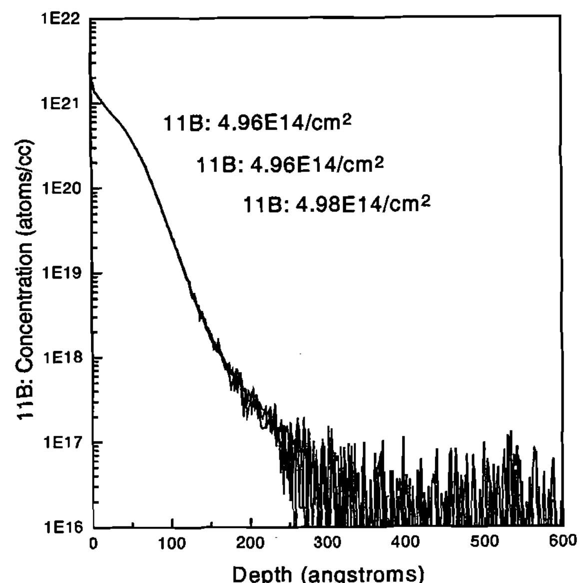

FIG. 3. SIMS profiles of three analyses of sample L-80, an implant of 0.5 keV ^{11}B in Si. The doses as measured by SIMS are shown on the plot. The dose determined from $^{11}B(p,\alpha)^8Be$ nuclear reaction analysis was 4.78E14/cm^2.

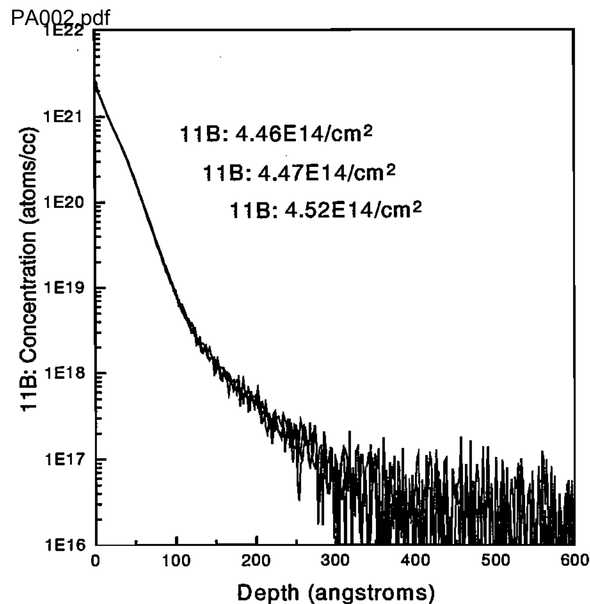

FIG. 4. SIMS profiles of three analyses of sample L-82, an implant of 0.25 keV ^{11}B in Si. The doses as measured by SIMS are shown on the plot. The dose determined from $^{11}B(p,\alpha)^{8}Be$ nuclear reaction analysis was 4.59E14/cm^2.

proton charge accumulation of the sample of 200 μC. Thus, for the lowest dose sample, L-76, we accumulated an additional 200 μC of charge to reduce the counting errors. The relative standard deviation between the two 200 μC charge integrations for samples L-76 was 2.9%. This indicates that the errors introduced by the nuclear reaction analysis (NRA) counting statistics are minor when compared to the potential inaccuracies of the SIMS measurements. The SIMS measurements have at least three possible sources of error. The first is an error introduced into the total integrated ^{11}B dose by the inaccuracy of the sputtering rate in the beginning stages of the analysis. We have shown conclusively[6] that, using the sputtering conditions of this work, the measured profile is too shallow by approximately 2.5 nm. All of the error comes within the initial 5 nm of sputtering. It has been shown that the sensitivity factor for boron relative to silicon in the initial stages of sputtering, during which the sputter rate is changing, compensates for the error introduced into the dose integration by the inaccurate depth scale of the profile. However, the absolute accuracy of SIMS-determined doses had not been measured prior to this work for ultralow-energy B implants in which a large fraction of the total dose resides within the top 5 nm of the silicon where the inaccuracy of the depth scale is greatest. However, we see from the accuracy of the SIMS-determined doses that any error introduced into the SIMS measurements by the inaccuracy of the depth scale in the initial stages of sputtering is very small.

The second possible source of error in the SIMS measurements is in the accurate measurement of the very high B concentrations that are found at the surface of ultralow-energy implants. The surface B concentration for the sample implanted at 0.25 keV is between 2E21/cm^{3}and 3E21/cm^3. This is approximately 5 at. %. The standard used to establish the SIMS instrumental sensitivity uses a ^{11}B concentration 200 times lower than this. It is generally assumed that SIMS measurements can be subject to error when the concentrations to be measured are above the "dilute limit," which is generally taken to be 1 at. %. Our measurements show, however, that even for boron concentrations five times greater than the dilute limit, accurate B doses can still be measured when using the measurement protocol described here.

The third possible source of error is due to the presence of an oxide on the surface of the wafers after implantation. It has been shown that oxides of greater than 1 nm in thickness can be present on wafers after implant, even if the wafers were HF-etched just prior to implant. Oxides are known to have a very large enhancement effect on B sensitivity when sputtered from Si, and one might expect an affect on the quantification when sputtering in this oxide since the instrument calibration is performed using a standard Si, not SiO_2. The use of oxygen flooding is supposed to do away with this problem since the sputtered surface is continuously being converted to SiO_2, including the surface of the standard when it is analyzed. Again, however, no independent confirmation of this assumption has been published. This present work suggests that this assumption is valid.

This study also sheds light on an often-discussed feature of SIMS profiles of ultralow-energy B implants, namely, the peak which is always detected at the surface. This feature is easily seen in the profile for 1.0 keV B shown in Fig. 2. TRIM (transport of ion through matter) calculations predict that no peak should exist at the surface for such an implant. However, the SIMS-measured dose of this sample (as well as all other samples) is only correct if all of the surface peak is integrated to be included in the measured dose. The surface peak has been discussed previously[7] and it is thought that it may be due to a redistribution of subsurface B to the surface during the initial stages of sputtering. This remains to be

TABLE I. Comparison of doses as determined by $^{11}B(p,\alpha)^{8}Be$ nuclear reaction analysis and SIMS.

Sample ID	Energy (keV)	Nominal dose (E14/cm^2)	NRA dose (E14/cm^2)	Ave. SIMS dose (E14/cm^2)	% error of SIMS
SPC	1.5	5.0	5.78	5.74±1.5%	−0.7
L-76	1.0	5.0	3.86	3.86±0.6%	0%
L-80	0.5	5.0	4.78	4.97±0.2%	+4.0%
L-82	0.25	5.0	4.59	4.48±0.7%	−2.4%
IB	0.5	10.0	8.80	8.65±0.9%	−7.7%
+0.12% ave. error					

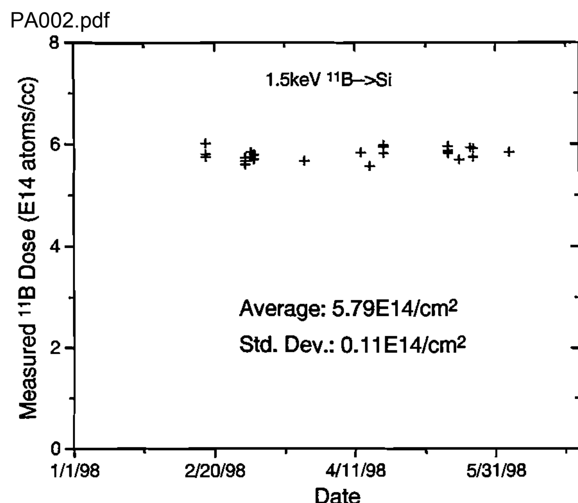

FIG. 5. Plot of SIMS-measured dose on our statistical process control sample over a five month period in 1998. The dose of this sample was measured by $^{11}B(p,\alpha)^{8}Be$ nuclear reaction analysis at the end of May 1998 and found to be 5.78E14/cm^2.

proven, but this work shows that it justified to include the surface peak in the total dose calculation.

The surface peak for these ultralow-energy implants includes some ^{11}B due to air exposure of the Si surface. This would be counted by the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction and the SIMS, but it would not be included in the dose integration of the implant. One might expect this to lead to a disagreement between the implanted dose and the NRA-measured dose. This, however, is not the case here because the air-exposure contamination includes both ^{10}B and ^{11}B, while the implantation only introduces ^{11}B. SIMS detects both isotopes separately and we find that the amount of ^{10}B from air exposure is so small that the associated ^{11}B from air exposure is at least an order of magnitude lower in concentration than the ^{11}B from the implant.

The long-term accuracy of our dose measurements has also been examined. One of the samples which was included in this study, sample "SPC," is a statistical process control sample which we analyze with each group of ultralow-energy B samples measured by SIMS. Figure 5 shows the values for the integrated dose for this sample which we have measured over a five-month period in 1998. The average value of 5.79E14/cm^2 is virtually identical to the dose measured by $^{11}B(p,\alpha)^{8}Be$ nuclear reaction analysis which is shown in Table I. It is also in good agreement with the average value which was determined by SIMS in this study which is also shown in Table I. We hasten to point out, however, that the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction analysis was not carried out on this sample until the end of the time period shown in Fig. 5. It was only then that we learned that the values of which we were obtaining by SIMS for the dose of this sample were correct.

V. CONCLUSION

We have shown that the total integrated doses for B in ultralow-energy implants can be determined with an accuracy of better than 5% using secondary ion spectrometry with oblique incidence O_2^+ primary ion bombardment and using oxygen flooding to stabilize the ion yields in the first several nanometers of sputtering. The problem of an inaccuracy in the depth scale over this initial depth interval does not introduce an inaccuracy in the integrated B dose. In addition, the concentrations of B at the surface of up to 5 at. % do not appear to present a problem with SIMS quantification, even when a dilute concentration B standard is used for calibration.

One must remember that in using the sputtering conditions of this work, there is an inaccuracy in the depth scale of the analyses (profiles are 2.5 nm too shallow). It has been shown conclusively,[6] however, that one *can* sputter Si using conditions which do *not* result in such inaccuracies. It is yet to be determined whether one will still be able to determine accurate B doses when the sputtering conditions are chosen such that there is *no* inaccuracy in the depth scale in the initial stages of sputtering. We are in the process of performing such experiments to answer this question.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Scott Baumann and Roger Bleiler of Evans Texas for obtaining samples L-76, L-80, and L-82 for this work. Discussions with Steve Smith, Gary Mount, Chuck Hitzman, Mike Edgell, and Dick Hockett of Charles Evans and Associates and Sukanta Biswas and Steve Littlewood of Evans Europa were also helpful. One of the authors (C.W.M.) also wishes to acknowledge early discussions with Joe Kirchhoff of Charles Evans and Associates about the usefulness of this nuclear reaction for accurate ^{11}B dose determinations.

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