Depth Profiling of Boron in Silicon by High-resolution Medium Energy Elastic Recoil Detection Analysis

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(Received 19 September 2012; Accepted 18 November 2012; Published 22 December 2012)

The feasibility of the high-resolution medium energy elastic recoil detection analysis using a sector type magnetic spectrometer was studied for the depth profiling of boron in silicon. Two different methods were examined to reject the scattered probe ions. One is installation of a thin mylar foil in front of the focal plane detector of the spectrometer. The other is the use of He$^+$ ions as a probe. The pros and cons of these two methods as well as high-resolution RBS were discussed based on the experimental results. It was demonstrated that the use of He$^+$ ions as a probe is the best method among these three methods.

[DOI: 10.1380/ejssnt.2012.655]

Keywords: High-resolution ERDA; High-resolution RBS; Boron in Silicon; Depth profiling; Charge state fraction

I. INTRODUCTION

The scaling of semiconductor devices requires analysis techniques allowing the characterization of surface and interface structures with sub-nanometer depth resolution [1]. Secondary ion mass spectrometry (SIMS) has been almost exclusively used for these characterizations, especially the depth profiling of dopant atoms such as phosphorous, sulfur, and boron in microelectronics devices. In the near-surface and interface regions, however, SIMS suffers from errors in the depth and concentration due to the changes in sputtering yields and stationary surface concentration of the implanted primary ions when going from one matrix to the second one [2]. Due to these surface transient and matrix effects, alternative techniques are highly desired for the research and development of the microelectronics devices.

High-resolution Rutherford backscattering spectroscopy (HRBS) is a powerful surface analysis technique [3–11], which has better depth resolution compared to the conventional RBS. We have developed a compact HRBS system, which employs a 90° sector type magnetic spectrometer instead of a silicon surface barrier detector [12]. It allows quantitative and non-destructive depth profiling of constituent elements with sub-nm depth resolution within a reasonably short measurement time (typically 10-20 min) without any special pre-treatment of the sample. However, the typical sensitivity of HRBS for light elements, such as boron, is ~1 at.%, which is not good enough for some applications, such as applications in microelectronics industry [13].

Elastic recoil detection analysis (ERDA) is more suitable to analyze the light elements than RBS. Dollinger et al. demonstrated that depth profiling of boron in silicon can be performed with sub-nanometer depth resolution and high sensitivity of ~0.01 at.% by using their high-resolution ERDA (HERDA) setup [1, 14]. To establish the sub nanometer depth resolution, they used high energy heavy ions (e.g. 40 MeV Au) as a probe and the energy spectrum of recoiled ions is measured by a sophisticated magnetic spectrometer, which was originally developed for the research of nuclear physics. Although the performance of their HERDA is excellent, they need a large facility including a high energy accelerator and a large magnetic spectrometer. If much smaller equipment can be used for the analysis of light elements with depth resolution and sensitivity comparable to their system, it should be useful. It was already demonstrated that our compact HRBS system can be used for high-resolution ERDA. Hydrogen depth profiling was performed with sub-nm depth resolution and a sensitivity of 0.1 at. % at 15, 16. However, there are several issues to be solved to analyze other light elements heavier than hydrogen, such as boron.

In our hydrogen analysis, we used an electrostatic deflector to reject the scattered probe ions. Unfortunately, the electrostatic deflector cannot separate recoiled boron ions from the scattered probe ions unless very heavy ions are used. Another issue is charge state fractions of recoiled ions. Because the magnetic spectrometer cannot measure recoiled ions of all charge states simultaneously, the information of charge state fractions of the recoiled ions is necessary for quantitative analysis. However, there is almost no measurement on the charge state fractions of light elements in the relevant energy region.

In this paper, we employ two different methods to reject probe ions in boron depth profiling using HERDA. One is the use of He$^+$ ions as a probe. The magnetic spectrometer itself can reject the scattered He ions when the magnetic field is adjusted for the recoiled boron ions. The other is the use of a mylar foil in front of the focal plane detector as is in the conventional ERDA. Feasibility of these methods is examined and the pros and cons of these methods are discussed. The charge state fractions of the recoiled boron ions are also measured and the results

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are compared with an available semi-empirical formula to check the accuracy of the formula.

II. ELASTIC RECOIL DETECTION OF BORON

When light elements are analyzed using ERDA, the recoiled ions of the relevant element should be distinguished from both scattered probe ions and recoiled ions of other elements. In the high resolution ERDA system of Dollinger et al., a magnetic spectograph is used in combination with a hybrid position sensitive detector consisting of an ionization chamber for the measurement of the stopping power and a silicon surface barrier detector for the residual energy. This allows to analyze the nuclear charge or the mass of the recoiled ion unambiguously with an excellent energy resolution. Such a hybrid detector, however, cannot be used to analyze recoiled ions with energies lower than MeV. Thus this approach cannot be used in our medium energy ERDA.

Here, we propose a new approach to reject the scattered probe ions. Let us consider the analysis of boron doped in silicon using our medium energy ERDA. In standard ERDA, probe ions heavier than the relevant elements are usually used. In our new approach, we choose lighter probe ions instead of heavy ions. The advantage of the light probe ion is that the scattered probe ions do not interfere with the energy spectrum of the relevant recoiled ions. For example, if 400 keV He ions are used and a typical recoil angle of 25° is chosen, the energy of 11B+ ions recoiled from the surface region is ~257 keV. When the magnetic field of the spectrometer is adjusted to detect these recoil ions, 4He+ ions of 707 keV (= 257 keV × 11/4) may be detected simultaneously. There is, however, no scattered He ion with energy higher than the incident energy (400 keV). As a result, the energy spectrum of the recoiled 11B+ ions can be measured without suffering from the scattered probe ions.

The second approach examined in this paper is the use of a thin foil to reject scattered probe ions. In the conventional ERDA, where hydrogen is analyzed using MeV He ions as a probe, a thin mylar foil of several μm thickness is installed in front of a silicon surface barrier detector. The mylar foil, however, deteriorates the energy resolution of the detector. In our medium energy ERDA, this method might be also effective. However, if the mylar foil is installed before the magnetic spectrometer the energy resolution is seriously deteriorated. In order to avoid the deterioration, the foil should be installed in front of the position sensitive detector which is placed on the focal plane of the spectrometer. Let us estimate the approximate thickness of the mylar foil when a 320 keV Ar+ ion beam is used as a probe for boron analysis. The energy of the boron ions recoiled from the surface region at 30° is ~163 keV. When the magnetic field of the spectrometer is adjusted to detect these 11B+ ions, scattered Ar+ ions of ~45 ( = 163 × 11/40) keV interfere with the boron signal. The projected range of 163 keV 11B+ in mylar (ρ=1.4) is calculated to be 0.64 μm using the SRIM code while that of 45 keV Ar+ is 0.07 μm. Thus, a mylar foil of several tenth μm thickness is suitable for rejection of the scattered probe Ar ions.

III. EXPERIMENTAL

Using a 400 keV He+ ion beam as a probe, HRBS and HERDA measurements were performed to measure boron profiles in boron implanted silicon samples with a compact HRBS system at Kyoto university [12]. In the HERDA measurement, B+ ions recoiled at 25° were measured by a 90° sector type magnetic spectrometer. Boron profiles were also measured by HRBS using the same equipment. The He+ ions scattered at 50° were measured by the same magnetic spectrometer.

The second approach of the HERDA measurements was performed using a HRBS500 system (Kobe Steel, Ltd.) [17]. A beam of 320 keV Ar+ ions was irradiated and boron ions recoiled at 30° were measured by the 90° sector type magnetic spectrometer. To reject the scattered Ar+ ions, a mylar foil of 0.7 μm thickness was set in front of a focal plane detector. Although a mylar foil thinner than 0.64 μm is better for the present experimental conditions as was discussed in the previous section, we chose 0.7 μm for the reason of handling.

Two types of boron doped silicon samples were prepared by plasma doping and ion implantation. The plasma doping sample was prepared in the following way. After the implantation of 12 keV Ge+ ions at a fluence of 5 × 1014 ions/cm², a Si(001) wafer was exposed to BF3 plasma for 75 sec. The amount of the doped boron was about 5 × 1015 atoms/cm², and both 11B and 10B were doped in proportion to their natural abundance. The other sample was prepared by ion implantation of 1 keV B+ ions at a fluence of 3 × 1016 atoms/cm². Because 11B+ and 10B+ ions were not separated in the implantation, this sample also contains both 11B and 10B in proportion to the natural abundance.

IV. BORON ANALYSIS WITH HRBS

The sample prepared by the plasma doping was measured by HRBS. An example of the observed spectrum is shown in Fig. 1. The measurement was performed under the [111] channeling condition to reduce the silicon background signal. The arrows indicate the elastic binary collision energies for constituent elements. There are 11B and 10B peaks at 305 and 298 keV, respectively. The observed boron signal is, however, weak compared to the silicon background even under the present channeling conditions. In order to obtain good statistics, the spectrum was accumulated for 11 hours. Thanks to the channeling effect, the boron signal can be clearly seen although the boron atoms in the substitutional sites cannot be measured under channeling conditions. Note that the silicon background spectrum shows an oscillatory structure which is a characteristic feature of channeling spectra. Due to this oscillatory structure, the background subtraction procedure has a large uncertainty. Assuming that the background can be approximated by a straight line shown in Fig. 1, the boron spectrum is extracted from the observed spectrum.

The depth profile of 11B was derived from the extracted boron spectrum and the result is shown by closed circles in Fig. 2 together with the derived silicon profile (solid line).
The boron profile has a peak at a depth ~1.8 nm which coincides with the SiO₂/Si interface. The depth resolution at the surface was estimated from the shape of the leading edge. The obtained depth resolution is ~0.7 nm, which is mainly determined by the energy resolution of the spectrometer. This good depth resolution, however, deteriorates with depth mainly due to energy loss straggling and multiple scattering. The depth resolution at a depth of 5 nm was estimated to be 2.3 nm using a Monte Carlo simulation code of CORTEO [18], which includes both energy loss straggling and the multiple scattering.

Because there is a large uncertainty in the estimation of the silicon background spectrum, the error in the boron concentration originates mainly from the uncertainty in the estimation of the silicon background, which determines the sensitivity of boron. The estimated sensitivity is ~1 at.% in the present case. Note that if channeling technique is not employed the silicon background is more than one order of magnitude larger than the channeling spectrum and the sensitivity is several times worse than the channeling measurement.

V. BORON ANALYSIS BY HE⁺ PROBE ERDA

The plasma doped Si was irradiated with 400 keV He⁺ ions and the ions recoiled at 25° with an exit angle of 10° with respect to the surface plane were measured by the magnetic spectrometer. An example of the observed spectrum accumulated for 5 hours is shown in Fig. 3. Note that the energy scale shown here was derived assuming that the recoiled ions are ¹¹B⁺. There is a broad peak around 250 keV and a small peak at 268 keV. The arrows indicate the expected positions of ¹⁰B⁺, ¹¹B⁺, and ¹²C⁺ ions recoiled from the surface. The position of the observed small peak (~268 keV) agrees with that of the ¹²C⁺ ions recoiled from the surface, indicating that the origin of this small peak is a surface contamination layer containing organic molecules. The broad peak seen at ~250 keV corresponds to the recoiled ¹⁰B and ¹¹B ions.

As was discussed in the experimental section, there should be no scattered He ions in the observed spectrum. There is, however, a rather large background shown by a dashed line in Fig. 3. A possible origin of the observed background is Si⁺ ions recoiled from the sample. The energy of the ²⁸Si⁺ ions, which overlap with 250 keV ¹¹B⁺ ions, is 98 keV (= 11/28 × 250 keV), which is lower than the energy of ²⁸Si⁺ ions recoiled from the surface. This suggests that the Si⁺ ions recoiled from the inside of the sample are the origin of the observed background. Although the present measurement indicates that the background cannot be completely removed even in the He-probe ERDA, the observed background can be well approximated by a straight line as is shown in Fig. 3. This allows reliable background subtraction as compared to the HRBS measurement (see the oscillatory structure of the
background in Fig. 1). The estimated sensitivity of boron is about 1 at.\% in the present case, which is almost the same as that of HRBS shown in the previous section, although the measurement time is more than twice shorter than that of the HRBS measurement. It is also noteworthy that the present ERDA measurement was done under non-channeling conditions differently from the HRBS measurement in the previous section. Thus, all boron atoms including those in the substitutional sites can be analyzed in the present ERDA measurement.

The background is subtracted from the observed spectrum and the resulting boron spectrum is shown in Fig. 4. The $^{11}$B spectrum was separated from the $^{10}$B spectrum in the following way. Because $^{10}$B signals recoiled from the surface appear at 244 keV, the spectrum in the energy region larger than 245 keV consists of only $^{11}$B signals. Therefore, the depth profile of $^{11}$B in the corresponding surface region can be derived from this energy region. Assuming that $^{10}$B and $^{11}$B atoms exist in proportion to the natural abundance, the spectrum of $^{10}$B in the same surface region can be calculated from the obtained $^{11}$B profile. By subtracting the estimated $^{10}$B contribution from the observed spectrum, the $^{11}$B spectrum in the next sub-surface region can be obtained. Repeating this procedure the $^{11}$B spectrum can be separated from the $^{10}$B spectrum. The results are shown by solid lines in Fig. 4. The depth profile of $^{11}$B was derived from the obtained $^{11}$B spectrum and is shown in Fig. 2 by open circles. The profile agrees with that measured by HRBS (solid circles) very well. The leading edge of the ERDA profile is, however, sharper than the HRBS profile and a shoulder is seen more clearly at a depth ~0.3 nm in the ERDA profile, indicating that the depth resolution of ERDA is better than that of HRBS. The depth resolution is estimated to be 0.5 nm from the shape of the leading edge. This depth resolution (0.5 nm) is comparable with that of the sophisticated HERDA measurements [14].

![FIG. 4: The boron spectrum derived from the ERDA spectrum shown in Fig. 3 by subtracting the background. The $^{11}$B spectrum was separated from the $^{10}$B spectrum by assuming that $^{11}$B and $^{11}$B isotopes exist in proportion to the natural abundance. The separated $^{11}$B and $^{10}$B spectra were shown by thin and thick solid lines respectively.](image1)

![FIG. 5: An example of the Ar$^+$ probe ERDA spectrum for B-doped Si(001) prepared by ion implantation. The incident ion was 320 keV Ar$^+$, the recoiled angle is 30° and the exit angle was 15°. To reject the scattered Ar$^+$ ions, 0.7 μm thick mylar foil was installed in front of a focal plane detector.](image2)

![FIG. 6: The equilibrium charge state fractions of boron ions estimated using the semi-empirical formula by Zaidins (lines). Charge state fractions measured in the present work are shown by open circle (B$^0$), full circle (B$^+$), full triangle (B$^{2+}$), and full square (B$^{3+}$).](image3)

**VI. BORON ANALYSIS BY AR$^+$ PROBE ERDA**

The ion implanted boron with energy of 1 keV in Si (the fluence $3 \times 10^{16}$ cm$^{-2}$) was irradiated with 320 keV Ar$^+$ ions and the recoiled ions at 30° with the exit angle of 15° were measured by the 90° sector type magnetic spectrometer. To reject the scattered Ar$^+$ ions, 0.7 μm thick mylar foil was installed in front of a focal plane detector. An example of observed spectrum is shown in Fig. 5. There are two broad peaks corresponding to $^{10}$B and $^{11}$B ions at 138 and 158 keV, respectively. There is almost no background, indicating that the scattered Ar together with the recoiled Si ions can be efficiently removed by the mylar foil.

In addition to the almost complete reduction of the background, the Ar$^+$ probe ERDA has another advantage, namely larger recoil cross sections compared with...
the He$^+$ probe ERDA. This leads to better sensitivity. Although the spectrum shown in Fig. 5 was accumulated for only 21 sec the estimated sensitivity is $\sim$0.7 at.%. The sensitivity can be improved to 0.1 at.% when the accumulation time is 10 min. There are, of course, some drawbacks. The main drawback is its relatively poor depth resolution. The observed boron peak has a large tail towards higher energies, which is attributed to the effect of multiple scattering. The multiple scattering deteriorates the depth resolution seriously. We estimated the energy resolutions for both He-probe ERDA and Ar-probe ERDA using the Monte Carlo simulation code of CORTEO [18], which includes the multiple scattering. The estimated depth resolutions are 0.4 and 0.5 nm at the surface and 3.0 and 6.9 nm at the depth 5 nm for the present He-probe ERDA and Ar-probe ERDA, respectively. The calculated depth resolution for He-probe ERDA is in good agreement with the observed result (0.5 nm). Although the depth resolution for Ar-probe ERDA is comparable to that of He-probe ERDA at the surface, it deteriorates more rapidly with increasing depth.

VII. CHARGE STATE FRACTIONS OF RECOILED BORON ION

For quantification, the information of charge state fractions of the recoiled B ions is important. The equilibrium charge state fractions of boron ions estimated using the semi-empirical formula by Zaidins [19] are shown in Fig. 6. The fraction of B$^+$ is dominant and shows almost constant at the energy region ranging from 200 to 400 keV and decreases rapidly at energies below 200 keV. As the experimental value of the charge state fractions of boron at the energies less than 200 keV was not reported, we tried to measure it using the boron implanted silicon sample. A beam of 320 keV Ar$^+$ ion was irradiated and recoiled B ions at 30$^\circ$ was measured by the 90$^\circ$ sector type magnetic spectrometer with 0.7 $\mu$m thick mylar foil in front of focal plane detector. The energy spectrum of B$^+$, B$^{2+}$, and B$^{3+}$ were measured by adjusting the magnetic field of the spectrometer corresponding to the each charge state. The measured charge state fractions were plotted in Fig. 6. As the recoiled neutral boron ions cannot be measured by the spectrometer, the charge state fraction of B$^0$ was estimated by assuming the charge state fraction ratio of B$^0$ to B$^+$ is equal to the value given by the semi-empirical formula of Zaidins. As shown in Fig. 6, the measured charge state fractions agree with the semi-empirical formula. This indicates that the semi-empirical formula is reliable even in this low energy region.

VIII. CONCLUSIONS

Boron depth profiling was performed by high-resolution RBS and two different high-resolution ERDA, namely He-probe ERDA and Ar-probe ERDA. Concerning the depth resolution, He-probe ERDA provides the best resolution (0.5 nm) at the surface. The resolution of Ar-probe ERDA is slightly worse than the He-probe ERDA and rapidly deteriorates with depth due to the multiple scattering.

The HRBS spectrum has a large background even if the spectrum is measured under channeling conditions. The background has an oscillatory structure which makes the accurate separation of the boron signals from the background very difficult. This results in a relatively large error in the boron concentration and a poor sensitivity. The estimated sensitivity is about 1 at.% even for a long measurement time (11 hours) under channeling conditions. The spectrum of He-probe ERDA also has a background. However, the signal to background ratio is much better than HRBS and the background can be approximated by a simple straight line. This guarantees better sensitivity compared to HRBS. The sensitivity is estimated to be about 1 at.% for the measurement of 5 hours under non-channeling conditions. On the other hand, the Ar-probe ERDA provides almost background free boron spectra and the recoil cross sections are much larger than He-probe ERDA. This results in a good sensitivity. The estimated sensitivity is $\sim$0.1 at.% even at a reasonably short measurement time of 10 min. Ar-probe ERDA, however, suffers from multiple scattering and the depth resolution deteriorates very rapidly with depth.

Summarizing these results, He-probe ERDA has the best depth resolution and a reasonably good sensitivity, indicating that He-probe ERDA is the best method unless a very good sensitivity is required. If better sensitivity is required, the sensitivity of He-probe ERDA can be improved by installing a thin mylar foil in front of the detector as was done in Ar-probe ERDA.

Acknowledgments

The authors are grateful to Dr. Tomita for providing the Mylar foil and B-implanted Si (001) and Prof. Vanderforst for the B-doped Si (001). And also thank Mr. Mure (Kobe Steel Ltd.) for the Ar$^+$ probe ERDA measurements. This work was supported in part by Grant-in-Aid for Scientific Research from JSPS.

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