Technical Report

Reference Materials for SIMS Depth Profiling Analysis

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Secondary ion mass spectrometry(SIMS) is widely used for the in-depth analysis of minor impurities in solid materials. However, the distribution of constituent elements is seriously distorted by ion beam sputtering. Therefore, well-defined standard procedures and certified reference materials are required to get a depth profile close to the original one in SIMS depth profiling

KRISS established an ion beam sputter deposition system and certification method for standard reference material. The thickness and concentration of doping element were certified by high resolution TEM and inductively coupled plasma mass spectrometry (ICP-MS) with isotope dilution method. Three kinds of KRISS CRMs for sputter depth profiling were invented and developed for the international standard procedures.

1. Introduction

SIMS is an useful technique for the in-depth analysis of minor impurities in the field of semiconductor and new material because of its high sensitivity and detection capability of all elements including hydrogen. However, the surface deformation by collision cascade due to ion beam bombardment is an obstacle for the improvement of depth resolution. Therefore, the improvement of depth resolution is one of the most important issues in sputter depth profiling. Ion beam mixing, surface segregation, preferential sputtering and surface topographic development are the major factors that determine the depth resolution. Sputtering parameters such as the ion species, kinetic energy and angle of incidence must be optimized to improve depth resolution.

Although the quantitative analysis by SIMS is very difficult because the ionization yield of sputtered secondary particles can change by several orders of magnitude, SIMS is also useful for the quantitative analysis of minor impurities, where the matrix effect can be ignored.

Standard procedures and related reference materials are required for the standardization of surface analysis. International standardization activity for surface chemical analysis is being performed by the international organization for standardization (ISO), technical committee TC201. Recently, several standard procedures for sputter depth profiling have been developed.[1,2] ISO-14606 describes the guidelines for the optimization of sputter depth profiling parameters to achieve optimum depth resolution in XPS, AES and SIMS depth profiling. ISO/DIS-20341 specifies a method for evaluating the depth resolution parameters. ISO-14237 is an international standard procedure for the SIMS quantitative analysis of B in silicon.

In the case of depth profiling, well-defined standard reference materials were developed to minimize depth resolution, calibrate depth scale and evaluate the depth resolution capability. The surfaces of these materials must be flat and the interfaces must be sharp. Moreover, the surface modification by ion beam sputtering must be minimized. Several standard specimens have been developed by national standardization organizations such as National Institute of Standards and Technology (NIST, USA), National Physical Laboratories (NPL, UK), Korea Research Institute of Standards and Science (KRISS, Korea) and National Institute of Materials and Chemical Research (NIMC, Japan).

Amorphous Ta_2O_5 on Ta (NPL CRM No. S7B83 ; BCR No. 261)[3], polycrystalline Ni/Cr multilayers on Si (NIST SRM 2135)[4] and AlAs/GaAs superlattices (NIMC) [5,6] have been developed as standard reference materials for sputter depth profiling by XPS, AES and SIMS. NIST SRM 2136 is a marker type multilayer consisting of 7 Cr layers separated by very thin

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Cr_2O_3 layers.[7]. The oxide marker layers can be easily identified by enhancement of Cr^+ signal at the oxide layers.

Reference materials for SIMS quantification are generally fabricated by ion implantation because it is easy to choose the doping elements and substrate materials. NIST developed an ion implanted reference material for the quantitative SIMS analysis of boron in silicon NIST SRM 2137 is a single crystal silicon implanted with the isotope ^{10}B.

The international standard procedures and related reference materials can provide an important basis for improving the reliability of the depth profiling results. Recently a thin film growth chamber was established in KRISS and many kinds of reference materials for sputter depth profiling analysis have been developed. In this paper, three types of KRISS CRMs for sputter depth profiling and the related ISO standard procedures will be introduced.

2. Fabrication and Characterization

Thin films were grown by ion beam sputter deposition (IBSD) method. Target material is sputtered by 1 keV Ar^+ ion beam and deposited on a substrate wafer as shown in Figure 1. The ion beam sputter deposition chamber was connected to a multi-technique surface analysis system.[8] The thin films grown at the deposition chamber could be transferred to the analysis chamber without being exposed to air, and therefore the original chemical state, composition and impurities could be analyzed by *in-situ* XPS.

Various kinds of thin films can be grown by the combination of the target materials. Pure metallic thin films can be grown by sputtering and deposition of pure metal targets.

Oxide thin films can be grown by reactive sputter deposition of pure metals under oxygen gas flow. Multilayer thin films can be grown by alternating deposition of two target materials using a rotatable target holder as shown in Figure 2(b). Binary alloys can be grown by sputtering the two adjacent targets fixed at one side of the target holder. The relative composition of the two elements can be exactly controlled as the relative sputtering area of the two targets varies by moving the targets as shown in Figure 2(a).

The thickness of the thin film layer was controlled by the growth time. The growth rate was calibrated by TEM measurement of a preliminary thin film grown in a given time. The surface native oxide layer of substrate wafer was eliminated by rinsing in dilute HF solution. The thickness of the standard specimen for depth profiling was measured by high resolution transmission electron microscopy (HR-TEM), where the distance between the crystal planes can

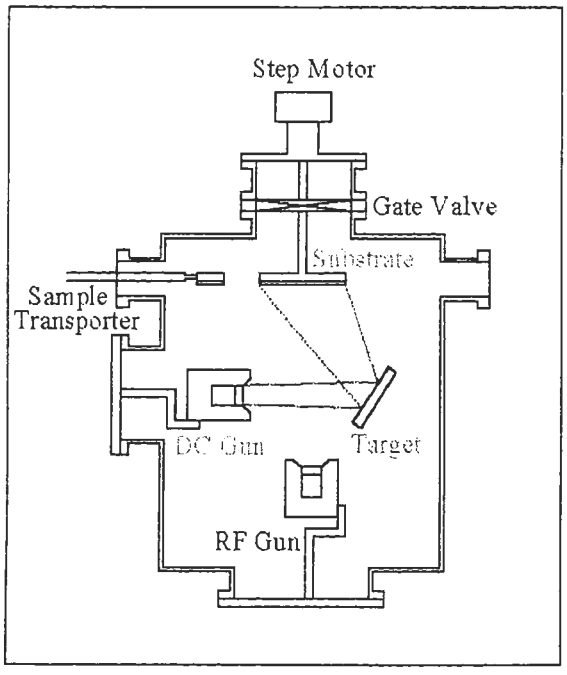

Figure 1. Schematic diagram of the ion beam sputter deposition (IBSD) system.

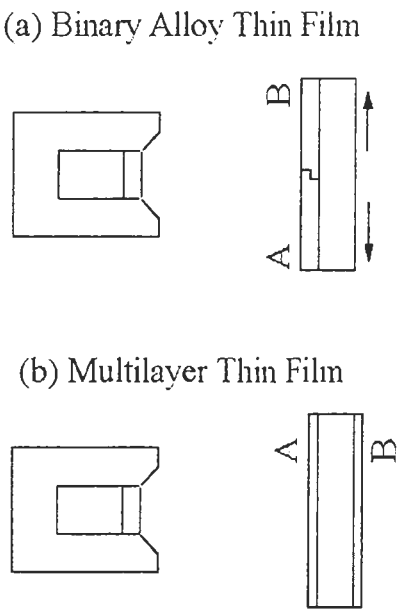

Figure 2. Schematic diagram of target holder for alloy(a) and multiplayer(b) growth.

be a good internal standard for the measurement of the film thickness.

The substrate was rotated with a speed of 30 rpm during thin film growth to improve the homogeneity and to minimize the surface roughness. The thin film was grown on silicon wafers and the wafer was divided into 10 mm x 10 mm specimens. The specimens taken from the center and edge of the wafer are not used as standard specimens, so that the variation of the thickness of the standard specimens is less than 1%.

Table 1. List of CRMs for sputter depth profiling developed by KRISS.

Use	CRM No.	Structure
Depth Profiling	KRISS CRM 103-04-101	Ta_2O_5/Ta Multilayer
SIMS Depth Profiling	KRISS CRM 103-04-100	Ta_2O_5/SiO_2 Multilayer
	KRISS CRM 103-04-102	Si/GaAs doped Si Multilayer
	KRISS CRM 103-04-103	Si/B-doped Si Multilayer
SIMS Quantification	KRISS CRM 103-04-300	B doped Si Thin Film

3. Reference Materials for Depth Profiling

In order to achieve improved depth resolution and accurate depth scale, sputter depth profiling parameters must be optimized by reference materials. For this purpose, many kind of multilayer systems such as metal/metal, metal/oxide, oxide/oxide and some epitaxial superlattices are required.

KRISS has developed three kinds of reference materials for sputter depth profiling as shown in Table 1. First group is multilayer for depth profiling by XPS, AES and SIMS. Second group is delta-doped multiplayer for the evaluation of SIMS depth resolution. The last one is uniformly doped Si thin films for quantitative analysis by SIMS.

(1) CRMs for depth profiling by XPS, AES and SIMS

Multilayer thin films with sharp interfaces are generally used in sputter depth profiling using XPS, AES and SIMS. The depth resolution is generally defined from the distance where the intensity changes from 84% to 16% of the peak intensity.[9] In the cases of depth profiling by XPS and AES this conventional definition is somewhat good for the evaluation of depth resolution because the matrix effect is not serious. However, the matrix change at a sharp interface results in troublesome interface artifacts in SIMS depth profiling. Therefore, it is very difficult to evaluate the SIMS depth resolution with a sharp interface.

ISO-14606 describes the guidelines for the optimization of sputter depth profiling parameters using superlattices and other multilayered systems in order to achieve optimum depth resolution in XPS, AES and SIMS depth profiling. For this standard procedure, Ni/Cr multiplayer (NIST SRM 2135), Ta_2O_5/Ta multilayer (KRISS CRM 103-04-101) and AlAs/GaAs superlattice (NIMC) were recommended as reference materials.

The Ta_2O_5/Ta multilayer CRM consists of alternating 5 Ta_2O_5 and 5 Ta layers. The crystal structure of Ta layer is polycrystalline and that of Ta_2O_5 layer is amorphous. Figure 3 shows SIMS depth profiles of the Ta_2O_5/Ta multilayer by Cameca IMS-4f. It shows appropriate dynamic range of Ta intensity for the 84-16% definition of depth resolution. Depth resolution is slightly deteriorated with sputter depth.

SIMS depth profiling was also performed by using argon ion beams. Depth resolution could be calculated at all incidence angles, because the

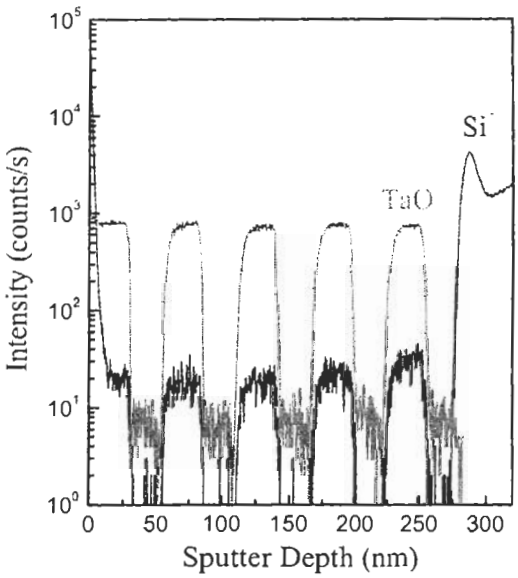

Figure 3. SIMS depth profiling of the Ta_2O_5/Ta multilayer by 7.5 keV Cs^+ ion beam. (4.5 keV bias, 52.2 ° incidence angle)

dynamic range of Ta^+ ion intensity at the Ta_2O_5/Ta interfaces are large enough to define the depth resolution. Depth resolutions at the first Ta_2O_5/Ta interfaces(31 nm) show similar values at the range of 1.8 - 2.2 nm at all incidence angles. The interface widths gradually increase with sputter depth and the degradation of the depth resolution is much severer at lower incidence angles due to the surface topographic development.

However, depth resolution can not be defined in the depth profiles by O_2^+ ion beam at near normal incidence angles because there is no large variation of Ta^+ ion intensity between the Ta_2O_5 and Ta layers as a result of severe oxidation of Ta surface by sputterin g with oxygen ion beam.
Although the dynamic range of Ta is not large enough, profiles at glancing incidence angles above 45° show sharp interfaces to define the depth resolution. The depth resolution seems to be somewhat deteriorated with the increase of incidence angle due to the surface topographic development.(Figure 4)

SIMS depth profiles by O_2^+ ion beam show abnormal interface artifacts at the Ta/Si interfaces. The Ta^+ ion intensity abnormally fluctuates near the Ta/Si interface. This abnormal interface

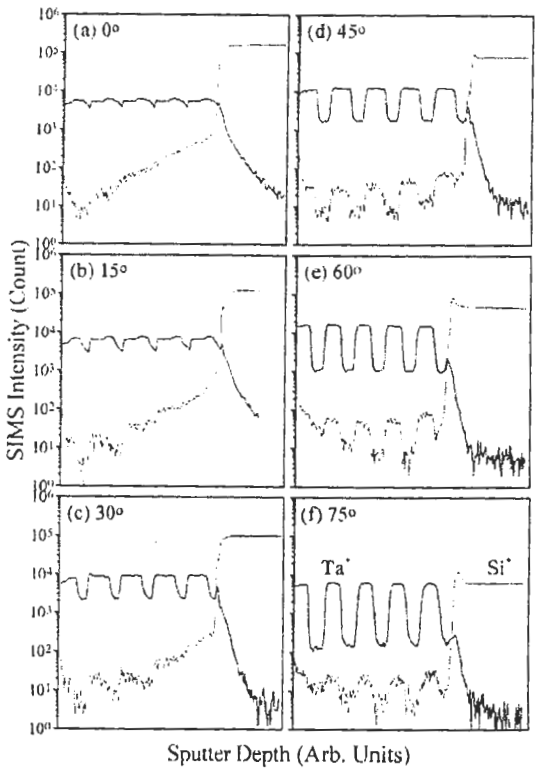

Figure 4. SIMS depth profiles of the Ta_2O_5/Ta multilayer thin film by 7 keV O_2^+ ion beam of various incidence angles

artifact has been found to be ascribed to the formation of crater-type topography which is developed on a flat surface where compressive stress can be accumulated sufficiently.[10,11] The abnormal interface artifact means that surface topography is not significantly developed on Ta_2O_5/Ta multilayer after sputtering with oxygen ion beam..

Surface topographic development was studied by AFM. The average roughness slightly increased from 0.6 to 1.4 nm after sputtering to the last Ta_2O_5/Ta interface by oxygen ion beam as the incidence angle increase from 0° to 75°. However, in the case of argon ion beam, the surface roughness decreased from 6.9 nm to 1.1 nm as the incidence angle increased from 0° to 75°.
These differences in surface topographic development due to different ion species can be explained by the crystallinity effect and surface inhomogeneity in chemical state due to ion beam bombardment.

(2) CRMs for SIMS depth profiling

Bombardment by energetic ions distorts the original profiles due to the momentum transfer. Therefore many efforts have been focused to the improvement of depth resolution. The 84-16% description of depth resolution in the multilayer thin films with sharp interfaces is not a good barometer for the evaluation of depth resolution in SIMS where reactive oxygen ions are mainly used to enhance the secondary ion yield. The matrix change at a sharp interface affects SIMS depth profiles through formation of interface artifacts so that it is very difficult to evaluate the SIMS depth resolution. To avoid the interface artifacts due to matrix change, multilayers separated with very thin marker layers can be used. In this delta-doped multilayers, full width at half-maximum (FWHM), the steepness of the leading/trailing edge of a sharp profile and the exponential decay length can be used as means to evaluate the SIMS depth resolution.[12,13]

The international standard procedure ISO/DIS-20341 specifies a method for estimating depth resolution parameters which are the leading edge decay length, the trailing edge decay length and the Gaussian broadening in SIMS depth profiling. This standard procedure requires well defined delta-doped multilayers. Ideal delta-layers have single atomic layer thickness. However, it is not always possible to make delta-layers or prove the single atomic layer thickness.

In order to be used as a delta-layer, the

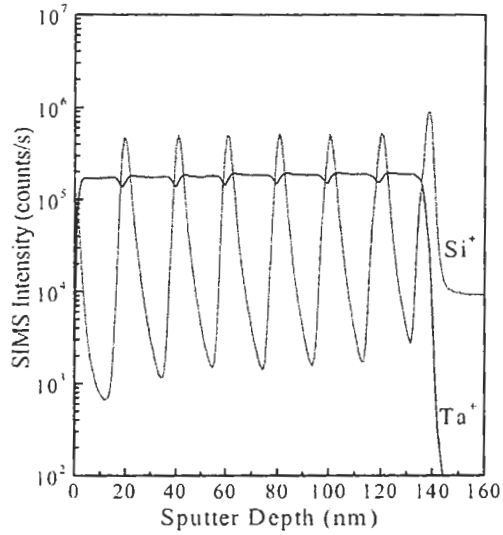

Figure 5. A SIMS depth profile of the Ta_2O_5/SiO_2 multilayer by 7.5 keV Ar^+ ion beam (4.5 keV Bias, 52.2° incidence angle)

following criteria must be satisfied. The matrix of sputtered surface layers shall not change during SIMS depth profiling so that no changes occur in any SIMS matrix effects or in the erosion rate during depth profiling. The surface and the delta-layers shall be flat and parallel to each other. The thickness of the doped delta-layers shall be sufficiently thin. The spacing between adjacent delta-layers shall be large enough so that the secondary ion intensity at the valley between layers is less than 1% of the peak intensity.

A Ta_2O_5/SiO_2 multilayer (KRISS CRM 103-04-100) was developed to minimize matrix effect and topographic development. Generally, the matrix effect can be minimized at the interface between the two fully oxidized materials.[14] Surface topographic development is also restrained at the surface of amorphous oxide layer.[15] 7 Ta_2O_5 layers were separated by 6 SiO_2 layers of 1 nm as shown in Figure 5. This CRM is not appropriate as a candidate for an ideal delta- doped multilayer reference material because the matrix Ta peak intensity fluctuates at the marker SiO_2 layers.

GaAs doped Si delta multilayer (KRISS CRM 103-04-102) was grown on a Si(100) wafer as shown in Figure 6.[16] A Si wafer was mounted on one side of the rotatable target holder and a Si wafer attached with a small piece (10 mm x 10 mm) of GaAs was mounted on the other side. By rotating the target holder, multilayers of Si and GaAs doped delta Si could be deposited. The CRM consists of 6 Si layers of about 83.8 nm separated by 5 GaAs doped Si layers of about 0.7 nm. The composition of delta-doped layers was estimated to be 24% GaAs by *in situ* XPS analysis by analyzing a 10 nm thick GaAs-doped Si layer

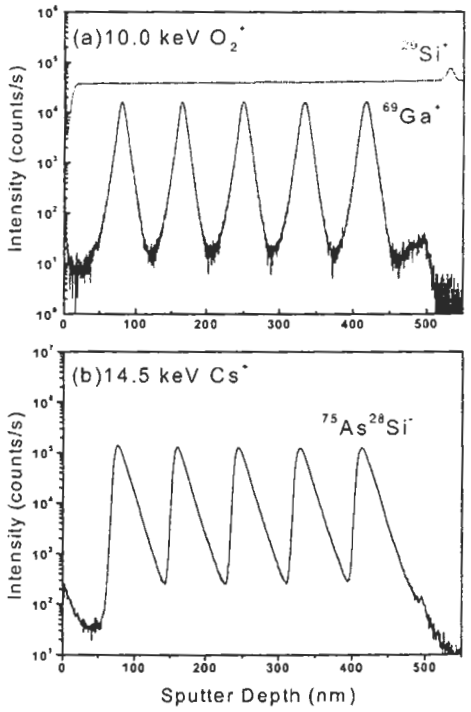

Figure 6. A positive(a) and negative(b) SIMS depth profiles of the GaAs doped Si delta multilayer.

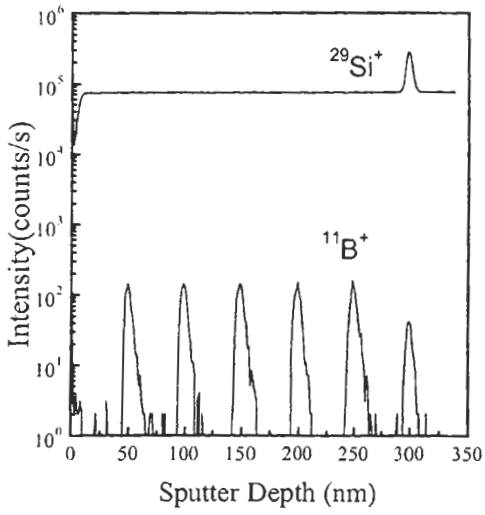

Figure 7. A SIMS depth profile of the B doped Si delta multiplayer by Cameca IMS-4f.
(7.5 keV O_2^+, 52.2° incidence angle)

analyzing a 10 nm thick GaAs-doped Si layer grown under the same conditions. The total thickness was measured by TEM and the thickness of each layer was estimated by the growth time and confirmed by SIMS analysis.

The accurate measurement of boron distribution in silicon is very important because B is one of the most important doping elements in semiconductor industry. Therefore, we developed a B doped delta Si multilayer (KRISS CRM 103-04-103) as a new candidate for the delta doped multiplayer reference material. A silicon wafer attached with a piece of BN of about 3 mm × 3 mm size was used as a target for B doped Si layer. The Si signal was not fluctuate at the deltalayers as shown in Figure 7. It shows much narrower delta layers than those of the GaAs doped Si delta multiplayer. This CRM will be useful for the evaluation of the SIMS depth resolution. In this CRM, the surface native oxide layer was not eliminated because it can be used as a marker layer of the interface.

(3) CRMs for SIMS quantification

Reference materials for SIMS quantification are generally fabricated by the ion implantation because it is easy to choose the doping elements and substrate materials. NIST SRM 2137 which consists of a single crystal silicon substrate ion-implanted with the isotope ^{10}B is one of the representative certified reference materials for quantitative SIMS analysis. SIMS quantification using an ion implanted reference material requires a rather complex calibration procedure because the in-depth distribution of implanted element is non-uniform. Whole range of the implanted zone must be profiled to sum up the number of the implanted atoms and the sputtered depth must be precisely determined directly or indirectly by such as profiler to estimate the analyzed volume.

ISO-14237 is a new international standard procedure for the quantitative SIMS analysis of boron in silicon. This document describes a new method to compensate the problems of the ion implanted references. It requires uniformly doped Si specimens as secondary reference materials which are used in daily analyses. The boron atomic concentration of the secondary reference materials must be certified by a primary reference material. According to the ISO document, NIST SRM 2137 is the only certified reference material (CRM) which is used as a primary reference material.

In the development of a new reference material for SIMS quantification, the certification of the doping level is very important. In the most of the ion implanted reference materials, the doping level of the implanted atoms is measured by ion dosimetry. Although the ion dosimetry method is simple, it is not so correct to be used as a certification method. In this point, the retained dose of ^{10}B atoms in the NIST SRM-2137 was certified by neutron depth profiling method.

If the concentration of doping elements can be certified, uniformly doped Si will be much more correct and convenient. Homma et. al. have developed B-doped bulk Si as a new type of reference material for SIMS quantification, where the doping level of B atoms were estimated by measurement of carrier density.

KRISS developed an uniformly doped Si thin film (KRISS-CRM 103-04-300) as a reference material for SIMS quantification of boron in silicon. The boron doped silicon thin films were fabricated by ion beam sputter deposition. The film thickness was measured by high resolution transmission electron microscopy (HR-TEM) and then the total numbers of atoms in a fixed volume could be measured by inductively coupled plasma mass spectrometry (ICP-MS) with isotope dilution method.[17]

Boron concentration was measured by SIMS

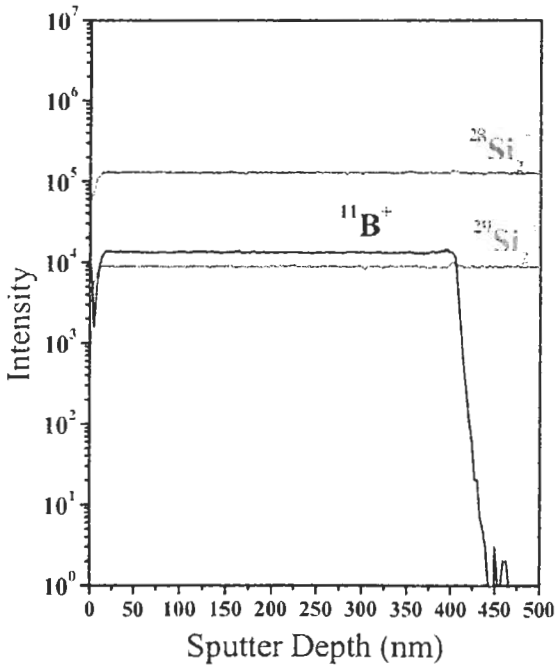

Figure 8. A SIMS depth profile of the B doped Si thin film by O_2^+ ion beam.

to compare with the results by ICP-MS. Figure 8 shows a SIMS depth profile of the KRISS-CRM 103-04-300 obtained by Cameca ims-4f. SIMS quantification has performed by using NIST SRM-2137 where the implanted ^{10}B ion dose is 1,018 $x10^{15}$ atom/cm^3. The boron concentration measured by SIMS well agreed with the ICP-MS data ($7.01x10^{19}$atoms/cm^3) within the difference of about 3%.

In this CRM, the relative sensitivity factor (RSF) of B can be easily calculated from the relative intensity of B and Si matrix. The RSF can be obtained at any point of the SIMS depth profile because the intensity of B and Si are constant with depth.

From these results we can say that the new reference material will provide more accurate measurement of dopant concentration as well as much simpler calibration. Moreover the uniformly doped Si thin film can be used as a reference material for depth profiling because the interface is very sharp as shown in Figure 8.

4. Conclusions

Development of well-defined standard reference materials and standard procedures are required for standardization of surface analysis.

KRISS established an ion beam sputter deposition system and developed many kinds of reference materials for surface analysis. The concentration of the uniformly-doped silicon thin films for SIMS quantification was measured by inductively coupled plasma mass spectrometry (ICP-MS) and the thickness was certified by high-resolution transmission electron microscopy (HR-TEM). KRISS CRMs were invented to used as reference materials for international standard procedures. Three types of CRMs found to be useful for the optimization of experimental parameters in AES, XPS and SIMS depth profiling, evaluation of SIMS depth resolution and SIMS quantification.

Acknowledgements

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