Development of a Certified Reference Material with Delta-Doped Boron Nitride Layers for Surface Depth-Profile Analysis*

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The certified reference material (NMIJ CRM 5206-a) is composed of a Si substrate with homogenously doped arsenic, and multiple alternately deposited boron nitride (BN) layers and Si layers. The designed thicknesses of the Si and BN layers were 8 nm and 0.05 nm, respectively. The thickness of each layer was measured using X-ray reflectometry (XRR), and the periodicity of the distance between the delta BN layers was determined to be 8.3 nm. The expanded uncertainty was 0.2 nm and was calculated using a coverage factor (k) of two that gives a level of confidence of approximately 95%. The concentration of the As atoms in the Si substrate, measured by instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectrometry (ICP-MS), was determined to be 0.80 g/kg with an uncertainty of 0.04 g/kg (k = 2). For the calibration of the developed reference material, three institutes with two types of secondary ion mass spectrometry (SIMS) instruments derived the SIMS depth profiles of the implanted arsenic atoms. The results were compared, and it was observed that the relative standard deviation (RSD) of the profile parameters was approximately 10%. [DOI: 10.1380/ejssnt.2016.125]

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I. INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a useful technique for analyzing the surface composition of a material. To obtain an accurate SIMS analysis, certified reference materials (CRMs) with multilayer structures, such as the NMIJ CRM 5202-a with a SiO₂ (20 nm)/Si(20 nm) multilayer [1], and the NMIJ CRM 5203-a with a GaAs(10 nm)/AlAs(10 nm) superlattice have been developed.

Advanced fabrication techniques for semiconductor devices have witnessed an improvement in the precision of the dopant control. The concentration of the channel-dopant has been increasing, but the depth of the contact junction has been decreasing according to the international technology roadmap for semiconductors (ITRS) [2]. Moreover, the structure of the advanced transistor has been shifting from a planar 2D structure to a nonplanar 3D structure, such as the FinFETs [3] that are expected to provide future scalability and electrostatic control. To fabricate 3D-structured FinFETs, higher precision in the dopant control is essential [4]. Along with the dopant control, high precision in dopant characterization will also be essential for the fabrication. Several characterization techniques such as the atom probe [5], low electron energy EDX, and through-fin SIMS have been studied [6].

To improve the precision of the SIMS analysis, the realization of both the depth resolution and the sputtering rate stability by a calibration procedure will be significant. At the early stage of the sputtering, both the secondary ion yield and sputtering rate are not constant, and a dynamic equilibrium between sputtering and atomic mixing is not established [7, 8]. This non-equilibrium region, so-called the transient region, is not negligibly shallow for practical analysis because the dopant-implanted depth has been equivalently ultra shallow. The formation of the transient region is caused by the ion irradiation conditions; therefore, the calibration is increasingly important.

The standard materials were developed for the calibration of the depth analysis, and the shallowly arsenic-implanted CRMs with a density of 3 x 10¹⁵ [9] and 6 x 10¹⁴ atoms/cm² [10] were supplied. With these reference materials, all the sputtered arsenic atoms can be calibrated by sputtering-out the entire arsenic-implanted region.

Another type of the standard material has a multilayer structure that has delta-doped layers considerably thinner than the other layers [7, 11–18]. The advantage of this structure is that an almost constant sputtering rate can be obtained during the sputtering of the multilayer, and the delta layer can be a depth scale, if the distance between the delta-layers is measured accurately.

In this report, the development of a CRM with a multilayer structure composed of a Si layer and a delta-layer made of boron nitride (BN) is described. The designed thickness of the delta layer is proportional to 0.05 nm. The substrate is a homogenously arsenic-doped Si with an arsenic concentration of ~ 10¹⁵ atoms/cm³. Owing to this structure and concentration, both the depth and the concentration of the ultra-shallow profiles can be calibrated with one sample. We also carried out a round-robin test

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II. EXPERIMENTS

A. Fabrication of a multilayer structure

Arsenic-doped Si(100) wafers with resistivity of approximately 0.005 Ω·cm and a diameter of 100 mm, were used as the substrate. One wafer was used as a CRM and another as a standard sample for the round-robin test. The arsenic concentrations were on the order of 10\(^{-15}\) atoms/cm\(^3\). Multiple layers of boron nitride (BN) films and Si films were deposited alternately by the magnetron sputtering method. The designed thickness of the Si layers and the delta BN layers were 8 nm and 0.05 nm, respectively. As shown in Fig. 1, delta BN layers separated the four Si layers and the Si substrate. After the multilayer fabrication, the wafers were cut into samples with a size of 7.5 mm × 15 mm.

B. Characterization of the fabricated standard material

To verify the quality of the fabricated materials, multiple surface analysis methods were utilized. Transmission electron microscopy (TEM), scanning TEM (STEM), and SIMS were used to evaluate the abruptness of the interfaces and the uniformity of the arsenic distribution on the substrate. The periodicity of the delta BN layers was determined using X-ray reflectometry (XRR); the arsenic concentration was determined by instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectrometry (ICP-MS). The number of measured samples were four for the XRR, three for the INAA, and four for the ICP-MS.

For the thickness measurement, a traceable XRR instrument [19] with an angle self-calibration system was used. The uncertainty of the measured angle was less than 1 arcsecond [20]. The Cu-K\(_\alpha\) X-ray source had an uncertainty of 3.8×10\(^{-4}\) in Δλ/λ. The scanning range of the 2θ angle was 0°–7° with a resolution of 0.01°.

The INAA experiments were performed at the Kyoto University Research Reactor Institute (KURRI). Radioactivation via neutron beam irradiation was carried out with a neutron flux of 5.5 × 10\(^{12}\) cm\(^{-2}\)s\(^{-1}\) over an irradiation time of 10 min and every sample was measured three times. Four standard samples with controlled arsenic weights were fabricated from a NIST SRM 3103a, an arsenic standard solution with a concentration of 9.999 mg/g. As an internal reference, a controlled volume of gold standard solution (NIST SRM 3121) was added to the measurement samples and the arsenic standard samples. The intensities of the γ-ray emissions of the \(^{76}\)As (559 keV) and the \(^{198}\)Au (411 keV) atoms were measured. The calibration of the signal intensities was performed considering three factors: the counting loss, the intensity decay during the measurement, and the intensity decay during the period between the termination of the radioactivation and the start of the measurement.

An ICP-MS analysis was followed to determine the arsenic concentration, wherein the sample was enclosed in a perfluoralkoxy (PFA) vessel with 5 mL of HNO\(_3\) and 1 mL of HF solution, followed by a microwave-assisted digestion. An \(^{89}\)Y solution (concentration of 3 ng/g) was used as an internal standard. The ICP-MS instrument (7500C, Agilent) was equipped with a glass nebulizer (100 μL) and a Scott-type spray chamber (2°C). The typical operating parameters were as follows: the incident radio frequency (RF) power was 1.6 kW, outer Ar gas-flow rate was 15 L·min\(^{-1}\), intermediate Ar gas-flow rate was 0.9 L·min\(^{-1}\), carrier Ar gas-flow rate was 0.8 L·min\(^{-1}\), and the make-up Ar gas-flow rate was 0.4 mL·min\(^{-1}\). The measurements were performed in a collision mode with He gas. A gravimetric preparation method was used to ensure SI traceability and a Japan calibration service system (JCSS) standard solution with an arsenic concentration of 1003 mg/L was used.

SIMS analysis was performed with a Cs\(^{+}\) ion primary beam of 350 eV. The signals of \(^{75}\)As\(^{28}\)Si\(^{+}\), \(^{28}\)Si\(^{30}\)Si\(^{+}\), and \(^{11}\)B\(^{28}\)Si\(^{−}\) were measured.

With a TEM (JEOL, JEM2100F, 200 kV) and a STEM (JEOL, ARM-200F, 200 kV), cross-sectional images of the multilayers were obtained. Magnification calibration was performed using a (004) lattice distance of 0.13576 nm as a reference.

C. Round-robin test for the depth profile of the arsenic-implanted Si

A shallowly arsenic-doped sample with an As\(^{+}\) implantation at an energy of 1 keV was prepared. The concentration was defined to be 1.056×10\(^{15}\) atoms/cm\(^2\) by a total-reflection X-ray fluorescence (TXRF) calibrated by the NMIJ CRM 5603-a. Three institutes were involved in this SIMS comparison test with two types of instruments: an ADEPT 1010 (ULVAC PHI) and a SIMS 4550 (CAMECA). The incident angles were 60° and 50°, re-

FIG. 1. Schematic view of the reference materials composed of a Si substrate with homogenously doped arsenic and multiple layers of alternately deposited delta layers made of boron nitride (BN) and a Si film layers.
FIG. 2. Measured XRR spectrum and best-fitted simulated spectrum with BN-layer thicknesses of 0.3 nm (red line), 0.5 nm (green line), and 1.0 nm (blue line). The inset is an illustration of the multilayer structure used in the best-fit evaluation procedure. Distance 1 and Distance 2 are defined as the sum of the thicknesses of the BN delta layer and the Si layer beneath the BN layer.

spectively. The primary ion was Cs\(^+\) with an energy of 350 eV. The developed material calibrated the depth scale and the arsenic sensitivity.

III. RESULTS AND DISCUSSIONS

A. Characterization of the multilayer

For the XRR analysis, we used a multilayer structure that had SiO\(_2\) layers on the top surface and just above the Si substrate, as shown in the inset of Fig. 2. The simulated spectrum based on this model structure was generated and fitted to the XRR measurement spectra. The fitting parameters were the film thickness, film density, and the roughness at the surface and the interface. The density of the Si substrate was assumed to be 2.330 g/cm\(^3\). Finally, the best-fit spectrum was determined. The model structure in Fig. 2 had a lower fitting residual error than the multilayer structure without the SiO\(_2\) layers.

All the best-fitted spectra derived for BN-layer thicknesses less than 1.2 nm had almost the same squared sum errors and all the simulated spectra for different BN-layer thicknesses produced the same results. For example, three simulated spectra with BN-layer thicknesses of 0.3, 0.5, or 1.0 nm coincided with each other, as shown in Fig. 2. In this study, the XRR analysis could not determine the exact thickness of the BN layer. However, the thickness of the BN layer was limited to less than 1.2 nm.

Another parameter of the fitting solution, the BN film density, exhibited a gradual increase as the thickness of the BN layers decreased. When the thicknesses of the BN layers were less than 0.2 nm, the film density became considerably larger than the BN crystal density; this is not acceptable. Therefore, the BN-layer thickness is expected to be greater than 0.2 nm. Additionally, the BN layer roughness parameter forces the BN-layer thickness to be greater than 0.3 nm. The above considerations led to the conclusion that the range of the BN-layer thickness should be between 0.3 nm–1.2 nm.

We evaluated the film thicknesses of the Si and BN layers for BN-layer thicknesses ranging from 0.3 nm to 1.2 nm with 0.1 nm increments. Distance 1 and Distance 2 in the inset of Fig. 2 showed almost the same value. Then, we defined the periodicity of the BN layers as the average of the two resultant distances and the periodicities for each BN layer thickness were between 8.34–8.37 nm. As the periodicities were almost equal, the average periodicity was defined as a reference value of the CRM. It is noted that the BN-layer thickness is one of the uncertainty sources because any value for the BN-layer thickness between 0.3 nm–1.2 nm is possible.

The analytical uncertainty was calculated based on the guide to the expression of uncertainty in measurement (GUM) [21]. The main sources of uncertainty were the deviation between the Distance 1 and the Distance 2, original location of the sample in the wafer, and the measurement repeatability. Other sources of uncertainty were the BN-layer that may have the thickness between 0.3 nm–1.2 nm, the scanning angle reproducibility, the accuracy of the fitting analysis, and the wavelength of the X-ray source.

Finally, the BN-layer periodicity was determined to be 8.3 nm, as a reference value of the CRM. The expanded uncertainty was 0.2 nm and was calculated using a coverage factor (\(k\)) of two, with a confidence level of approximately 95%.

The long-term stability of the multilayer films was confirmed by an XRR analysis. Annual XRR analysis, over a period of 5 years, showed that the periodicity of the delta BN layers remained within the range of the expanded un-
The high-angle annular dark-field (HAADF)-STEM image in Fig. 3 depicts the BN layers as distinct bright lines. The contrast of the BN layers was 5% brighter than the Si layers. The distance between the BN layers was evaluated to be between 8.3 nm–8.4 nm that was consistent with the XRR results. Interestingly, the BN layers appeared as bright, wide lines. The lines were wider than the designed thickness of 0.05 nm, i.e., 0.9–1.2 nm at a full width at the half maximum (FWHM) of the line contrast. The lines had a contrast brighter by 5% than the Si layers despite the absence of metals such as Fe, Cr, and Ni in these layers. Further investigation is necessary to explain and support this result.

### B. Determination of the arsenic concentration

To evaluate the arsenic concentration, INAA analysis was utilized. The mass of the As was calculated using

\[
m_{\text{As}} = \frac{1}{a} \left( \frac{R_{0,\text{As}}}{R_{0,\text{Au}}/m_{\text{Au}}} - b \right)
\]

where \( R_{0,\text{As}} \) is the intensity of the arsenic signal, \( R_{0,\text{Au}}/m_{\text{Au}} \) is the intensity of the Au signal per unit mass, and \( a \) and \( b \) are the slope and intercept of the calibration curve, respectively. The intensities of the γ-ray emissions tended to vary because the irradiance intensity of the neutron beam varied with time, with flux variations in the irradiating location. To suppress these variations, the Au signal was used as an internal standard. The main sources of the uncertainty were the prepared standard solutions (0.34% RSD), the calibration curve (0.99% RSD), and the repeatability and reproducibility (0.34% RSD). Traceability was maintained using the arsenic standard solution NIST SRM 3103a. Further, the INAA measurement determined the arsenic concentration as 0.80 g/kg with an uncertainty of 0.02 g/kg (\( k = 2 \)).

The arsenic concentration was also determined by an ICP-MS analysis. It used a JCSS standard solution as the calibration source. The validity of the analytical procedure was confirmed by the measurement of the arsenic concentration of a NMIJ CRM 5604-a with a reference value of 78.6 ng/cm\(^2\) and an uncertainty of 2.1 ng/cm\(^2\) (\( k = 2 \)). The main sources of the uncertainty were the standard solution (0.30% RSD) and the coefficients of the calibration curve (0.72%). Other factors were the analytical uncertainty, the weight set uncertainty, and the diluting fluid. Further, the ICP-MS measurements determined the concentration as 0.797 g/kg with an uncertainty of 0.016 g/kg (\( k = 2 \)).

Both the determined arsenic concentrations were in agreement with each other. The final arsenic concentration was defined as the weighted mean in which the weight coefficients were the inverse of the squared uncertainty. Finally, the reference value of the CRM was determined to be 0.80 g/kg.

Another Si wafer was also analyzed using the same procedure, and its arsenic concentration was 0.77 g/kg. This wafer was used as the reference material for the SIMS round-robin test which is described in section 3.4.

### C. Depth-profile analysis

The SIMS depth profile of the developed sample is shown in Fig. 4(a). The four peaks of the \(^{11}\text{B}^{28}\text{Si}^-\) signal correspond to the BN delta layers and the flat \(^{28}\text{Si}^{75}\text{As}^-\) signal region corresponds to the Si substrate. The \(^{11}\text{B}^{28}\text{Si}^-\) peaks have a long trailing edge; however, these edges had an almost equal decay length of 9.0 ± 0.1 nm/decade. The distance between the first peak and the second peak was the same as that between the second and the third. Therefore, the transient region had already vanished with the appearance of the first BN layer and a constant sputtering rate was maintained between the first peak and the third peak. The arsenic intensity cor-
The energy of the arsenic was 1 keV, with a density of \(1.056 \times 10^{15}\) atoms/cm\(^2\). An analysis of the shallowly implanted arsenic by Institute A resulted in a peak of \(8.3\) nm, but the third institute showed \(1.24\) nm. The average intercepts were 2.39 and 2.38 nm, with a standard deviation of 8.7% in RSD that was consistent with the calibrated value of \(1.056 \times 10^{15}\) atoms/cm\(^2\).

Comparing these depth profiles, the depth where the arsenic concentration was of \(1.4 \times 10^{19}\) atoms/cm\(^3\), was approximately 10 nm, and the dispersion of the depth was 6% in RSD. The variation had been 14% in RSD in the previous round-robin test that had been carried out by four institutes with a Cs\(^+\) ion beam of 500 eV, without the use of a reference material. Thus, the reference material improved the accuracy of the SIMS analysis.

To further characterize the accuracy of the derived depth profile, three parameters were evaluated: the total number of implanted arsenic atoms (NAs), the peak concentration (Cpeak), and the depth at the peak (Dpeak). The average NAs was \(1.10 \times 10^{15}\) atoms/cm\(^2\) with a deviation of 8.7% in RSD that was consistent with the calibrated value of \(1.056 \times 10^{15}\) atoms/cm\(^2\). The deviations of the other parameters were 9.8% for the Cpeak and 12% for the Dpeak, respectively.

The measurement accuracy, at this moment, cannot be improved further. In Fig. 6, at depths greater than approximately 10 nm, the concentration has considerable variations. One of the reasons is the differences in the incident angles of the primary beam. A smaller incident angle of its primary energy tends to cause a lower depth resolution, and the depth profile has a long trailing edge in the deep region. Hence, the calibration method for the incident angle effect would be important for an accurate measurement. Another reason might be the differences in the signal background that depends upon the individual instruments. Additionally, the evaluation of the highly doped arsenic concentration from the high intensity \(^{75}\text{As}^{28}\text{Si}^-\) signal could be affected by signal saturation; this has to be considered for an accurate measurement. Besides, the beam current stability is essential for an accurate analysis. In this study, the stability determined by one institute was limited to 5% and it was clarified using the reference material. Therefore, regular calibration with a reference material will be practically beneficial for an accurate SIMS analysis.

### IV. SUMMARY

A certified reference material (CRM), NMIJ CRM 5206-a, was developed as a reference material for the SIMS analysis. It consisted of BN delta layers and a substrate with a high arsenic concentration and can calibrate both the etching rate and arsenic sensitivity. The reference value is the BN-layer periodicity that is \(8.3\) nm with an expanded uncertainty of \(0.2\) nm \((k = 2)\). Another reference value is the arsenic concentration that is \(0.80\) g/kg with an uncertainty of \(0.04\) g/kg \((k = 2)\). The accuracy of the depth profile of the shallowly doped arsenic can be improved using a calibration based on the reference material.

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