# Sputter Depth Profiling by SIMS; Calibration of SIMS Depth Scale Using Multi-layer Reference Materials

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(Received: January 19, 2009; Accepted: February 20, 2009)

In-depth distribution of doping elements in shallow depth region is an important role of secondary ion mass spectrometry (SIMS) for the development of next-generation semiconductor devices. KRISS has developed two types of multi-layer reference materials by ion beam sputter deposition. A multiple delta-layer reference material where the layers of one element are very thin can be used to evaluate SIMS depth resolution, to calibrate the depth scale and to monitor sputtering uniformity. The scale of a stylus profilometer can be also calibrated by comparison of the crater depths measured by a stylus profilometer and the certified thickness of the reference material measured by high resolution TEM. In a Korean round robin test for the scale calibration of a stylus profilometer using a Si/Ge multiple delta-layer (MDL), the average slope of the linear fitting results between the measured depth and the nominal depth was 0.989 with the standard deviation of 0.05. In depth scale calibration using a Si/Ge multi-layer reference material showed that the determination of interface position is very important to calibrate the sputtering rates of two different constituent materials. Especially, it is critical to define the positions of interfaces in a SIMS depth profile with interface artifacts.

## 1. Introduction

Although SIMS is a useful technique for the in-depth analysis of constituent elements, the determination of depth scale is very complicated.[1-3] Change of sputtering rate in shallow depth region is a great difficulty in metrology for next-generation semiconductor process. [4,5]

Depth scale in a SIMS depth profile is generally calibrated by the measurement of crater depth using a stylus profilometer or an optical interferometer. Calibration methods for depth scale in depth profiling analysis are described in ISO/TR-15969.[6] The delta-layers in a MDL film can be used as marker layers for the calibration of depth scale and evaluation of depth resolution.[7,8] If the positions of delta-layers in a MDL certified reference material (CRM) are certified, SIMS depth scale and the vertical scale in step-height measurement can be calibrated from the certified positions of the delta-layers. Recently, Si/B-doped Si and Si/Ge MDLs were developed as CRMs for the calibration of SIMS depth scale.[9,10]

Interface artifact is a troublesome problem for the calibration of SIMS depth scale in multi-layer (ML) films.[1] The origin of interface artifacts in a SIMS depth profile of a Pt/Co multi-layer using a $C_{60}$ source was found to be matrix effect. [11] Several ML reference materials have been developed by national measurement institutes. Polycrystalline Ni/Cr multi-layers [12], AlAs/GaAs superlattices [13,14] and $Ta_2O_5$/Ta multi-layer [15] have been developed for depth scale calibration or determination of sputtering rate.

In this paper, methods to calibrate SIMS depth scale using two kinds of reference materials are introduced.

## 2. Fabrication of the samples

A Si/Ge MDL and a Si/Ge ML films were grown by ion beam sputter deposition (IBSD) system in KRISS. The target material is sputtered by a 1 keV $Ar^+$ ion beam produced by a Kaufmann-type DC ion gun and deposited on a substrate at room temperature. The film can be grown on a 150 mm diameter Si wafer rotating with a speed of 30 revolutions per minute to improve the homogeneity of film thickness. Si/Ge multi-layer films are grown by alternating deposition of Si and Ge targets using a rotatable target holder. The relative film thickness was controlled by the growth rate calibrated by high resolution transmission electron microscopy (HR-TEM) measurement of a thin film grown in a known time.

Figure 1 shows TEM images of the Si/Ge MDL (a) and the Si/Ge ML (b) films. In the Si/Ge MDL, the Si layers of about 39 nm are separated by Ge delta-layers of about 0.4 nm thickness. In the Si/Ge ML film, the Si and Ge layers of about 38 nm were deposited on Si (100) wafer.

The certified film thickness and uncertainty of the two films are tabulated in Table 1. The film thickness was determined by HR-TEM. The crystalline lattice planes of Si (100) substrate are used as an internal standard for the measurement of film thickness.

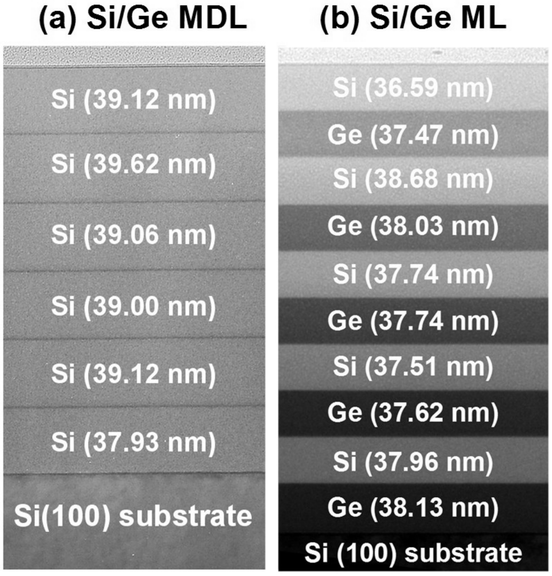


**Fig. 1** Certification of the film thickness by HR-TEM based on the Si lattice constant.

**Table 1** Thickness and uncertainty of the Si/Ge MDL and ML films measured by HR-TEM. The layer numbers were designated from surface.

| Si/Ge MDL | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Si thickness | 39.12 | 39.62 | 39.06 | 39.00 | 39.12 | 37.93 |
| *U* (nm) | 0.26 | 0.21 | 0.22 | 0.19 | 0.18 | 0.23 |

| Si/Ge ML | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Si thickness | 36.59 | 38.68 | 37.74 | 37.51 | 37.96 |
| *U* (nm) | 0.75 | 0.75 | 0.74 | 0.75 | 0.75 |
| Ge thickness | 37.47 | 38.03 | 37.74 | 37.62 | 38.13 |
| *U* (nm) | 0.77 | 0.74 | 0.76 | 0.75 | 0.77 |

In the TEM measurement, the combined standard uncertainty $U_c$ is calculated from the equation $U_c^2 = U_m^2 + U_r^2$. The first term ($U_m$) is the standard uncertainty from the thickness measurement in a TEM image. The second term is the standard uncertainty ($U_r$) of the reference layer based on the measurement of the distance between 50 Si lattice planes. The expanded uncertainty $U = kU_c$, where k is a coverage factor equivalent to approximately a 95 % confidence interval, are tabulated in Table 1 with the certified film thicknesses.

## 3. Results and discussion

### 3.1 Measurement of crater depth by a stylus

The measurement of crater depth is a general method to calibrate SIMS depth scale as described in ISO/TR-15969. Figure 2 shows the method to measure the crater depth by a mechanical stylus profilometer. Crater depth is measured from the average distance between the original surface (region B or C) and the crater bottom (region A) from which the measured signal is derived. Leveling of the profile so that regions B and C are at the same height, and setting the width of region A equal to the dimension of the SIMS analysis region, are important points to be recommended for the accurate calibration of SIMS depth scale.

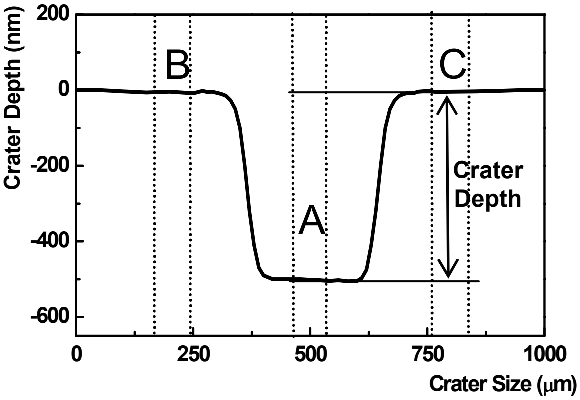


**Fig. 2** Measurement of crater depth by a stylus profilometry.

The crater depth was measured by an alpha step IQ (KLA Tencor, USA) in KRISS. The vertical scale of the stylus profilometer was calibrated using a standard material with a certified step-height of 89.4 nm and an expanded uncertainty of 1.2 nm. The standard deviation was about 0.34 nm when the step-height was measured 12 times.

In the crater depth measurement by a stylus profilometer, the standard uncertainty is calculated from the equation $U_c^2 = U_r^2 + U_m^2$. $U_r$ is the relative standard uncertainty of repeated step-height measurements combined with the stated relative standard uncertainty of the certified value. $U_m$ is the standard uncertainty of depth calibration using a step-height standard. The measurement uncertainty ($U_m$) is derived from the standard deviation ($S_m$) divided by the square root of the number of measurements. The expanded uncertainty in the measurement of crater depth by a KRISS stylus profilometer was 1.5 nm in 95 % confidence.

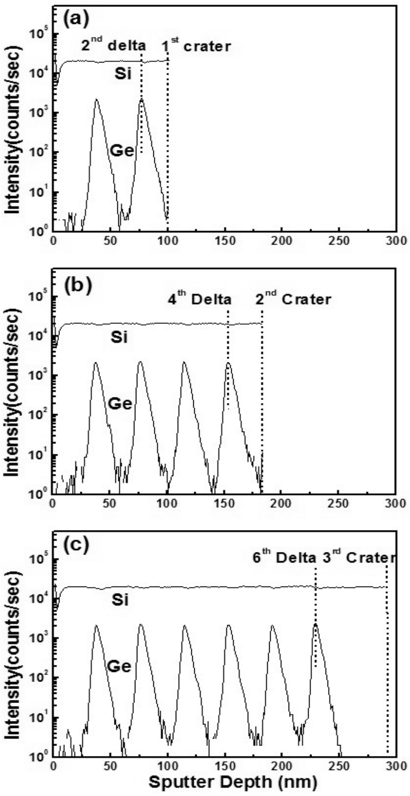
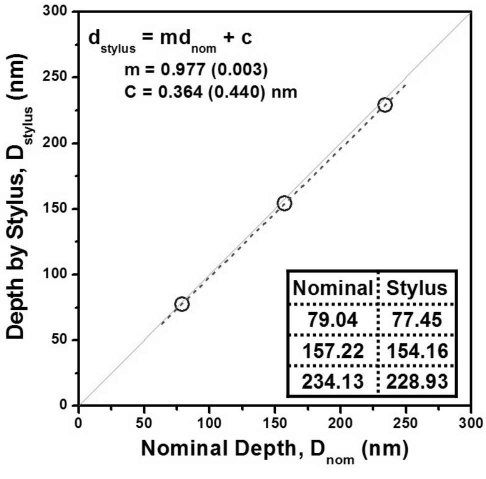


**Fig. 3** SIMS depth profiles of the Si/Ge MDL with different depths by 2 keV $O_2^+$ ions .



| Nominal | Stylus |
|---|---|
| 79.04 | 77.45 |
| 157.22 | 154.16 |
| 234.13 | 228.93 |

**Fig. 4** An example of depth scale calibration of a stylus profilometer.

### 3.2 Calibration of depth scale by a Si/Ge MDL

Figure 3 shows SIMS depth profiles of the Si/Ge multiple delta-layer measured by Cameca ims-7f SIMS. $O_2^+$ ion beam of 2 keV was used as a sputtering source. The delta-layers in the Si/Ge MDL film can act as marker layers to convert sputter time to sputter depth. The crater depth of the Si/Ge MDL film can be determined from the certified depth of Ge delta-layers and the measurement of depth by a stylus profilometer.

Figure 3 and 4 show an example of depth scale calibration of a stylus profilometer. The positions of the delta-layers can be determined at local maximum where the intensity of Ge is maximized and at half maximum where the intensity of Ge signal decreases to half of the maximum intensity on the trailing edge.

The depth of delta-layer was determined at the peak maxima as shown in Figure 3. The result of the straight line fit of the two series of different depths is expressed by the following equation.

$$d_{\text{stylus}} = md_{\text{nom}} + c \text{ ------------------------- } (1)$$

Here, the offset $c$ is the excess depth when the nominal depth calibrated by HR-TEM and SIMS is extrapolated to zero and the slope $m$ is a scaling constant. The table in Figure 4 shows that the slope m and the offset c are determined to be 0.977 ± 0.003 and 0.364 nm ± 0.440 nm, respectively. The real crater depth can be derived by equation (1) from the slope m and offset value $c$.

### 3.3 Round robin test for the calibration of SIMS depth scale by a MDL film

Korean round robin test for the calibration of SIMS depth scale has been performed using the Si/Ge MDL film. 12 laboratories were participated in the RRT as tabulated in Table 2. 10 magnetic sector SIMS, 1 quadrupole SIMS and 1 TOF SIMS were used in this RRT. Three craters with different depth were formed by SIMS depth profiling as shown in Figure 3 and the depths of the 2nd, 4th and 6th delta-layers determined by the measurement of the crater depths using a stylus profilometer or an optical interferometer were compared with the certified depths in Table 1. The positions of the delta-layers were determined by the depths at the local maximum

The slope m shows a wide range between 0.871 and 1.099. The average of the slope and the offset values are 0.989 and 0.050 nm, respectively. If the minimum and maximum values of the slopes are eliminated, the average slope of 0.990 is similar to that without elimination, however, the offset value is greatly improved to 0.020 nm.

**Table 2** List of the participants in the RRT

| Laboratory | Participants |
|---|---|
| Hynix Semiconductor | C. S. Jeong, J. H. Kim |
| ETRI | S. K. Kim |
| KBSI | T. E. Hong |
| LG Elite | J. W. Lee |
| KRISS | K. J. Kim |
| Samsung SDI | M. K. Park |
| Samsung LCD | J. H. Moon |
| SAIT | J. W. Won |
| KIST | Y. H. Lee |
| Dongbu HiTek Co. | Y. J. Jung |
| RIST | J. N. Kim |
| Samsung Electronics | J. S. Lee |

**Table 3** RRT results.

| Delta-layer | 2nd (nm) | 4th (nm) | 6th (nm) | slope | offset (nm) |
|---|---|---|---|---|---|
| Nom. depth | 79.0 | 157.2 | 234.1 | - | - |
| 1 | 73.9 | 151.0 | 226.0 | 0.981 | -3.48 |
| 2 | 79.1 | 157.3 | 234.8 | 1.000 | -0.35 |
| 3 | 85.3 | 169.5 | 247.2 | 1.044 | 3.66 |
| 4 | 84.7 | 170.7 | 255.1 | 1.099 | -2.11 |
| 5 | 76.2 | 152.2 | 230.9 | 0.997 | -3.28 |
| 6 | 77.3 | 153.9 | 229.6 | 0.982 | -0.36 |
| 7 | 75.5 | 153.8 | 228.2 | 0.985 | -1.89 |
| 8 | 76.7 | 155.8 | 232.3 | 1.003 | -2.38 |
| 9 | 81.8 | 163.1 | 232.0 | 0.969 | 7.02 |
| 10 | 71.4 | 147.8 | 221.8 | 0.970 | -5.06 |
| 11 | 68.7 | 145.8 | 219.6 | 0.973 | -7.87 |
| 12 | 73.3 | 138.4 | 208.3 | 0.871 | 3.49 |
| 13 | 77.0 | 157.1 | 229.9 | 0.986 | 0.08 |
| Ave. (nm) | 77.0 | 155.1 | 230.4 | 0.989 | -0.96 |
| Stdev (nm) | 4.8 | 9.0 | 11.6 | 0.050 | - |

These result means that the scales of profilometers of Korean industries are well maintained using step-height standards. Another important point is that the Si/Ge MDL CRM film can be used to calibrate the scale of stylus profilometer and to confirm the certified scale of step-height standards.

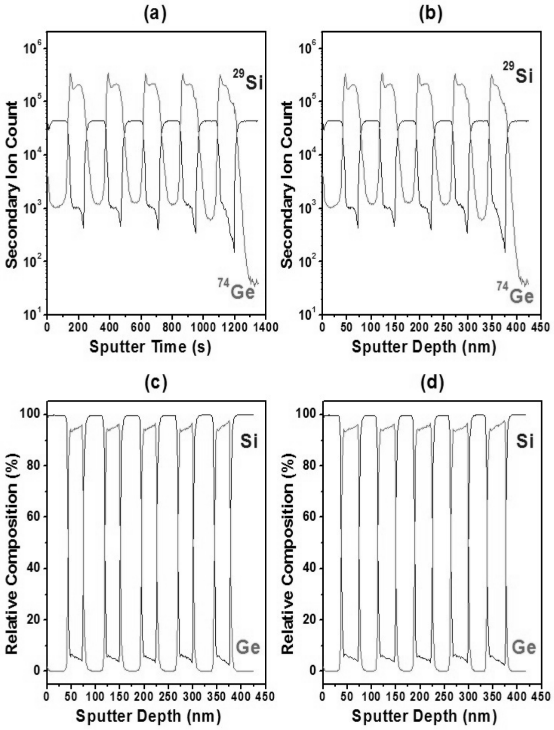


**Fig. 5** SIMS depth profiles of the Si/Ge ML using 2 keV $O_2^+$ ions. (a) raw profile, (b) depth calibrated profile, (c) composition calibrated profile, (d) sputtering rate difference calibrated profile.

### 3.4 Calibration of depth scale by a Si/Ge ML

Figure 5 shows the original SIMS profile and the converted profiles of the Si/Ge multi-layer film analyzed by Cameca IMS 7f SIMS in KRISS using 2 keV oxygen ion beam. Calibration of SIMS depth scale of a Si/Ge ML film is more complicated than that of a MDL because of the interface artifact. However, the original profile can be converted to a compositional depth profile by the following three step conversion.

*Step 1; Calibration of total sputter depth*
*(a) → (b)*

The depth scale of the original depth profile (a) can be converted from sputter time to sputter depth by measuring the crater depth using a stylus profilometer or an optical interferometer.

*Step 2; Conversion to composition profile*
*(b) → (c)*

The second step to calibrate the depth scale is the conversion of an original SIMS profile to compositional profile. This step is essential to determine the positions of the interfaces by elimination of the interface artifacts in the Si/Ge and Ge/Si interfaces. The interface artifact was reported to be eliminated by conversion to compositional profile. [11] This step requires an alloy film with composition of about 50 %.

A $Si_{52.4}Ge_{47.6}$ alloy film was fabricated by ion beam sputtering deposition and the composition was analyzed by Rutherford backscattering spectroscopy (RBS) as shown in Figure 6. Determination of the relative sensitivity factor (RSF) of Si and Ge is the first step for the conversion to a compositional profile. The RSFs of Si ($R_{Si}$) and Ge ($R_{Ge}$) were measured from the average ion intensity of Si ($I_{Si}$) and Ge ($I_{Ge}$) divided by the measured composition of Si ($C_{Si}$) and Ge ($C_{Ge}$) over the depth interval from 30 nm to 120 nm by the following equations as shown in Figure 7.

$$R_{Si} = (I_{Si} / C_{Si}) \quad \text{------------------------} \quad (2)$$

$$R_{Ge} = (I_{Ge} / C_{Ge}) \quad \text{------------------------} \quad (3)$$

The original SIMS depth profile can be converted to a compositional SIMS profile from the following equations.

$$X_{Si}^{unk} = \frac{(I_{Si}^{unk} / R_{Si})}{(I_{Si}^{unk} / R_{Si}) + (I_{Ge}^{unk} / R_{Ge})} \quad \text{-------} \quad (4)$$

$$X_{Si}^{unk} = \frac{I_{Si}^{unk}}{I_{Si}^{unk} + I_{Ge}^{unk} / R} \quad \text{------------------} \quad (5)$$

$$R = \frac{R_{Ge}}{R_{Si}} \quad \text{----------------------------------} \quad (6)$$

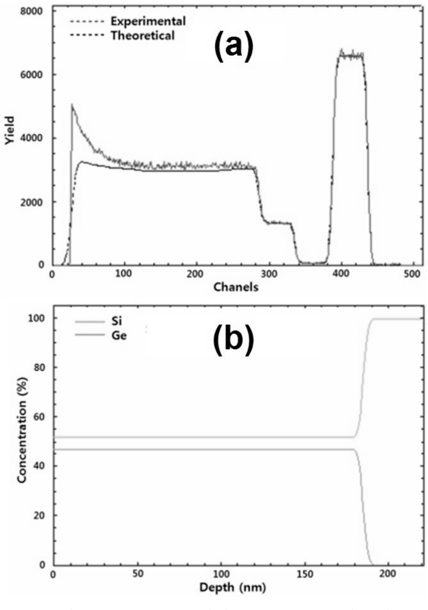


**Fig. 6** The composition(a) and depth(b) profile of a $Si_{52.4}Ge_{47.6}$ alloy film measured by RBS.

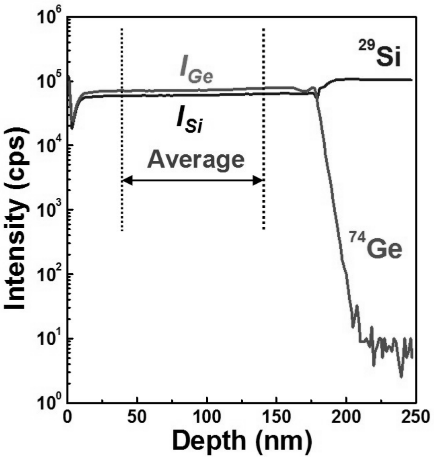


**Fig. 7** The original SIMS depth profile of the $Si_{52.4}Ge_{47.6}$ alloy film and the conversion region.

The SIMS intensity of the original profile was converted to the relative composition by the measured R value of 1.309.

The compositional profile of the Si/Ge ML in Figure 5 (c) shows that the positions of interfaces can be well determined without suffering from the effect of interface artifact. Although the compositions of Si and Ge are not close to 100 %, the position of interfaces can be clearly determined.

*Step 3; Calibration of sputtering rate of layers (c) → (d)*

The sputtering rates of the constituent elements are generally different each other. The sputtering rate depends on the detailed parameters of sputtering condition. The compositional profile of the Si/Ge ML in Figure 5 (c) shows a distorted depth scale due to the different sputtering rates of Si and Ge layers. The relative sputtering rates of Si and Ge layers can be derived from the certified thicknesses and the sputtering times of Si and Ge layers. The sputtering rate of Ge is much higher than that of Si as shown in Figure 5 (c). The cause of the slow sputtering of Si is oxidation of Si during sputtering with oxygen ion beam. Si surface is successively oxidized during sputtering with oxygen ion beam. The oxygen atoms are involved into the sputtered substrate surface and sputtered out to diminish the total surface momentum. As a result, the sputtering of Si layer is delayed due to the preferential sputtering of oxygen atoms from the oxidized silicon surface. On the other hand, this effect can be negligible at the sputtering of Ge layers.

The sputtering rates of Si and Ge layers are

0.271 nm/s and 0.375 nm/s, respectively. The distorted depth scale in Figure 5 (c) can be converted to a reasonable calibrated depth scale by compensating the above sputtering rates of Si and Ge layers as shown in Figure 5 (d).

## 4. Coclusions

A Si/Ge multiple delta-layer (MDL) and a Si/Ge multi-layer (ML) films were fabricated by ion beam sputter deposition as reference materials to calibrate the depth scale of SIMS and a stylus profilometer. The thicknesses of the layers were certified by high resolution TEM. The certified positions of the delta-layers in the Si/Ge MDL film can be useful marker layers to calibrate the depth scale. The multiple delta-layer film could be usefully applied to calibrate the depth scale of SIMS depth profiles as defined ISO/TR-15969.

Korean round robin test for the scale calibration of a stylus profilometer using a Si/Ge multiple delta-layer showed an average slope of 0.989 with the standard deviation of 0.05 from the linear fitting results between the measured depth and the nominal depth. The vertical scale of a stylus profilometer could be traceable to the length unit using a multiple delta-layer film with a certified film thickness.

In depth scale calibration using a Si/Ge multi-layer reference material, the positions of interfaces were successfully determined by conversion of the original profile to a composition profile using relative sensitivity factors of Si and Ge. In this process, the severe interface artifact due to matrix effect was compensated. The difference in the sputtering rates of Si and Ge layers could be also calibrated.

## 5. Acknowledgements

This research was partially supported by Ministry of Knowledge Economy, Korea, through system IC 2010 project and partly through the KRISS Project of Improvement of Measurement Reliability for Industry.

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