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WILEY SURFACE and INTERFACE ANALYSIS

RESEARCH ARTICLE

Round-robin test for the measurement of layer thickness of multilayer films by secondary ion mass spectrometry depth profiling

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An international round-robin test (RRT) was performed to investigate a method to determine the interface location and the layer thickness of multilayer films by secondary ion mass spectrometry (SIMS) depth profiling as a preliminary study to develop a new work item proposal in ISO/TC-201. Two types of reference materials were used in this RRT. A SiGe alloy ($Si_{52.4}Ge_{47.6}$) reference film was used to determine the relative sensitivity factors of Si and Ge. A Si/Ge multilayer reference film was used to determine the relative sputtering rates of the Si and Ge layers. The layer thicknesses were measured from the interfaces determined by a 50 atomic percent definition. Seven laboratories from 5 countries participated in this international RRT. The RRT reference expanded uncertainties for Si and Ge layers in a Si/Ge multilayer with similar thicknesses as the reference film were 0.76 and 1.17 nm, respectively. However, those in a thinner Si/Ge multilayer film were slightly larger at 1.04 and 1.59 nm, respectively. Most of the thickness ratios in the 2 Si/Ge multilayer films were consistent with the RRT reference value within their expanded uncertainties.

KEYWORDS

50 at% definition, interface location, multilayer, SIMS, thickness measurement

1 | INTRODUCTION

The thickness measurement of multilayer films is one of the most important measurement issues of surface analysis. Although secondary ion mass spectrometry (SIMS) is generally used for in-depth analysis of multilayer films, the determination of the layer thickness is not easy due to the difficulty in determining the interface location.[1-3]

Abnormal variation of the ion intensities near the interfaces due to the matrix effect is the main reason for this challenge,[4-6] which can be partially counterbalanced using relative sensitivity factors (RSFs) determined from certified alloy reference materials.[2,6,7]

International standards for step-by-step measurement processes have been developed by the International Organization for Standardization (ISO). Specifically, international standards on the applications of SIMS analysis have been developed in subcommittee SC6 (SIMS) of ISO technical committee TC-201 (surface chemical analysis).

In this study, an international round-robin test (RRT) was performed to develop a new work item proposal in ISO/TC-201 for the thickness measurement of multilayer films by SIMS. Two Si/Ge multilayer systems were manufactured with differing layer thicknesses. Although the reported layer thicknesses of the Si and Ge layers in the multilayer with similar thickness as the reference film showed consistent results with small uncertainty values, those in the thinner multilayer system were not so similar.

2 | OUTLINE OF THE ROUND-ROBIN TEST

2.1 | Objective

The objective of this RRT is to measure the layer thicknesses of Si/Ge multilayer films by SIMS depth profiling analysis. The measurand of this study is the layer thickness of Si/Ge multilayers in the unit of nanometer. The interface location is determined from the point where the atomic fractions of Si and Ge are each 50 atomic percent. This is possible by conversion of the raw depth profiles to compositional depth profiles using the RSFs determined from a reference alloy film. The layer thicknesses can be determined from the sputtering rates

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determined from a reference Si/Ge multilayer film with certified layer thicknesses.

2.2 | The specimens

Four specimens, a reference SiGe alloy film, a reference Si/Ge multilayer film, and 2 test Si/Ge multilayer films, were used for this RRT.

2.2.1 | Reference SiGe alloy film

A reference $Si_{52.4}Ge_{47.6}$ alloy film was used to determine the RSFs of Si and Ge. The atomic fraction of the alloy reference (AR) film was analyzed by Rutherford backscattering spectroscopy (Evans Analytical Group, USA). The expanded uncertainty in the atomic fractions of Si and Ge are ±1 at% with a coverage factor of 2.

2.2.2 | Reference Si/Ge multilayer film

A $(Si/Ge)_5$ multilayer film grown on a Si(100) substrate was used as a reference to determine the sputtering rates of Si and Ge. The layer thicknesses of the reference specimen were determined by high resolution transmission electron microscopy (HR-TEM) based on the lattice constant of the Si (100) substrate as shown in Table 1 and Figure 1. The expanded uncertainty of the certified thickness was expressed with the coverage factor (k = 2) at 95% confidence level.

2.2.3 | Test Si/Ge multilayer film

Two $(Si/Ge)_5/Si(100)$ multilayer films with unknown thicknesses were the test samples to determine the layer thicknesses. The layer thicknesses of the first test specimen (T1) were similar with those of the reference multilayer film. On the other hand, the layer thicknesses of the second test specimen (T2) were approximately half those of the reference multilayer film.

3 | RECOMMENDED MEASUREMENT PROCEDURE

3.1 | Determination of interface location

The locations of the interfaces should be carefully established to determine the layer thicknesses of Si/Ge multilayer films. This is possible by conversion of the raw depth profiles to compositional depth profiles using the RSFs of the constituent layer elements. The RSFs are determined from the average ion intensities in a SIMS depth profile of the reference $Si_{52.4}Ge_{47.6}$ alloy film. The average ion intensities of Si (I_{Si}) and Ge (I_{Ge}) are measured at the depth interval over the plateau region

TABLE 1 Layer thicknesses of the reference Si/Ge multilayer film by HR-TEM

	First	Second	Third	Fourth	Fifth
Thickness of Si layer (nm)	36.6	38.7	37.7	37.5	38.0
Expanded uncertainty (k = 2) *U* (nm)	0.8	0.8	0.7	0.8	0.8
Thickness of Ge layer (nm)	37.5	38.0	37.7	37.6	38.1
Expanded uncertainty (k = 2) *U* (nm)	0.8	0.7	0.8	0.8	0.8

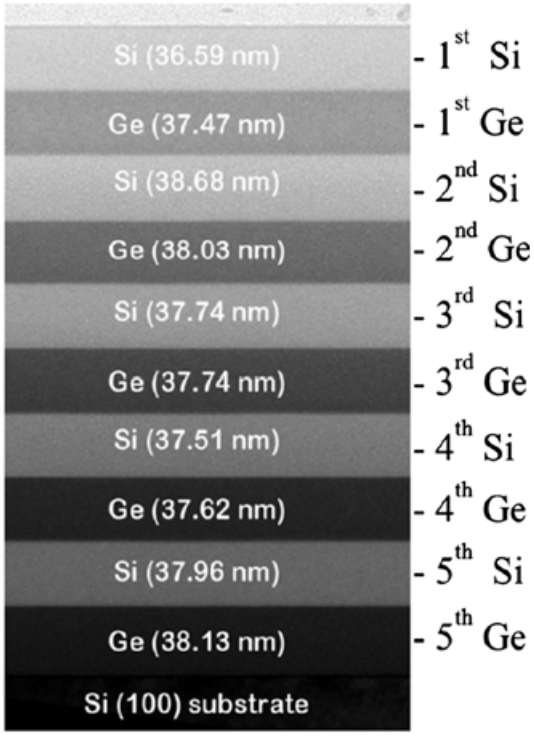

FIGURE 1 TEM images of the reference Si/Ge multilayer film

in which the ion intensities of Si and Ge are uniform as shown in Figure 2. The widest uniform range of average except the surface transient range and the interface is recommended.

The RSFs of Si (S_{Si}^{AR}) and Ge (S_{Ge}^{AR}) are determined by dividing the average ion intensities of Si Si (I_{Si}) and Ge (I_{Ge}) by the certified compositions of Si (C_{Si}) and Ge (C_{Ge}) using the following equations.

$$S_{Si}^{AR} = I_{Si}/C_{Si} = I_{Si}/0.524 \quad (1)$$

$$S_{Ge}^{AR} = I_{Ge}/C_{Ge} = I_{Ge}/0.476 \quad (2)$$

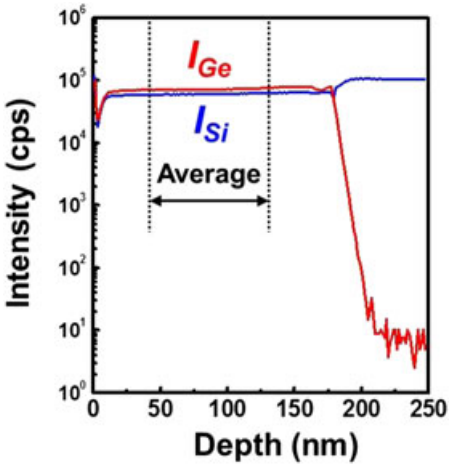

FIGURE 2 The average ion intensities of Si and Ge are measured over the depth interval at the plateau region where the ion intensities of Si and Ge are uniform with depth [Colour figure can be viewed at wileyonlinelibrary.com]

Individual ion intensities of Si (i_{Si}) and Ge (i_{Ge}) in a data cycle in the raw SIMS depth profile of the reference Si/Ge multilayer film are converted to individual atomic fractions of Si (x_{Si}) and Ge (x_{Ge}) from the RSFs of Si (S_{Si}^{AR}) and Ge (S_{Ge}^{AR}) via the following equation as shown in Figure 3B.

$$x_{Si} = \frac{\left(i_{Si}/S_{Si}^{AR}\right)}{\left(i_{Si}/S_{Si}^{AR}\right) + \left(i_{Ge}/S_{Ge}^{AR}\right)} \times 100(at\%) \quad (3)$$

$$x_{Ge} = \frac{\left(i_{Ge}/S_{Ge}^{AR}\right)}{\left(i_{Si}/S_{Si}^{AR}\right) + \left(i_{Ge}/S_{Ge}^{AR}\right)} \times 100(at\%) \quad (4)$$

The locations of the interfaces in the compositional depth profile of the reference Si/Ge multilayer film are determined by a 50 atomic percent definition, which means that the interface by 50 at% definition is the point where the amount of the 2 layer materials are same. The interface position is easily determined from the broken line in Figure 3B, which corresponds to 50 atomic percent.

3.2 | Determination of layer thickness

The sputtering rates of Si (z_{Si}) and Ge (z_{Ge}) in the unit of nm/s are determined by dividing the certified thicknesses of Si (d_{Si}^{R}) and Ge (d_{Ge}^{R}) by the sputtering times of Si (t_{Si}^{R}) and Ge (t_{Ge}^{R}) layers of a reference Si/Ge multilayer film, where R refers to reference.

$$z_{Si} = d_{Si}^{R}/t_{Si}^{R} \quad (5)$$

$$z_{Ge} = d_{Ge}^{R}/t_{Ge}^{R} \quad (6)$$

The sputtering time of a Si layer (t_{Si}^{R}) is determined from the time interval from Ge/Si to Si/Ge interfaces and that of a Ge layer (t_{Ge}^{R}) is determined from the time period from Si/Ge to Ge/Si interfaces as shown in Figure 4. The average sputtering rates of Si ($\bar{z}_{Si}$) and Ge ($\bar{z}_{Ge}$) layers are determined from the average value of the sputtering rates of the 3 middle Si and Ge layers.

The layer thicknesses of Si (d_{Si}^{T}) and Ge (d_{Ge}^{T}) layers of the test Si/Ge multilayer films are determined by multiplying the average sputtering rates of Si ($\bar{z}_{Si}$) and Ge ($\bar{z}_{Ge}$) and the sputtering times of Si (t_{Si}^{T}) and Ge (t_{Ge}^{T}) layers of the test Si/Ge multilayer films.

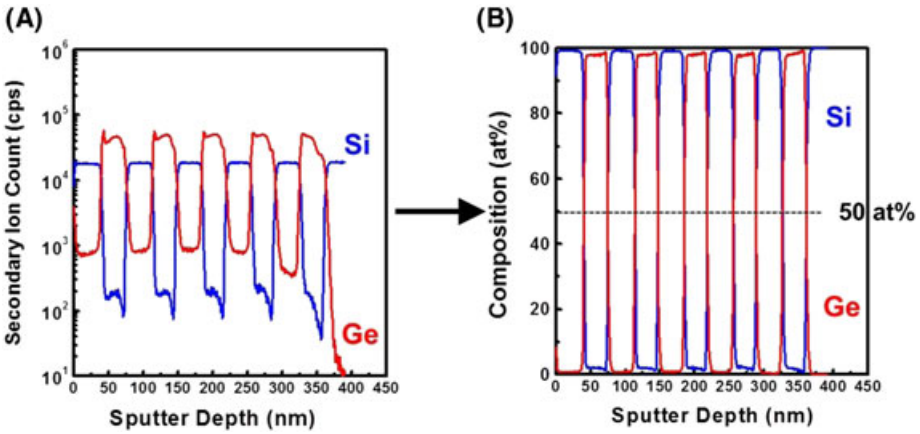

FIGURE 3 Conversion of A, a raw SIMS depth profile of the reference Si/Ge multilayer film to B, a compositional depth profile [Colour figure can be viewed at wileyonlinelibrary.com]

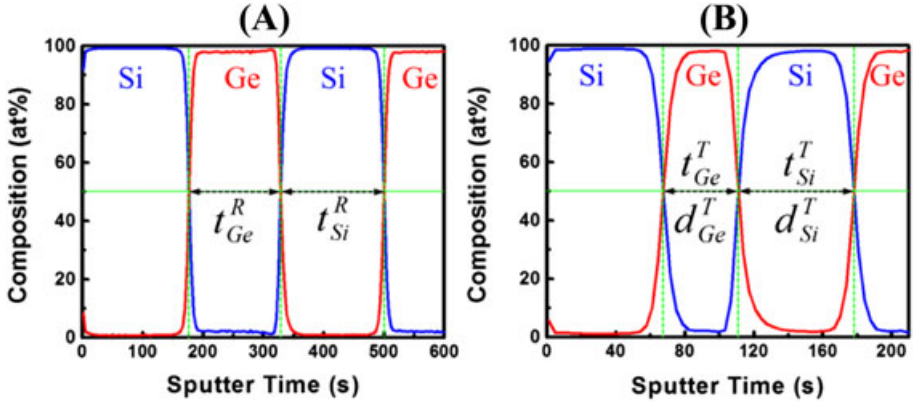

FIGURE 4 (a) Determination of the sputtering times of Si (t_{Si}^{R}) and Ge (t_{Ge}^{R}) layers in a compositional depth profile of a reference Si/Ge multilayer film and (B) determination of layer thicknesses of a Si layer (d_{Si}^{T}) and a Ge layer (d_{Ge}^{T}) from a depth profile of an unknown Si/Ge multilayer film [Colour figure can be viewed at wileyonlinelibrary.com]

$$d_{Si}^{T} = \bar{z}_{Si} \bullet t_{Si}^{T} \quad (7)$$

$$d_{Ge}^{T} = \bar{z}_{Ge} \bullet t_{Ge}^{T} \quad (8)$$

The SIMS depth profiles of the reference and the test multilayer sample should be obtained under the same sputtering and analysis conditions to minimize the measurement uncertainties. Measurement should be repeated more than 5 times to reduce the statistical uncertainties.

4 | RESULTS AND DISCUSSIONS

4.1 | Participants and experimental conditions

Table 2 lists the participants and the key experimental parameters used in this international RRT. Seven laboratories from 5 countries participated in this study. Three types of SIMS machines with quadrupole, magnetic sector, and time-of flight mass analyzers were used. Oxygen and cesium ions were used with ion energies ranging from 0.5 to 3 keV and with the incidence angles ranging from 45° to 80° with respect to the surface normal.

4.2 | Reported data

Based on the measurement protocol for this RRT, the layer thicknesses of the second, third, and fourth Si and Ge layers were reported. Tables 3 and 4 show the reported layer thicknesses (d_i), the standard deviations (stdev), and relative standard deviations (RSD) of the Si and Ge layers in the T1 and T2 Si/Ge multilayers, respectively. The relative ratio of the layer thicknesses of Si and Ge layers (d_{Si} / d_{Ge}) is a parameter that can be used to investigate the feasibility of the method to determine the interface locations of multilayer films.

4.3 | Calculation of uncertainty

In this RRT, the relative combined standard uncertainty (u_c) in the measurement of layer thickness is determined by the following equation,

$$u_c^2 = u_{CRM}^2 + u_z^2 + u_t^2 \quad (9)$$

where u_{CRM}, u_z, and u_t are the relative standard uncertainties for the certified layer thicknesses of the multilayer reference film, for the average sputtering rate using the multilayer reference film and for the individual layer thicknesses of the multilayer test film, respectively. The expanded uncertainty (U) is expressed by the multiplication of the combined standard uncertainty (u_c) and the coverage factor (k) with a confidence level of 95%, where k is determined from the effective degrees of freedom.

$$U = ku_c \quad (10)$$

Table 5 shows the calculated expanded uncertainties (unit: nm) of the reported thicknesses of the third Si and Ge layers at 95% confi-

TABLE 2 Participants and key experimental parameters in this RRT

No.	Laboratory	Country	Instrument	Ion	Energy (keV)	Incidence angle (°)
1	Novati Tech.	USA	PHI ADEPT-1010	O_2^+	1.0	60
2	FBK	Italia	Cameca WF804	Cs^+	0.5	48
3	NTT	Japan	PHI ADEPT 1010	Cs^+	1.0	60
4	NIST	USA	Cameca IMS-1280[a]	O_2^+	3.0	55
5	Tsinghua Univ.	China	IONTOF TOF.SIMS 5-100	O_2^+	1.0	45
6	KRISS	Korea	Cameca IMS-7F	O_2^+	1.0	80
7	EAG	USA	PHI 6600	Cs^+	2.5	60

[a]Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

TABLE 3 Reported layer thicknesses (d_i) of the Si and Ge layers in the T1 Si/Ge multilayer film

Laboratory Number of measurement	Novati 5	FBK 6	NTT 5	NIST 5	TU 5	KRISS 5	EAG 5	Average	Stdev	RSD (%)
Second d_{Si}	38.30	38.57	36.90	39.05	38.53	37.95	39.60	38.41	0.85	2.22
Second d_{Ge}	36.20	37.92	34.60	37.81	34.49	36.57	38.00	36.51	1.51	4.14
Third d_{Si}	37.80	38.02	36.50	38.38	38.36	37.46	39.10	37.95	0.82	2.16
Third d_{Ge}	36.76	38.02	34.65	38.03	35.99	36.59	37.96	36.86	1.27	3.44
Fourth d_{Si}	36.10	38.10	35.44	38.25	36.48	36.38	38.90	37.09	1.31	3.52
Fourth d_{Ge}	37.40	37.91	34.74	37.63	41.74	36.51	37.80	37.68	2.11	5.59
Average d_{Si}	37.40	38.23	36.28	38.56	37.79	37.26	39.20	37.82	0.96	2.53
Average d_{Ge}	36.80	37.95	34.66	37.83	37.40	36.56	37.90	37.01	1.17	3.17
d_{Si}/d_{Ge}	1.02	1.01	1.05	1.02	1.01	1.02	1.03	1.02	0.01	1.35
Third d_{Si}/third d_{Ge}	1.03	1.00	1.05	1.01	1.07	1.02	1.03	1.03	0.02	2.31

TABLE 4 Reported layer thicknesses (d_i) of the Si and Ge layers in the T2 Si/Ge multilayer film

Laboratory Number of measurement	Novati 5	FBK 6	NTT 5	NIST 5	TU 5	KRISS 5	EAG 5	Average	Stdev	RSD (%)
Second d_{Si}	17.90	19.62	17.39	19.85	17.47	17.80	19.30	18.48	1.07	5.79
Second d_{Ge}	15.90	19.50	16.32	18.57	15.48	16.58	19.50	17.41	1.73	9.94
Third d_{Si}	18.16	20.00	17.54	20.36	17.93	18.33	19.70	18.86	1.13	5.98
Third d_{Ge}	16.52	20.07	16.95	19.06	15.97	16.87	19.92	17.91	1.72	9.60
Fourth d_{Si}	17.40	19.69	17.14	19.72	17.30	17.80	19.10	18.31	1.15	6.30
Fourth d_{Ge}	17.20	20.57	17.52	19.61	16.39	17.46	20.50	18.46	1.72	9.30
Average d_{Si}	17.80	19.77	17.36	19.98	17.56	17.97	19.30	18.53	1.11	5.99
Average d_{Ge}	16.50	20.05	16.93	19.08	15.95	16.97	20.00	17.93	1.73	9.66
d_{Si}/d_{Ge}	1.08	0.99	1.03	1.05	1.10	1.06	0.97	1.04	0.05	4.51
Third d_{Si}/Third d_{Ge}	1.10	1.00	1.04	1.07	1.12	1.09	0.99	1.06	0.05	4.74

TABLE 5 Calculated expanded uncertainties (nm) of the reported third Si and Ge layers in this RRT at 95% confidence level

Laboratory No. of measurements		Novati 5	FBK 6	NTT 5	NIST 5	TU 5	KRISS 5	EAG 5
T1	Third Si layer	0.83	1.21	0.86	0.97	0.70	0.74	0.75
	Third Ge layer	0.84	1.23	1.69	0.90	0.76	0.83	0.83
T2	Third Si layer	0.36	0.59	0.40	0.50	0.33	0.35	0.38
	Third Ge layer	0.36	0.62	0.69	0.43	0.35	0.38	0.43

dence level. The uncertainties mainly depend on the relative standard uncertainties for the certified layer thicknesses of the multilayer reference film.

4.4 | Round-robin test reference value and uncertainty

In the round-robin test performed by the same measurement method, the arithmetic mean can be used as a method to determine the RRT reference value because the uncertainties of the reported data are similar. In this RRT, the RRT reference thicknesses (d_{ref}) were calculated by the arithmetic mean method from the average values of the reported layer thicknesses, where m is the number of laboratories reporting measurement values.

$$d_{ref} = \sum_{i=1}^{m} d_i / m \tag{11}$$

The RRT reference expanded uncertainties (U_{ref}) of the RRT reference thicknesses shown in Table 6 were calculated from the standard deviations of the reported layer thicknesses (s) and the coverage factor (k).

$$u_{ref} = s(d_i)/\sqrt{m} \tag{12}$$

TABLE 6 RRT reference thicknesses and expanded uncertainties of the third Si and Ge layers in the 2 test Si/Ge multilayer films

First test specimen (T1)				Second test specimen (T2)			
d_{ref}^{Si}	U_{ref}^{Si}	d_{ref}^{Ge}	U_{ref}^{Ge}	d_{ref}^{Si}	U_{ref}^{Si}	d_{ref}^{Ge}	U_{ref}^{Ge}
37.95	0.76	36.86	1.17	18.86	1.04	17.91	1.59

$$U_{ref} = k u_{ref} \tag{13}$$

The RRT reference expanded uncertainties of the thick Si/Ge multilayer (first test specimen: T1) with similar thickness as the reference film are 0.76 and 1.17 nm for the third Si and Ge layers, respectively. The expanded uncertainties increase to 1.04 and 1.59 nm for the third Si and Ge layers of the thin Si/Ge multilayer (second test specimen: T2), respectively.

Figure 5 shows the reported layer thicknesses (d_i) and the expanded uncertainties (U_i) of the third Si and Ge layers. The solid blue lines and the broken red lines are the round-robin reference values and the round-robin expanded reference uncertainties, respectively. In the plot of the layer thickness of the T1 Si/Ge multilayer film with similar thickness to the reference film, most of the individual laboratory values are consistent with the reference value within their expanded uncertainties. However, most of the values for the layer thickness of the T2 Si/Ge multilayer film with reduced layer thicknesses are not consistent with the RRT reference value. It is possible that that the thickness could be more precisely determined from the determination of the total film thickness by measuring the crater depths.

In order to investigate the feasibility of the method, the relative ratios (d_{Si}/d_{Ge}) of film thicknesses were compared as shown in Tables 3 and 4 and Figure 5. In the case of this thickness ratio, the uncertainties were determined by combination of the uncertainties in the thickness measurements of the Si and Ge layers. Most of the thickness ratio values from individual laboratories for the T1 and T2 Si/Ge multilayer films are consistent with the RRT reference value within their uncertainty limits.

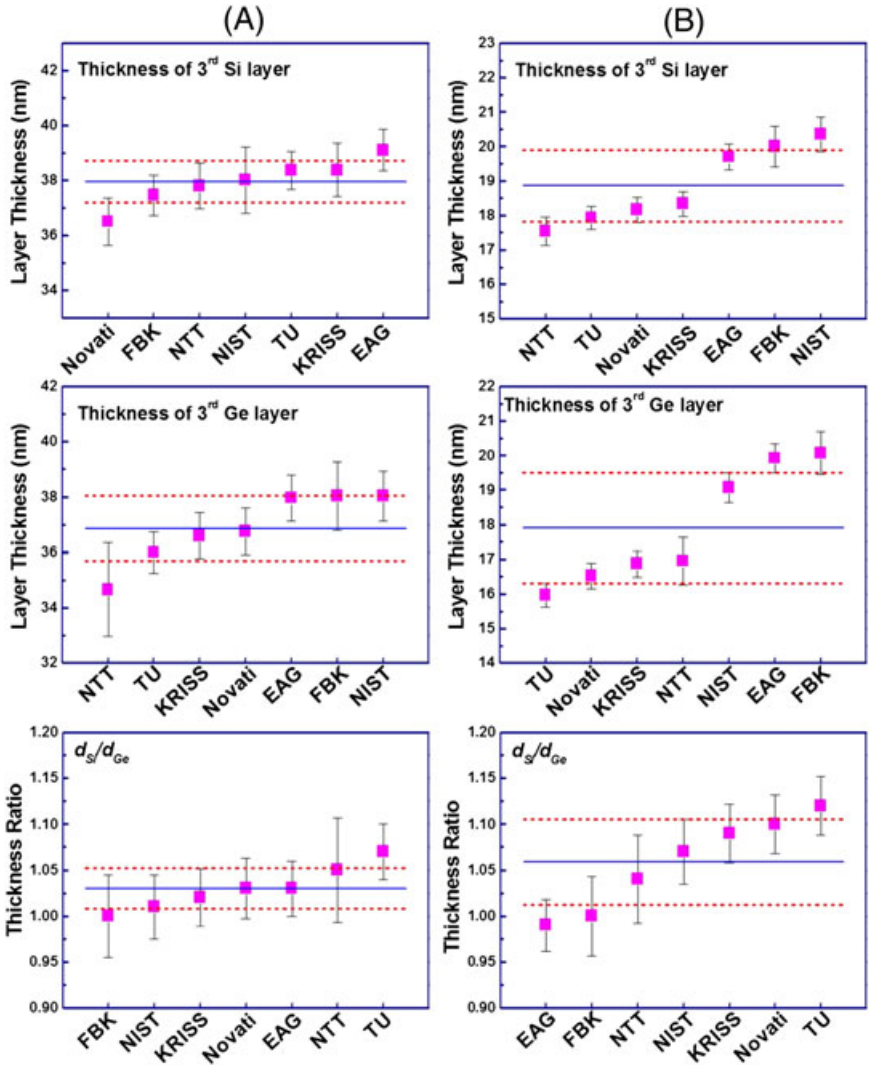

FIGURE 5 Reported layer thicknesses of the third Si and Ge layers in the (A) T1 and (B) T2 Si/Ge multilayer films with the RRT reference thicknesses and expanded uncertainties. The solid blue lines and the broken red lines are the round-robin reference values and the round-robin reference expanded uncertainties at 95% confidence, respectively [Colour figure can be viewed at wileyonlinelibrary.com]

5 | CONCLUSION

A method to determine the interface location and the layer thickness of Si/Ge multilayer films by SIMS depth profiling has been studied by an international RRT. The raw SIMS depth profiles of the Si/Ge multilayer films were converted to compositional depth profiles using the RSFs of Si and Ge derived from a SiGe alloy ($Si_{52.4}Ge_{47.6}$) reference film. The interface locations were determined in the compositional depth profiles by a 50 atomic percent definition. The layer thicknesses were determined from the interface locations.

The RRT reference expanded uncertainties for Si and Ge layers in the Si/Ge multilayer films increased from 0.76 nm and 1.17 nm to 1.04 nm and 1.59 nm as the layer thickness of the Si/Ge multilayer films decreased from the similar thickness of 38 nm to half of that value. As a result, the reported layer thicknesses of the Si and Ge layers in the T1 Si/Ge multilayer with similar thickness showed a good agreement and had small uncertainty values. However, those in the T2 Si/Ge multilayer with thinner thickness were not in good agreement.

This problem can be solved by using the relative ratio (d_{Si}/d_{Ge}) of layer thicknesses and an additional measurement of the crater depth. Most of the thickness ratios in the T1 and T2 Si/Ge multilayer films agree with the RRT reference value within the stated uncertainties.

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