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Nano-film thicknesses using X-ray reflectometry

SUPPLEMENTARY COMPARISON

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TCMM/APMP Supplementary Comparison (SC)
APMP.L-S6.6.n01
(Co-organized by KRISS and NMIJ)

Film-Thickness Measurement Using XRR
(X-Ray Reflectometry)

Final Report

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Contents

Abstract

A supplementary comparison (SC) on the measurement of film thickness using X-ray Reflectivity (XRR) was conducted within TCMM/APMP, as proposed and approved at the TCMM/APMP meeting in Singapore in 2018 and the TCMM-TCL/APMP joint meeting in Sydney 2019. The aim of this SC to perform an inter-laboratory comparison of nanoscale film thicknesses measurements by XRR among NMIs and to confirm the international equivalence of the reported measurement results.

Four NMIs – CMS, NIM, NMIJ, and KRISS – participated in the comparison using three specimens comprising single-layer and multilayer thin films with nominal thicknesses from 3 nm to 5 nm. The participating NMIs measured and reported film thicknesses values together with their associated measurement uncertainty. Comparison reference values (CRVs) were determined using an uncertainty-weighted mean method, and the degree of equivalence (DoE) and normalized error (E_n) values were evaluated.

The analysis of all specimens — specimens 1 and 2 consisting of single-layer HfO_2 films and specimen 3 being a multilayer AlAs/GaAs superlattice — demonstrated that the reported thickness measurements are mutually equivalent within their stated uncertainties.

1. Introduction

X-ray reflectivity (XRR) is a powerful technique for the determination of thickness, density, and surface and interface roughness of thin films. When X-rays are incident on the surface of a thin film deposited on a substrate at a grazing angle, they are reflected at both the surface and the interfaces. The reflected X-rays interfere with each other due to the path-length difference, producing thickness fringes (oscillations) in the reflectivity curve. The period of these oscillations is directly related to the film thickness. In the XRR measurements reported here, θ is the angle of incidence measured from the sample surface, and 2θ is the angle between the incident and reflected X-ray beams under the specular reflection condition.

XRR is applicable to a wide range of thin films that exhibit electron density contrast with respect to their substrate, and the measurable thickness range typically extends from approximately 1 nm up to 1 μm. Several analytical techniques, including XRR, spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS) , and transmission electron microscopy (TEM), have been used to measure nanoscale thin-film thicknesses. However, SE and XPS require additional information, such as the refractive index of the film or a thickness correction factor, which are often not independently known. In contrast, film thickness determination by XRR relies on the X-ray wavelength and angular scale, both of which can be calibrated, enabling a high level traceability. Furthermore, XRR is a non-destructive technique, unlike TEM, which requires destructive method for sample preparation. [1-8]

At the TCMM/APMP meeting held in Singapore on November 26, 2018, a supplementary comparison (SC) on nanoscale film thickness measurement using XRR among APMP NMIs was proposed, and the proposal was approved at the TCMM-TCL/APMP joint meeting in Sydney in 2019. Four NMIs — CMS (Chinese Taipei), NIM (China), NMIJ (Japan), and KRISS (Republic of Korea) — participated in the comparison, and three thin-film specimens were circulated. Two specimens consisted of single-layer HfO_2 films, and the specimen 3 was a multi-layer AlAs/GaAs superlattice. The nominal film thicknesses of the specimens range from 3 nm to 5 nm.

The participating NMIs reported film thickness values together with their associated measurement uncertainties. The reported results were compared, and comparison reference values (CRVs) were

determined using the uncertainty-weighted mean method. Degree of equivalence (DoE) and normalized error (E_n) values were subsequently evaluated to assess the equivalence of the reported measurement results.

Prior to the SC, the participating TCMM/APMP NMIs conducted a pilot study on film thickness measurement by XRR, and a workshop for the APMP TC Initiative (TCI) project was held in Beijing in 2018. During the pilot study and the workshop, film thickness measurements were compared, and detailed discussions were conducted on XRR data analysis methods, particularly with respect to simulation and fitting procedure for multilayer specimens. As a result, common analysis approaches were established and agreed upon by the participating NMIs. [9, 10]

2. Objectives of the SC

The objectives of the SC are to perform an interlaboratory comparison of nanoscale film thicknesses measurements using XRR and to confirm the international equivalence of the measurement results reported by APMP NMIs.

3. Participants

4 NMIs belonging to APMP participated in the SC and the NMIs are listed in the following Table 1. The contact details are given in the annex A1 of the technical protocol, which is attached as annex to this report.

Table 1 Participants

Country/ Economic Region	Institute	Acronym
China	National Institute of Metrology	NIM
Chinese Taipei	Center for Measurement Standards	CMS
Japan	National Metrology Institute of Japan	NMIJ
Korea, The Republic of	Korea Research Institute of Standards and Science	KRISS

4. Specimens

Three kinds of specimens were provided to the participants for comparison. Detailed descriptions of the specimens are summarized in Table 2.

specimen 1: 3 nm thick HfO_2 film on SiO_2 substrate

specimen 2: 5 nm thick HfO_2 film on SiO_2 substrate

specimen 3: AlAs (5 nm)/ GaAs (5 nm) multilayers on GaAs substrate

Specimens 1 and 2 were prepared with one sample each to avoid thickness variations among the

samples. They were circulated among NMIs to measure XRR curves and returned to KRISS for cleaning using the same procedure outlined in section 6.2. The cleaned specimens were then shipped to the next NMI for subsequent measurement. (A. Technical Protocol) Four samples of specimen 3 were prepared and shipped to each NMI.

Table 2 Detailed list of specimens

No	Specimen	Single /Multi-layer	Surface polishing	Specimen size (mm × mm)	Nominal Thickness (nm)	No. of Specimens	Provided by
1	HfO_2/SiO_2*	single	single sided	20 × 40	3	1	KRISS
2	HfO_2/SiO_2*	single	single sided	20 × 40	5	1	
3	3×(GaAs/AlAs)/GaAs**	multi	double sided	15 × 15	(5/5) x 3	4***	NMIJ

*: HfO_2 film on SiO_2 substrate

**: GaAs/AlAs/ GaAs/AlAs/ GaAs/AlAs/GaAs substrate

***: #1 (NIM), #2 (CMS), #3 (NMIJ), #4 (KRISS)

5. Measurement

5.1 Measurand

The measurand was the film thicknesses of the three specimens provided, expressed in nanometers (nm).

5.2 Method of measurement

Film thickness measurements were performed using XRR [11-15]. Information of the measurement instrument used by each NMI is summarized in Table 3.

5.3 Traceability

The traceability of film thickness measurement by XRR is established through the X-ray wavelength and the calibration of the angular scale. The X-ray wavelength was determined based on lattice constants of reference materials (e.g. silicon crystals), while the angular scale was calibrated using national angle standards or calibration systems traceable to such standards (e.g. autocollimators and interferometric methods). The traceability chains were established independently by each NMI according to their internal calibration practices.

5.4 Measurement conditions

The recommended XRR measurement conditions were as follows and are also summarized in Table 4:

- Measurement range: see Table 4
- Measurement step: see Table 4
- Counting time per step: see Table 4
- Preferred ambient temperature: room temperature
- Preferred ambient relative humidity: < 50 %
- No background correction (subtraction) was required.
- No specimen cleaning was required.
- Each specimen was placed on a specimen holder such that the long edge of the specimen was parallel to the direction of the X-ray beam.

Table 3 XRR measurement instruments of each NMI

	Measurement Instrument	**Manufacturer**	**X-ray**
NIM	X'pert PRO MRD	PANalytical	Cu $K\alpha_1$
CMS	X'pert PRO MRD	PANalytical	Cu $K\alpha_1$
NMIJ	Traceable X-ray reflectometer (Custom built)	Rigaku	Cu $K\alpha_1$
KRISS	KRISS X-Ray Reflectometer (Based on a modified Bruker D8)	Bruker	Cu $K\alpha_1$

Table 4 XRR measurement conditions

No	**Specimen**	**Meas. Range(°, 2θ)**	**Meas. step (°, 2θ)**	**Counting Time/step (s) in a continuous scan mode**
1	HfO_2/SiO_2	0.1 – 10	0.02	4
2	HfO_2/SiO_2	0.1 – 10	0.02	4
3	3×(GaAs/AlAs)/GaAs	0.1 – 10	0.01	≥ 2

6. Results

6.1 Specimen cleaning

To remove excess surface contamination that may distort the XRR profiles, specimens 1 and 2 were subject to the cleaning procedure described in [16] shown in Fig. 1 prior to measurement at each NMI. Following surface cleaning, XRR measurements were also conducted to confirm the consistency of the XRR profiles by the pilot laboratory. The cleaned specimens were then shipped to the next NMI for measurement (see Annex A of the technical protocol, included as an annex to this report). Figure 2 shows the XRR profiles of the specimen 2 by the pilot laboratory after cleaning, immediately before packing and shipment to each NMI. The results exhibit nearly identical profiles.

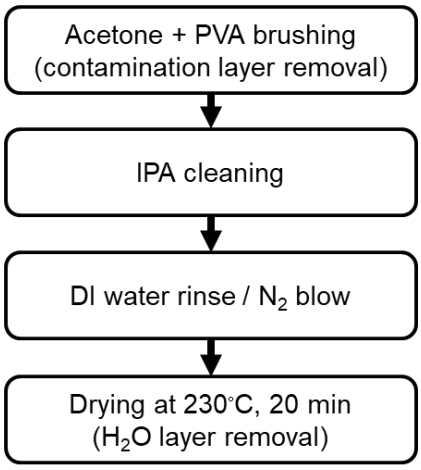


Fig. 1. Surface cleaning procedure for specimens 1 and 2 performed by the pilot laboratory prior to packing and shipment to each NMI.

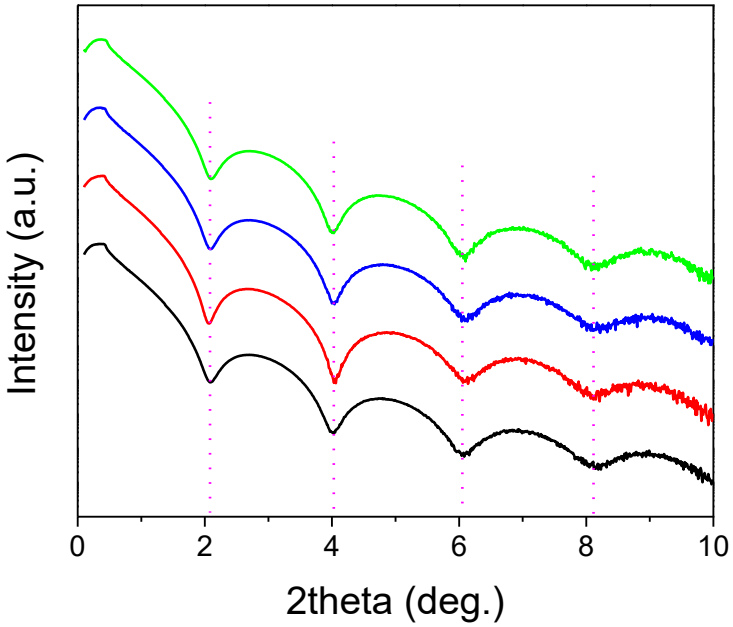


Fig. 2. XRR profiles of specimen 2 measured by pilot laboratory after cleaning, prior to packing and shipment to each NMI.

6.2 Reported results

The reported thicknesses (***t***) and expanded uncertainties (*U*) of the specimens from each NMI are summarized in Table 5. The expanded uncertainties were evaluated at a 95% confidence level. [17, 18]

Table 5 Thicknesses (***t***) and expanded uncertainties (*U*) for specimens 1, 2, and 3 submitted by each NMI.

NMIs	Specimen 1		Specimen 2		Specimen 3									
					AlAs 1*		AlAs 2*		AlAs 3*		GaAs 2*		GaAs 3*	
	t	*U*	***t***	*U*	***t***	*U*	***t***	*U*	***t***	*U*	***t***	*U*	***t***	*U*
	nm													
KRISS	2.59	0.05	4.43	0.05	5.08	0.06	5.06	0.06	5.05	0.05	4.95	0.05	4.94	0.05
NMIJ	2.59	0.05	4.43	0.10	5.10	0.06	5.07	0.06	5.05	0.06	4.94	0.06	4.93	0.06
CMS	2.59	0.05	4.43	0.05	5.10	0.05	5.09	0.05	5.10	0.05	4.91	0.05	4.91	0.05
NIM	2.58	0.04	4.40	0.05	5.08	0.05	5.07	0.06	5.06	0.06	4.93	0.06	4.92	0.06

*GaAs/AlAs 1/ GaAs 2/AlAs 2/ GaAs 3/AlAs 3/GaAs substrate

7. Estimation of Comparison Reference Values (CRVs) and Uncertainties

The Comparison Reference Values (CRVs) of the SC were calculated using the uncertainty-weighted mean method. For a set of n measured values $x_1, x_2, \dots, x_n$ with associated standard uncertainties $u(x_1), u(x_2), \dots, u(x_n)$, the uncertainty-weighted mean, x_{ref} (CRV) is given by [17-20]:

$$x_{ref} = \sum_{i=1}^{n} w_i \, x_i, \tag{7-1}$$

where

$$w_i = \frac{1/u(x_i)^2}{\sum_{j=1}^{n} 1/u(x_j)^2}, \tag{7-2}$$

is the weight of i-th measured value.
The standard uncertainty of the weighted mean, $u(x_{ref})$, is given by

$$\frac{1}{u^2(x_{ref})} = \sum_{i=1}^{n} \frac{1}{u^2(x_i)}. \tag{7-3}$$

The expanded uncertainty of the weighted mean, $U(x_{ref})$, is given by

$$U(x_{ref}) = k \cdot u(x_{ref}), \tag{7-4}$$

where k is the coverage factor, taken as $k = 2$.
The expanded uncertainty of each measured value, $U(x_i)$, is similarly given by

$$U(x_i) = k \cdot u(x_i), \tag{7-5}$$

where $k = 2$.

Using the measured results listed in Tables 5, CRVs (x_{ref}) and their expanded uncertainties ($U(x_{ref})$) calculated according to the above equations are summarized in Table 6.

Table 6 Comparison Reference Values (CRVs), x_{ref}, and expanded uncertainties ($U(x_{ref})$) for specimens 1, 2, and 3.

Specimens		CRV(= x_{ref})	$u(x_{ref})$	$U(x_{ref})$
		nm		
1		2.587	0.012	0.023
2		4.421	0.014	0.028
3	AlAs 1	5.090	0.014	0.027
	AlAs 2	5.074	0.014	0.028
	AlAs 3	5.067	0.014	0.027
	GaAs 2	4.932	0.014	0.027
	GaAs 3	4.925	0.014	0.027

7.1 Reported thickness (*t*) versus Comparison Reference Values (x_{ref}) for specimens 1 and 2

Figure 3 shows the reported thickness values from each NMI (Table 5), together with the estimated comparison reference values, x_{ref}, and their expanded uncertainties, $U(x_{ref})$, for specimens 1 and 2 (Table 6). In Fig. 3, the blue line represents the comparison reference value (x_{ref}), while the interval indicated by the red lines corresponds to $x_{ref} \pm U(x_{ref})$. The black squares with error bars represent the reported values $x_i \pm U(x_i)$. A detailed graphical explanation of the symbols in Fig. 3 is provided in Fig. 4.

As shown in Fig. 3, the reported thickness values from each NMI, together with their expanded uncertainties, overlap sufficiently with the intervals defined by the CRVs and their expanded uncertainties. The agreement between the participants is notably good relative to the reported uncertainties. This may primarily reflect the inherently high precision of XRR measurements, as well as the use of common measurement conditions and data analysis procedures. In addition, some components of the uncertainty, particularly those that cannot be directly evaluated experimentally, may have been conservatively estimated, leading to relatively large uncertainties compared to the observed dispersion of the results.

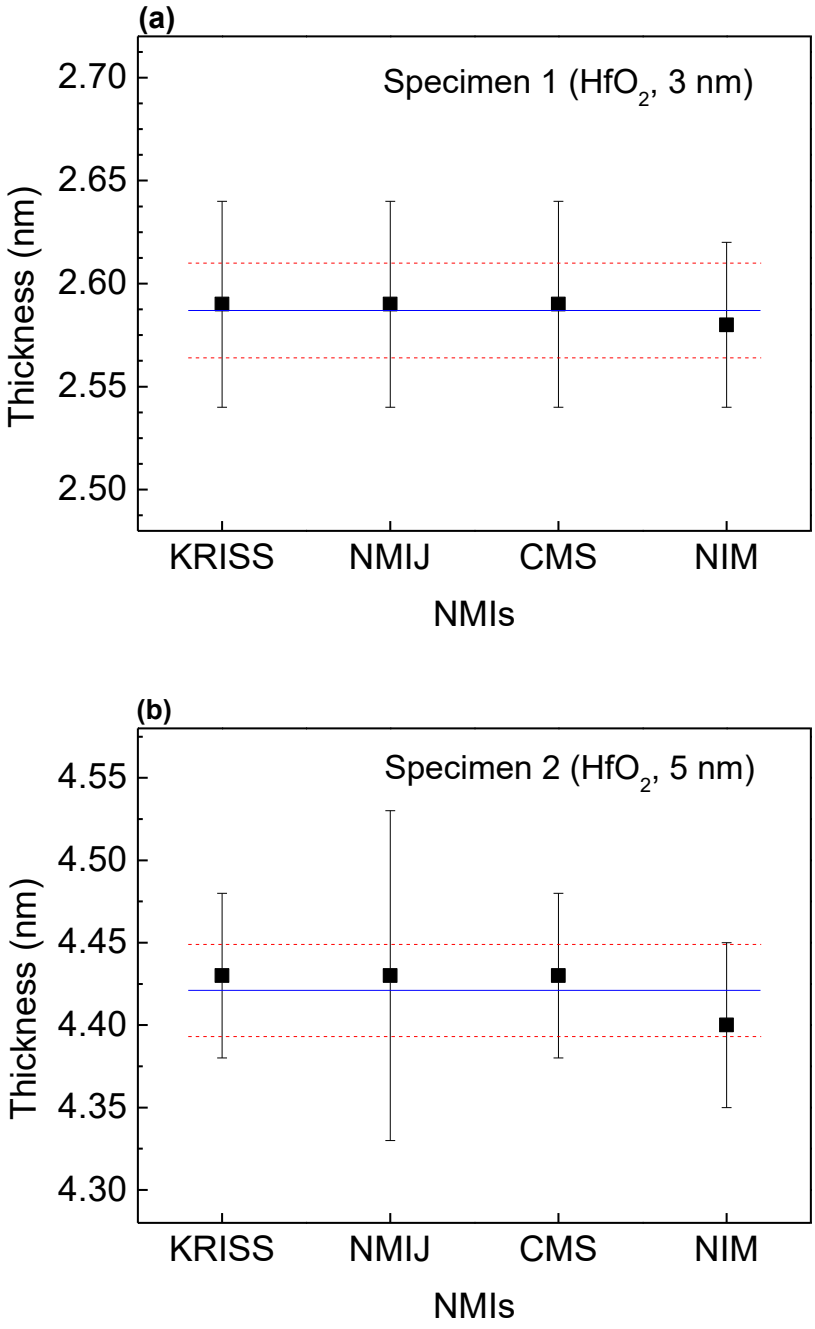


Fig. 3. Reported thickness values and comparison reference values, together with their expanded uncertainties for (a) specimen 1 and (b) specimen 2.

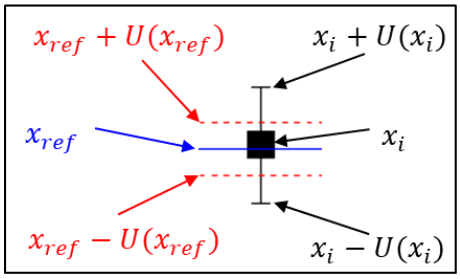
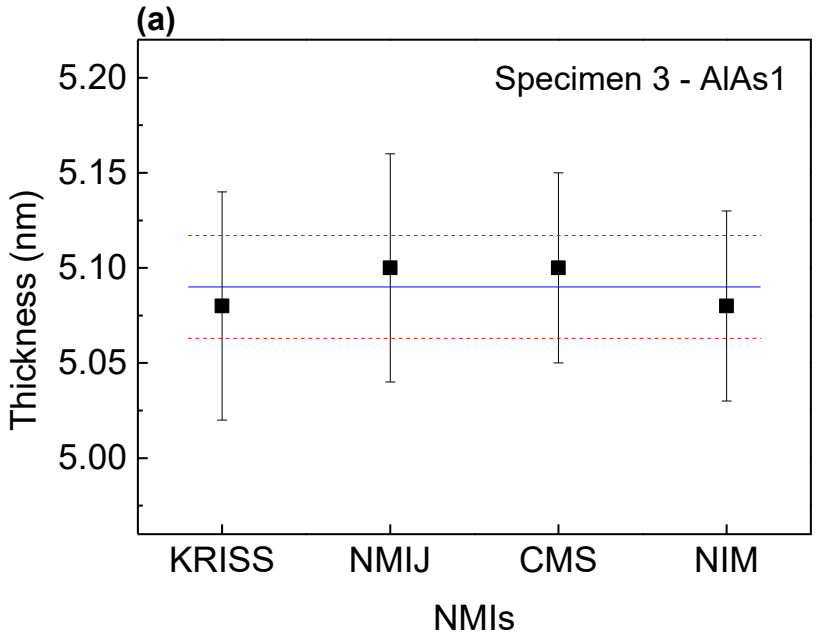


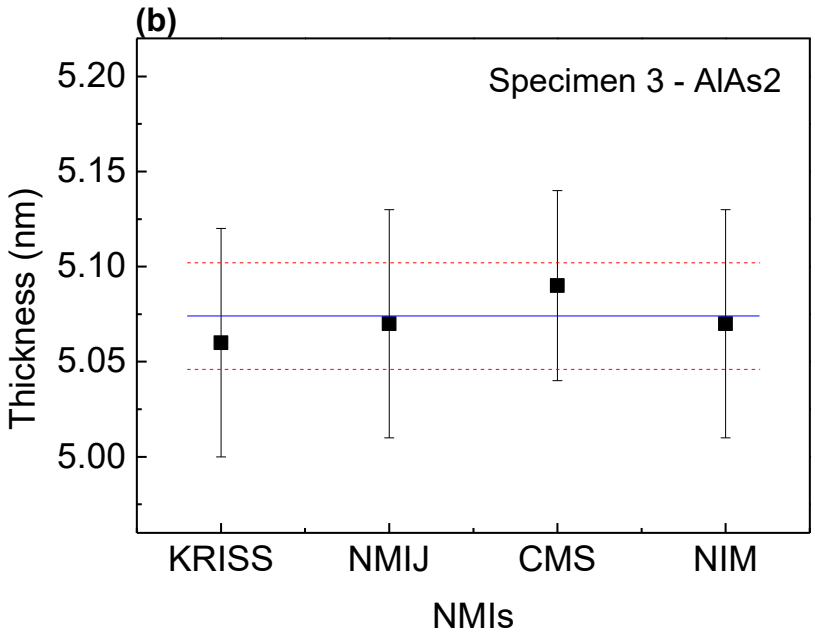
Fig. 4. Graphical legend explaining the symbols used in Fig. 3.

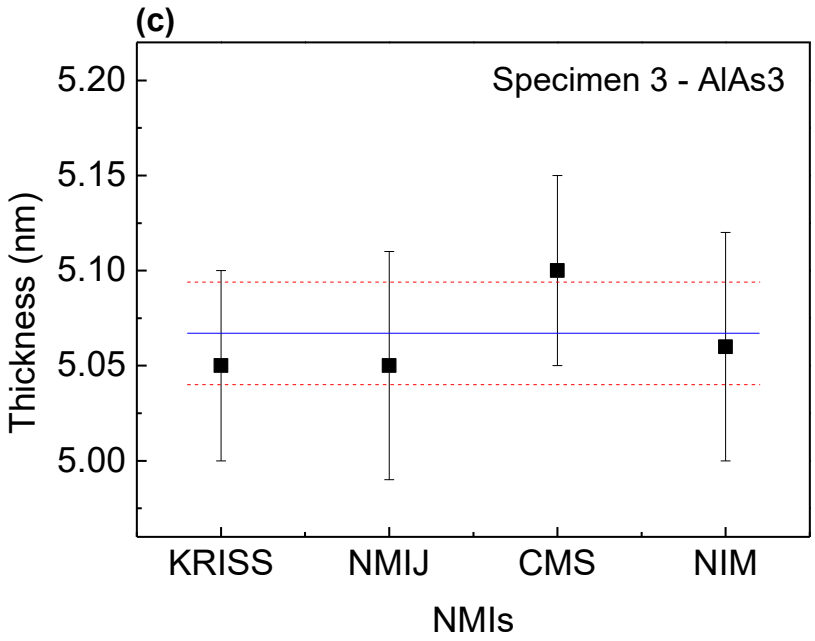
7.2 Reported thicknesses (*t*) versus Comparison Reference Values (x_{ref}) for specimen 3

Figure 5 also shows the reported thickness values from each NMI (Table 5), together with the estimated comparison reference values, x_{ref}, and their expanded uncertainties, $U(x_{ref})$, for the layers reported for specimen 3 (Table 6). The results for the uppermost GaAs layer (GaAs 1) are not included, because its thickness varies among the specimens due to the oxidation. The graphical representation of the symbols used in Fig. 5 is the same as that used in Fig. 3 and illustrated in Fig. 4.

As shown in Fig. 5, the reported thickness values for all included layers of specimen 3, together with their expanded uncertainties, sufficiently overlap with the intervals defined by the CRVs and their expanded uncertainties. A similarly good level of agreement relative to the reported uncertainties is observed for specimen 3. As discussed for specimens 1 and 2, this may be attributed to the high precision of XRR measurements and the conservative estimation of certain uncertainty components.




(b)
Specimen 3 - AlAs2
Thickness (nm)
5.20
5.15
5.10
5.05
5.00
KRISS
NMIJ
CMS
NIM
NMIs


(c)
Specimen 3 - AlAs3
Thickness (nm)
5.20
5.15
5.10
5.05
5.00
KRISS
NMIJ
CMS
NIM
NMIs

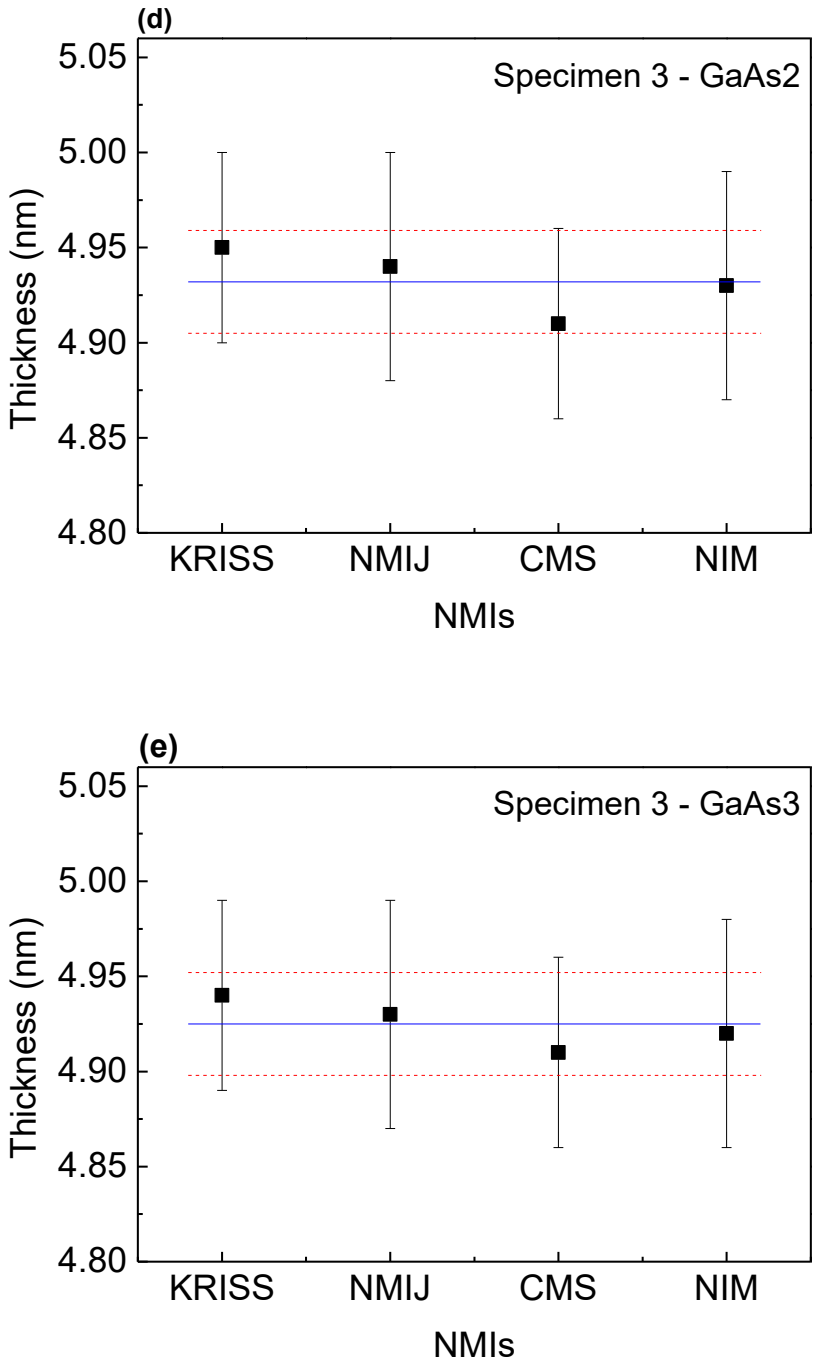


Fig. 5. Reported thickness values and comparison reference values, together with their expanded uncertainties, for each layer of specimen 3.

8. Equivalence Statements

The equivalence statements were calculated for each thickness result in accordance with BIPM guidelines [18, 20-22]. The degree of equivalence (DoE), denoted as d_i is calculated using the following expression:

$$d_i = x_i - x_{ref} \tag{8-1}$$

where x_i is reported result from an individual NMI and x_{ref} is the CRV.

The standard uncertainty of the degree of equivalences, $u(d_i)$, is obtained by combining the standard uncertainty of the individual reported value, $u(x_i)$, and the standard uncertainty of the CRV, $u(x_{ref})$. A coverage factor of k=2 is applied to calculate the expanded uncertainty of the degree of equivalence, $U(d_i)$, as given by:

$$u^2(d_i) = u^2(x_i) - u^2(x_{ref}) \tag{8-2}$$

$$U(d_i) = k \cdot u(d_i) \tag{8-3}$$

The normalized error, E_n is defined as:

$$E_n = \frac{d_i}{U(d_i)} = \frac{d_i}{2 \cdot u(d_i)} \tag{8-4}$$

If the absolute value $|E_n|$ for a reported result x_i exceeds 1, the result is considered to be inconsistent with the reference value within the standard uncertainties.

For specimens 1 and 2, the degrees of equivalences d_i, expanded uncertainties $U(d_i)$ and $|E_n|$ values were calculated using the above equations and are summarized in Table 7.

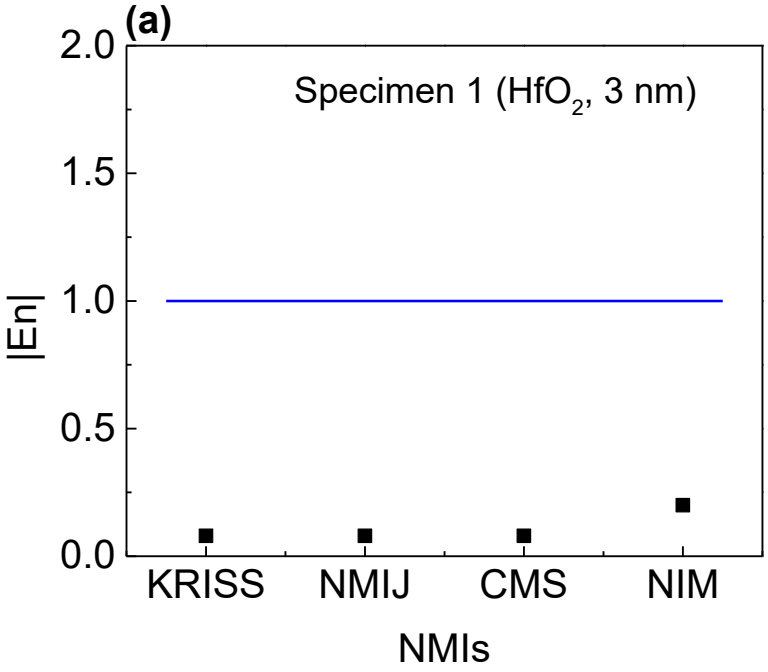
In addition, the degrees of equivalence d_i, expanded uncertainties $U(d_i)$, and $|E_n|$ values for specimen 3 are calculated and presented in Table 8(a) and 8(b).

8.1 E_n values for specimens 1 and 2

The $|E_n|$ values for specimens 1 and 2, as listed in Table 7, are plotted in Fig. 6. All $|E_n|$ values are less than 1, indicating that no outliers are present in the measurement results for specimens 1 and 2.

Table 7 Degrees of equivalence, expanded uncertainties, and $|E_n|$ values for specimens 1 and 2.

NMIs	Specimen 1 (x_{ref} = 2.587)					Specimen 2 (x_{ref} = 4.421)				
	$t\ (=x_i)$	$U(x_i)$	d_i	$U(d_i)$	$\lvert E_n \rvert$	$t\ (=x_i)$	$U(x_i)$	d_i	$U(d_i)$	$\lvert E_n \rvert$
	(nm)				-	(nm)				-
KRISS	2.59	0.05	0.003	0.044	0.08	4.43	0.05	0.009	0.042	0.22
NMIJ	2.59	0.05	0.003	0.044	0.08	4.43	0.10	0.009	0.096	0.10
CMS	2.59	0.05	0.003	0.044	0.08	4.43	0.05	0.009	0.042	0.22
NIM	2.58	0.04	-0.007	0.032	0.20	4.40	0.05	-0.021	0.042	0.50



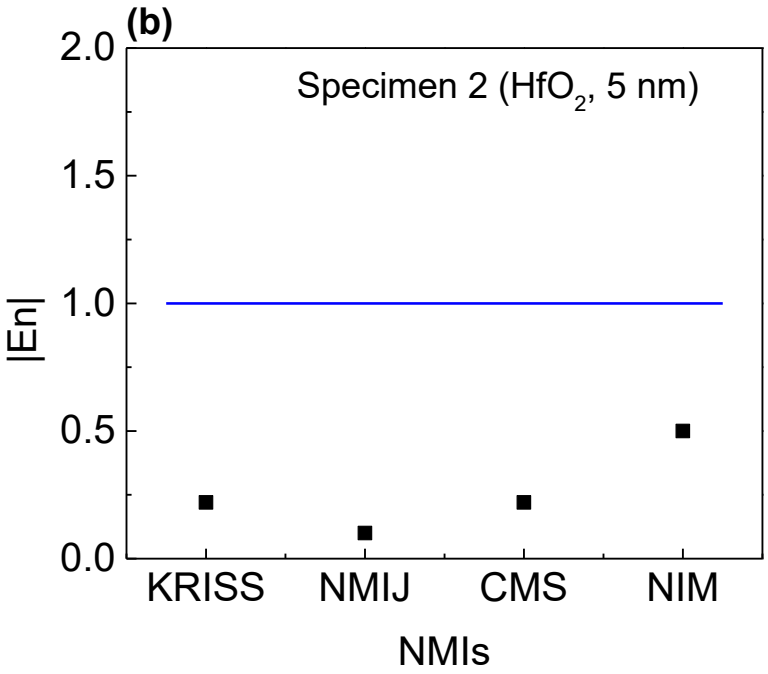


Fig. 6. $|E_n|$ values for (a) specimen 1 and (b) specimen 2.

8.2 E_n values for specimen 3

Table 8 lists the degrees of equivalence (d_i), expanded uncertainties ($U(d_i)$), and $|E_n|$ values for all layers of specimen 3, and the corresponding $|E_n|$ values are plotted in Fig. 7. Similar to the results shown in Fig. 6 for specimens 1 and 2, all $|E_n|$ values for the layers of specimen 3 are less than 1, indicating that no outliers are presented in the measured thickness values.

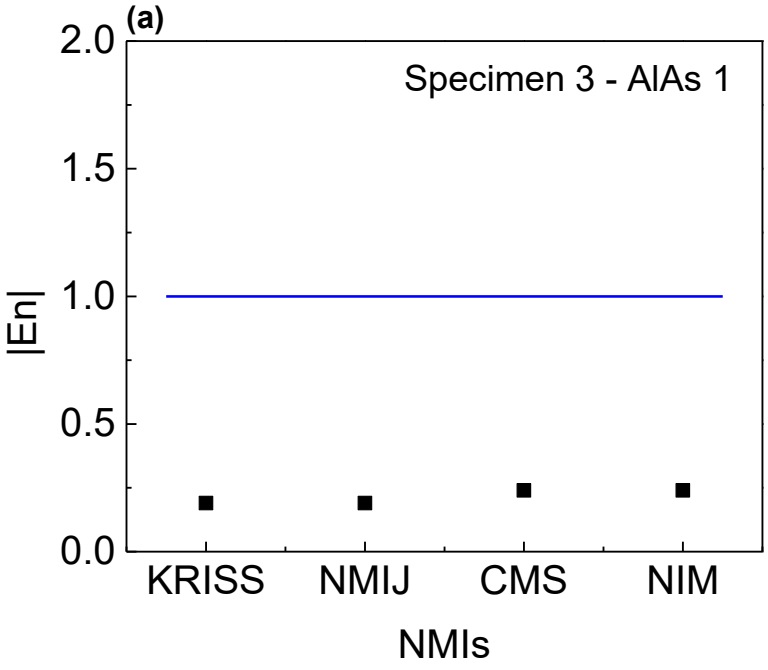
Table 8 Degrees of equivalence, expanded uncertainties, and $|E_n|$ values for (a) AlAs layers and (b) GaAs layers of specimen 3.

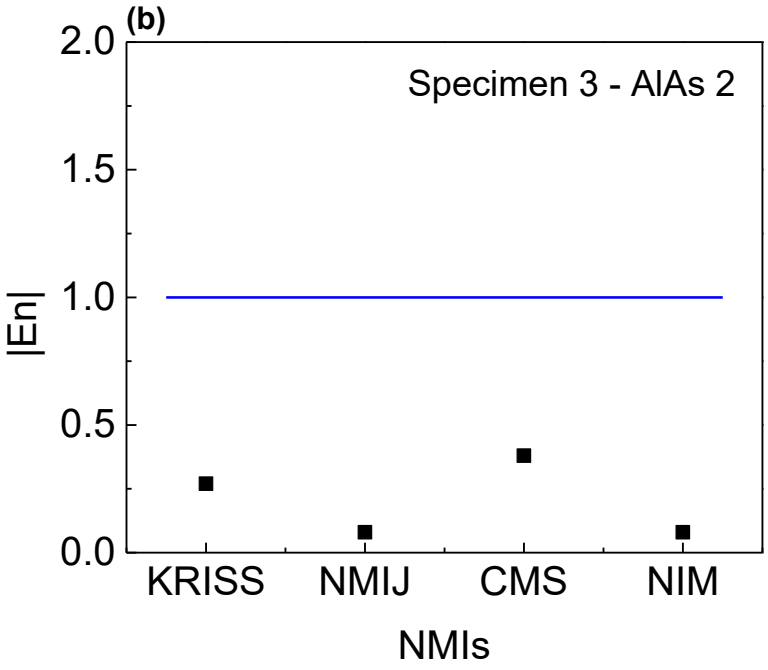
(a)

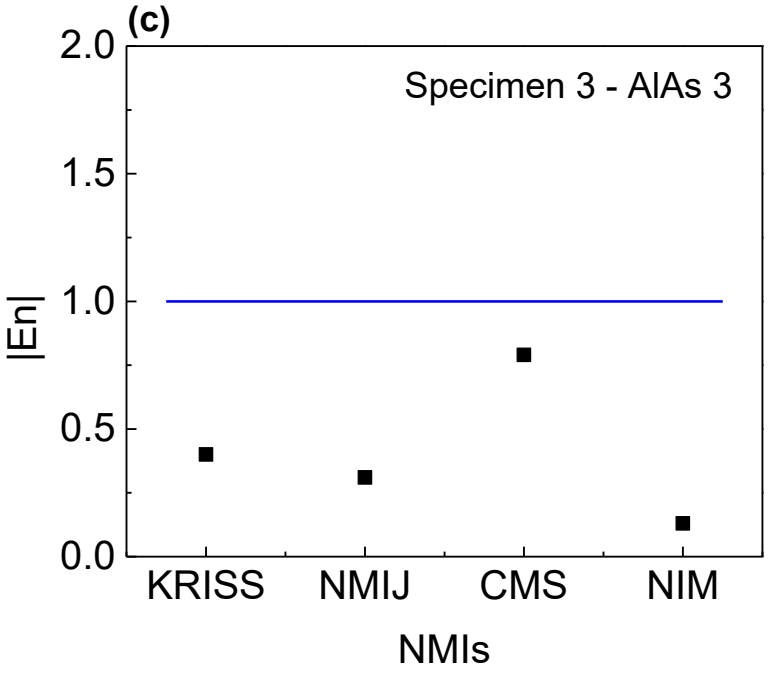
NMIs	Specimen 3														
	AlAs1 (x_{ref} = 5.090)					AlAs2 (x_{ref} = 5.074)					AlAs3 (x_{ref} = 5.067)				
	$t\,(=x_i)$	$U(x_i)$	d_i	$U(d_i)$	$\lvert E_n\rvert$	$t\,(=x_i)$	$U(x_i)$	d_i	$U(d_i)$	|En|	$t\,(=x_i)$	$U(x_i)$	d_i	$U(d_i)$	$\lvert E_n\rvert$
	nm				-	nm				-	nm				-
KRISS	5.08	0.06	-0.010	0.054	0.19	5.06	0.06	-0.014	0.053	0.27	5.05	0.05	-0.017	0.042	0.40
NMIJ	5.10	0.06	0.010	0.054	0.19	5.07	0.06	-0.004	0.053	0.08	5.05	0.06	-0.017	0.054	0.31
CMS	5.10	0.05	0.010	0.042	0.24	5.09	0.05	0.016	0.041	0.38	5.10	0.05	0.033	0.042	0.79
NIM	5.08	0.05	-0.010	0.042	0.24	5.07	0.06	-0.004	0.053	0.08	5.06	0.06	-0.007	0.054	0.13

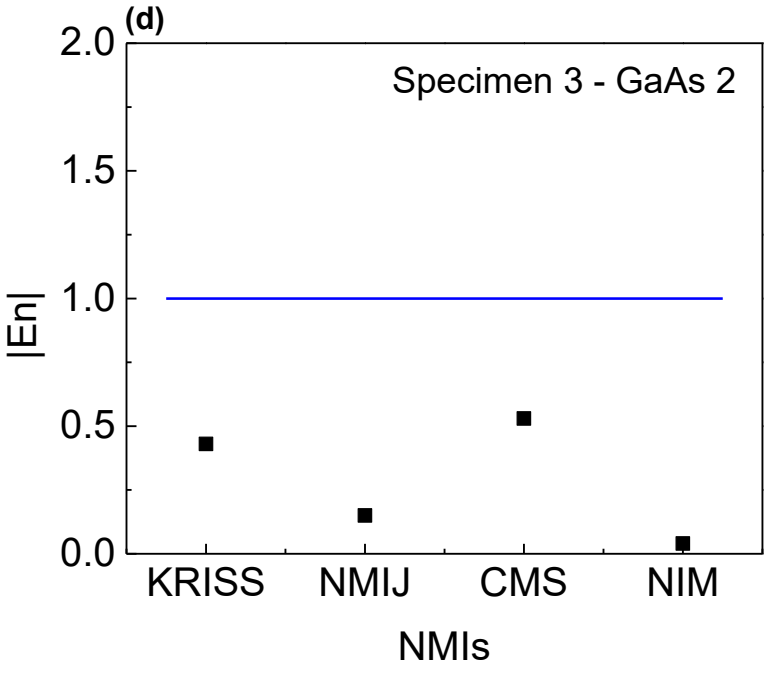
(b)

NMIs	Specimen 3									
	GaAs2 (x_{ref} = 4.932)					GaAs3 (x_{ref} = 4.925)				
	$t\,(=x_i)$	$U(x_i)$	d_i	$U(d_i)$	$\lvert E_n\rvert$	$t\,(=x_i)$	$U(x_i)$	d_i	$U(d_i)$	$\lvert E_n\rvert$
	nm				-	nm				-
KRISS	4.95	0.05	0.018	0.042	0.43	4.94	0.05	0.015	0.042	0.36
NMIJ	4.94	0.06	0.008	0.054	0.15	4.93	0.06	0.005	0.054	0.09
CMS	4.91	0.05	-0.022	0.042	0.53	4.91	0.05	-0.015	0.042	0.36
NIM	4.93	0.06	-0.002	0.054	0.04	4.92	0.06	-0.005	0.054	0.09


(a)
Specimen 3 - AlAs 1
2.0
1.5
1.0
0.5
0.0
|En|
KRISS
NMIJ
CMS
NIM
NMIs


(b)
Specimen 3 - AlAs 2
2.0
1.5
1.0
0.5
0.0
|En|
KRISS
NMIJ
CMS
NIM
NMIs


(c)
Specimen 3 - AlAs 3
2.0
1.5
1.0
0.5
0.0
|En|
KRISS
NMIJ
CMS
NIM
NMIs


(d)
Specimen 3 - GaAs 2
2.0
1.5
1.0
0.5
0.0
|En|
KRISS
NMIJ
CMS
NIM
NMIs

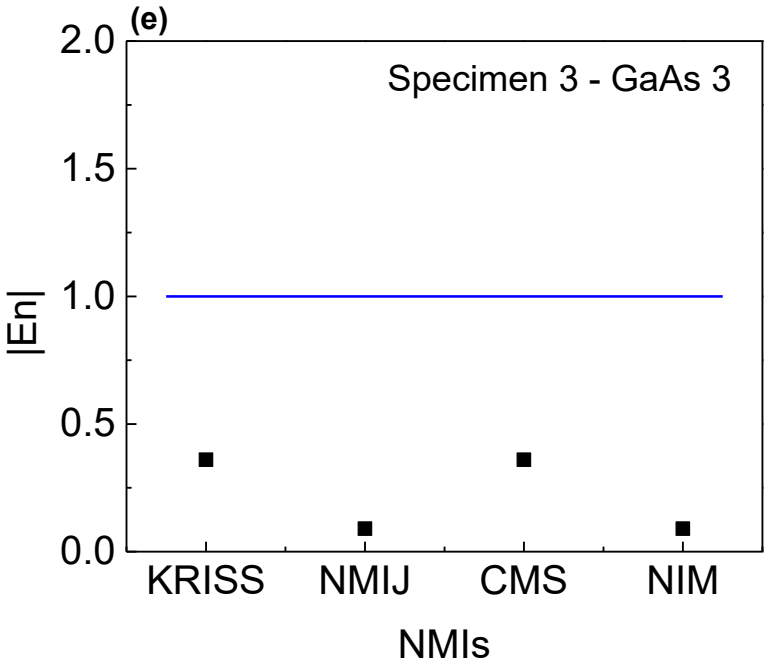
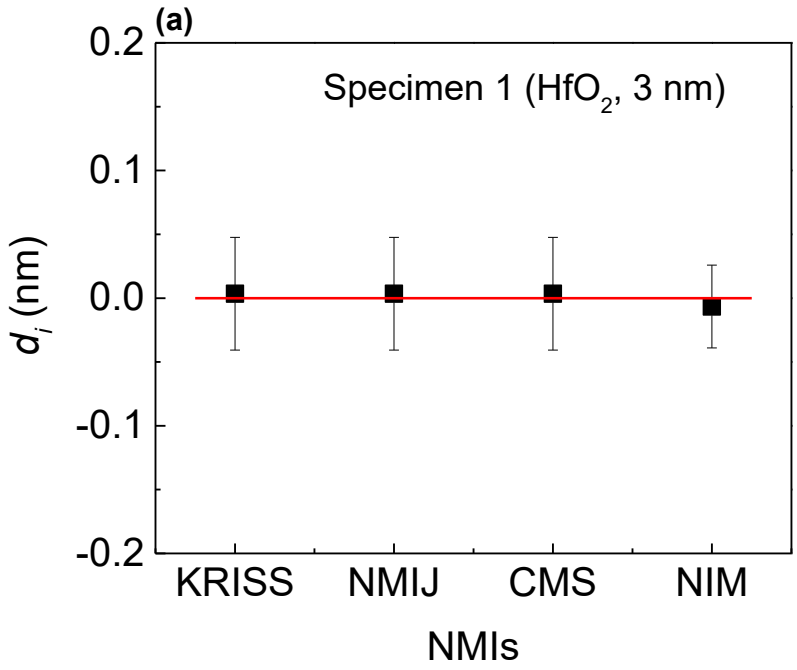


Fig. 7. $|E_n|$ values for all layers of specimen 3.

8.3 Degrees of equivalences (d_i) and uncertainties ($U(d_i)$) for specimen 1 and 2

The degrees of equivalence and their expanded uncertainties for specimen 1 and 2, as listed in Table 7, are plotted in Fig. 8. The red line represents the reference line with $d_i = 0$, while the black squares with error bars represent $d_i \pm U(d_i)$, as graphically illustrated in Fig. 9.

As shown in Fig. 8, although d_i values differ among the participating NMIs, the intervals defined by $d_i \pm U(d_i)$ overlap with the reference line $d_i = 0$ for each specimen. This indicates that the reported results are mutually equivalent within their respective uncertainties for each specimen.



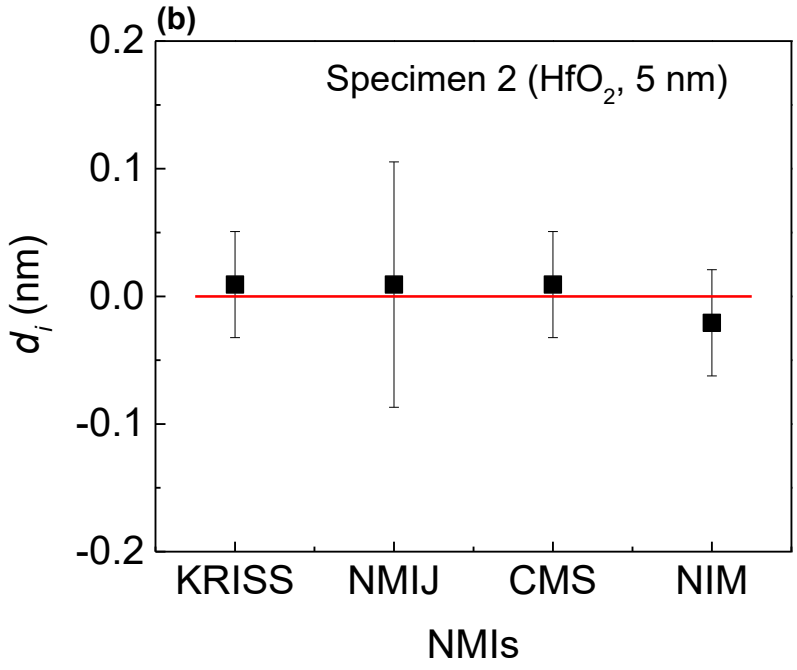


Fig. 8. Degrees of equivalence with expanded uncertainties relative to the reference line at $d_i = 0$ for (a) specimen 1 and (b) specimen 2.

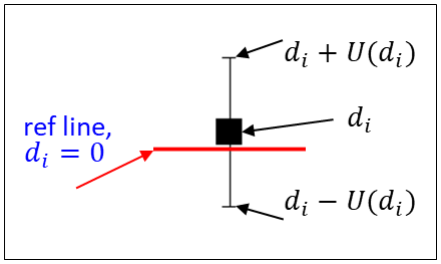
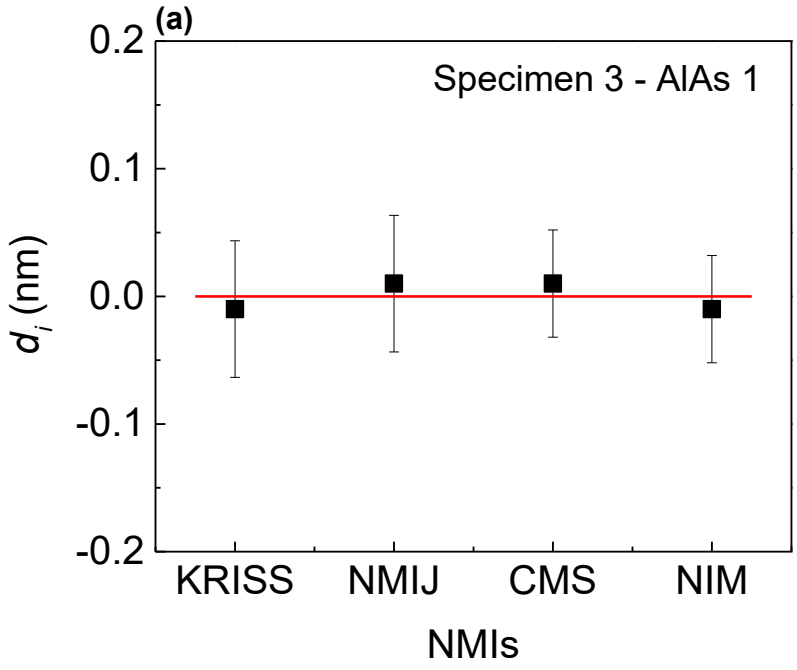


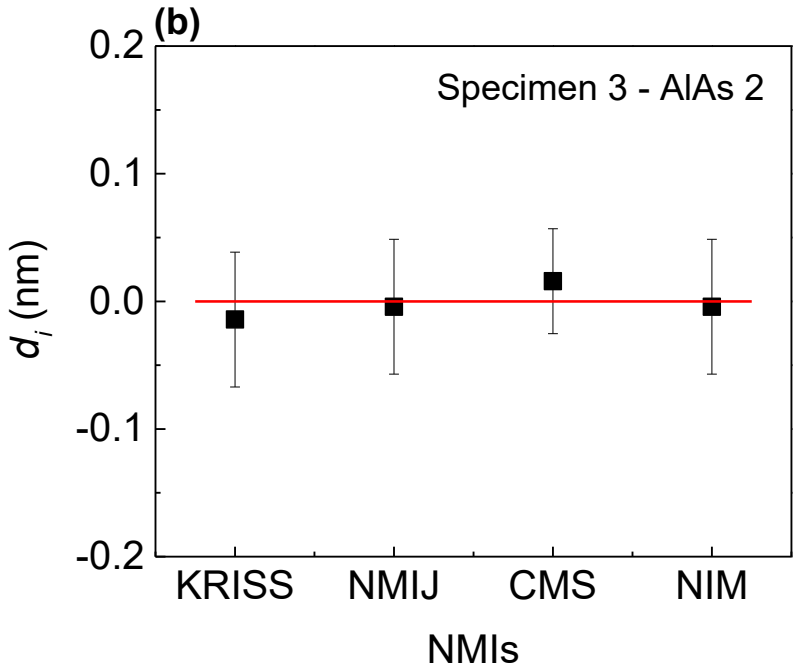
Fig. 9. Graphical legend explaining the symbols used in Fig. 8.

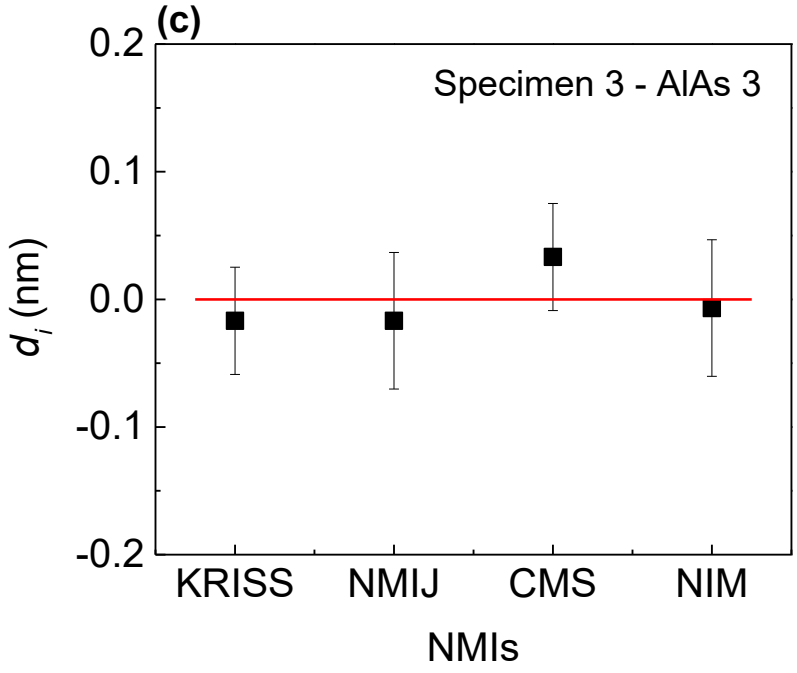
8.4 Degrees of equivalence (d_i) and uncertainties ($U(d_i)$) for specimen 3

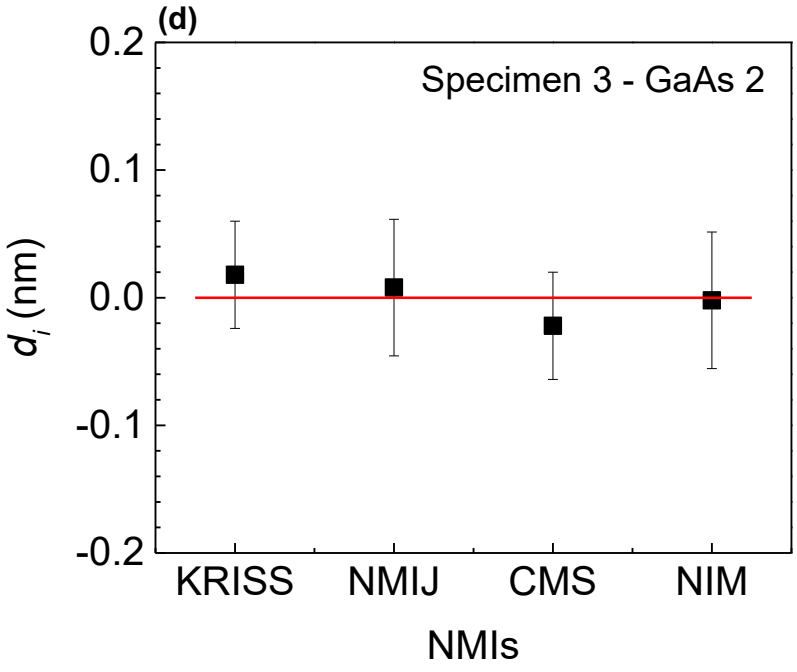
The degrees of equivalence and their expanded uncertainties for the layers of specimen 3, as presented in Table 8, are plotted in Fig. 10. Similar to Fig. 8, the red line represents the reference line at $d_i = 0$, while the black squares with error bars represent $d_i \pm U(d_i)$, as illustrated in Fig. 9.

As shown in Fig. 10, the intervals defined by $d_i \pm U(d_i)$ overlap with the reference line of $d_i = 0$ for each layer of specimen 3. This indicates that the reported results for all layers of specimen 3 are mutually equivalent within their respective uncertainties.


(a)
Specimen 3 - AlAs 1
0.2
0.1
0.0
-0.1
-0.2
d_i (nm)
KRISS
NMIJ
CMS
NIM
NMIs


(b)
Specimen 3 - AlAs 2
0.2
0.1
0.0
-0.1
-0.2
d_i (nm)
KRISS
NMIJ
CMS
NIM
NMIs


(c)
Specimen 3 - AlAs 3
0.2
0.1
0.0
-0.1
-0.2
d_i (nm)
KRISS
NMIJ
CMS
NIM
NMIs


(d)
Specimen 3 - GaAs 2
0.2
0.1
0.0
-0.1
-0.2
d_i (nm)
KRISS
NMIJ
CMS
NIM
NMIs

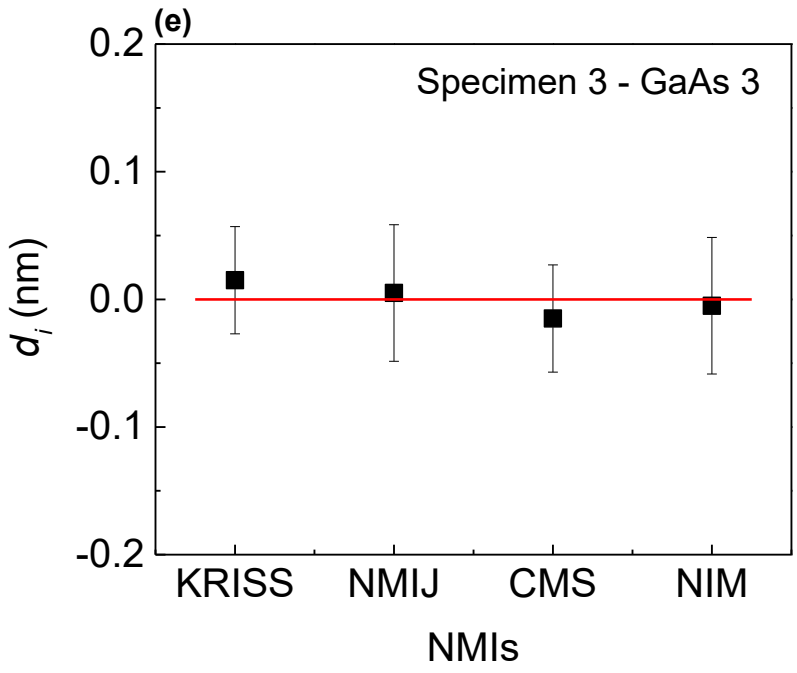


Fig. 10. Degrees of equivalence with expanded uncertainties relative to the reference line at $d_i = 0$ for each layer of specimen 3.

9. Conclusions

TCMM/APMP conducted a supplementary comparison (SC) on the measurement of nanoscale film thicknesses using X-ray reflectivity (XRR). The objectives of this SC were to perform an interlaboratory comparison of film thicknesses measured using XRR and to confirm the international equivalence of the measurement results reported by APMP NMIs.

Four NMIs – CMS, NIM, NMIJ and KRISS – participated in the comparison using three specimens. Two specimens consisted of single-layered HfO_2 films, and the third was a multi-layered AlAs/GaAs superlattice with three periods, having nominal film-thicknesses ranging from 3.0 nm to 5.0 nm.

The participating NMIs reported film thickness values together with their associated measurement uncertainties. The reported results were compared, and comparison reference values (CRVs) were determined using the uncertainty-weighted mean method. Degrees of equivalence (d_i) and normalized error (E_n) values were subsequently calculated.

For all measured thickness values of specimens 1, 2, and 3, the absolute values of $|E_n|$ were found to be less than 1, indicating the absence of outliers in the measured results. The reported thicknesses values, together with their uncertainty error bars, overlapped with the intervals defined by the CRVs and their expanded uncertainties for each specimen. These results demonstrate that reported measurements are mutually equivalent within their stated uncertainties. Furthermore, the intervals of $d_i \pm U(d_i)$ overlapped with the reference line at $d_i = 0$ for all specimens, indicating that the degrees of equivalence are consistent with zero within their respective uncertainties. This confirms the overall consistency and international equivalence of the film thickness measurements among the participating NMIs.

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ANNEX

Annex A. Technical Protocol

APMP Supplementary Comparison (SC): Film-Thickness Measurement Using XRR (X-Ray Reflectometry)

TECHNICAL PROTOCOL (Draft)

2019-2022 XRR Film-Thickness Comparison between APMP Laboratories

Pilot Laboratory: Korea Research Institute of Standards and Science (KRISS), 267 Gajeong-Ro, Yuseong-Gu, Daejeon 34113, Republic of Korea

Co-Pilot Laboratory: National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, 305-8565 Japan

Coordinators: Chang-Soo Kim (KRISS), e-mail: kimcs@kriss.re.kr

Yasushi Azuma (NMIJ), e-mail: azuma.y@aist.go.jp

Contents

1. Introduction

At the TCMM/APMP meeting held in Singapore on November 26, 2018, a supplementary comparison on nano-film-thickness measurement using XRR among APMP NMIs was proposed.

By means of the proposed comparison, the TCMM/APMP will provide a basis for establishing materials metrology on film thickness that is traceable to SI unit among the National Metrology Institutes in APMP.

The protocol outlined in this document was prepared following the measurement comparisons in the CIPM MRA [1] and the CCEM guidelines for planning, organizing, conducting and reporting key, supplementary and pilot comparisons [2].

2. Objectives of the SC

The objectives of the supplementary comparison (SC) are

- to make inter-laboratory comparison
- to confirm international equivalence

for nano-scale film thicknesses measured by XRR (X-Ray Reflectometry) among NMIs.

3. Measurand

The XRR film thicknesses of the three specimens provided, expressed in terms of the nm unit.

4. Specimens

Three specimens are provided for the comparison, 1) 3.0 nm thick HfO_2 on SiO_2, 2) 5.0 nm thick HfO_2 on SiO_2, 3) AlAs/GaAs multilayers on GaAs. Detailed descriptions of the specimens are summarized in Table 1.

***Table 1*:** Detailed information of specimens

No	Specimen	Single /Multi-layer	Surface polishing	Specimen size (mm × mm)	Nominal Thickness (nm)	Provided by
1	HfO_2/SiO_2*	single	single sided	20 × 40	3.0	KRISS, Korea
2	HfO_2/SiO_2*	single	single sided	20 × 40	5.0	KRISS, Korea
3	AlAs/GaAs**	multi	double sided	15 × 15	(5/5) x 3	NMIJ, Japan

*: SiO_2-substrate, **: GaAs/AlAs/ GaAs/AlAs/ GaAs/AlAs/GaAs-substrate,

5. Participants

The proposed participating institutes are listed in the following table. The contact details are given in Annex A1.

***Table 2*:** Participants

Country/ Economic Region	Institute	Acronym
China	National Institute of Metrology	NIM
Chinese Taipei	Center for Measurement Standards	CMS
Japan	National Metrology Institute of Japan	NMIJ
Korea, The Republic of	Korea Research Institute of Standards and Science	KRISS

6. Specimen delivery sequence and time schedule

XRR measurements and circulation of the specimens are scheduled to start in April 2022 and is planned to end in July 2022. The specimen delivery sequence to each participant and the detailed time schedule are given in Annex A2.

A period of three weeks is allowed for the measurements of the specimens at each laboratory, including the transit time. Also, a period of one week at KRISS is allowed for the cleaning and subsequent packing of the specimens.

7. Delivery and packing list

Specimens will be delivered in two ways. Package 1 containing specimens 1 and 2 (plus a pair of beam-stoppers) will be delivered from KRISS according to the time schedule in Annex A2. Package 2 containing specimen 3 will be delivered to all participants at the same time from NMIJ around in May.

A packing list for package 1 from KRISS is shown in Table 3, and a packing list for package 2 from NMIJ in Table 4.

Specimens 1 and 2 will be returned to KRISS, and the specimens will be delivered again to next NMI for the subsequent measurement in Annex A2 after cleaning.

***Table 3*:** Packing list for the package 1 from KRISS

No	Specimen	Single /Multi-layer	Surface polishing	Specimen size (mm × mm)	Nominal Thickness (nm)
1	HfO_2/SiO_2	single	single sided	20 × 40	3.0
2	HfO_2/SiO_2	single	single sided	20 × 40	5.0

***Table 4*:** Packing list for the package 2 from NMIJ

No	Specimen	Single /Multi-layer	Surface polishing	Specimen size (mm × mm)	Nominal Thickness (nm)	Specimen code
3	AlAs/GaAs	multi	double sided	15 × 15	(5/5) x 3	#1 (NIM) #2 (CMS) #3 (NMIJ) #4 (KRISS)

8. Measurement instructions

8.1 Unpacking

-. Please be very careful not to make any damages or cracks on the specimens during measurements and handlings.

-. On each specimen storage case, specimen 1, specimen 2, and specimen 3 are labeled, respectively.

-. Each specimen is stored in a conical-base tray with the thin-film side down, and the back side of the specimen is supported by a plastic spring.

-. Each specimen is vacuum-packed.

-. Specimens 1 (3.0 nm HfO_2) and 2 (5.0 nm HfO_2) are single-side-polished. Specimen 3 (AlAs/GaAs superlattice) is double-side-polished, but the thin-film(s) were deposited on one side. In order to distinguish the film surface, small marks were made at the backside corner.

-. The surfaces of the specimens 1, and 2 are cleaned before vacuum-packing at KRISS, while specimen 3 is left untouched as vacuum-packed by NMIJ. **The specimens are strongly recommended to be measured as fast as possible after delivery in order to avoid an excess surface contamination,** which may cause a distortion of X-ray reflectivity curves.

8.2 Method of measurement

X-Ray Reflectivity measurement method [3,4,5,6,7]

8.3 Measurement conditions

Recommended XRR measurement conditions are as follow, and also summarized in Table 5.

-. Measurement range: see Table 5
-. Measurement step: see Table 5
-. Counting time/step: see Table 5
-. Preferred ambient temperature: Room Temperature
-. Preferred ambient relative humidity: < 50 %
-. No background correction (subtraction) is required.
-. No specimen cleaning is required.
-. Each specimen is placed on a specimen holder, in which the long edge of the specimen is parallel to the direction of the X-Ray beam.

-. Brief instruction for use of the beam-stoppers provided

In order to make the same beam exposure conditions from different laboratories, the beam-stoppers may be used as shown in Figure 1.

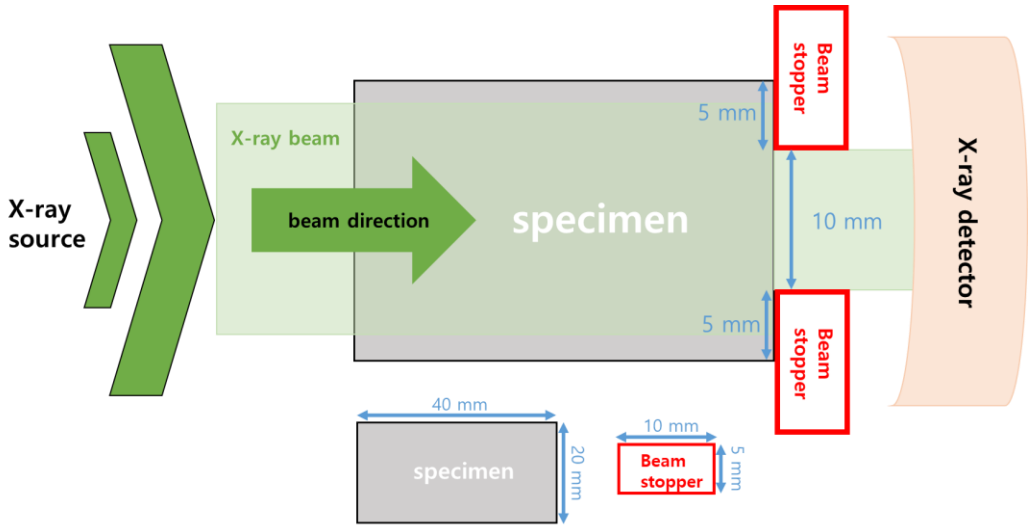


Figure 1. A schematic instruction diagram for the use of beam-stoppers

***Table 5*:** XRR measurement conditions

No	Specimen	Meas. Range(°, 2θ)	Meas. step (°, 2θ)	Counting Time/step (sec) in a continuous scan mode
1	HfO_2/SiO_2	0.1 - 10	0.02	4
2	HfO_2/SiO_2	0.1 – 10	0.02	4
3	AlAs/GaAs ML	0.1 - 10	0.01	≥ 2

9. Return of the specimens

After finishing XRR measurements of the specimens, please return specimens 1, and 2 in package 1 to KRISS as soon as possible. At KRISS, the specimens will be cleaned and vacuum-packed again with the same procedure as before, and shipped to the next laboratory (see Annex A2) for the subsequent measurement. For specimen 3, please return it to NMIJ.

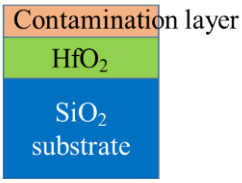
10. Data analysis

10.1 Model structures of the specimens for simulation and fit

Data analysis is conducted through simulation and fitting procedure.

10.1.1 For specimens 1, and 2, following model for layered structures is used for simulation and fit.

-. Specimen 1 and Specimen 2



10.1.2 For specimen 3, following model is used for the simulation and fit.

-. Specimen 3

Notes:

1. **If the above models do not produce good fittings, different models will be discussed among the participants.**
2. **A contamination layer on the top of the surface is assumed. (see 9.2)**

10.2 Tables of the results

After data analysis, the following tables are used for reporting.

-. Specimen 1

Meas. Date (yy/mm/dd)	Thickness (nm)			Roughness(rms)	Density(g/cm3)
	Nominal	Final	Uncertainty		
Contam. Layer ($C_6H_{14}O_2$)					
HfO_2	3.0				
SiO_2 Substrate					2.23

: not required

-. Specimen 2

Meas. Date (yy/mm/dd)	Thickness (nm)			Roughness(rms)	Density(g/cm3)
	Nominal	Final	Uncertainty		
Contam. Layer ($C_6H_{14}O_2$)					
HfO_2	5.0				
SiO_2 Substrate					2.23

-. Specimen 3

Meas. Date (yy/mm/dd)	Thickness (nm)			Roughness(rms)	Density(g/cm3)
	Nominal	Final	Uncertainty		
Contam. Layer ($C_6H_{14}O_2$)					
Oxide (GaAsO)	5.4				
GaAs					
AlAs	5.0				
GaAs	5.0				
AlAs	5.0				
GaAs	5.0				
AlAs	5.0				
GaAs Substrate					5.317

11. Uncertainty of measurement

A detailed uncertainty budget in accordance with the ISO Guide to the Expression of Uncertainty in Measurement [8] shall be reported for each specimen.

12. Method of computation of the Comparison Reference Value (CRV)

The proposed principles of the analysis for the Comparison Reference Value (CRV) are:

-. The results obtained by the pilot laboratory will be used to determine the thickness change of the films of the specimens, if any;

-. For the calculation of the CRV, the uncertainty weighted mean value over the laboratories will be used. The detailed method for the calculation of the CRV, however, will be discussed among the participants after the measurements.

13. Measurement report

Each participant is asked to submit a final printed and signed report by mail within one month after completing the measurements to the pilot lab. A copy of the report may also be sent by e-mail. In the case of differences between electronic and paper versions of the report, the signed paper form is considered to be the valid version. The report should contain at least the following:

-. Measurand (name of specimen, nominal value)
-.Traceability scheme. If the traceability to the SI is provided by another NMI, the name of the NMI should be stated (needed to identify possible sources of correlation).
-. The ambient conditions of the measurement; the mean temperature and humidity
-. Experimental details;
  - X-ray wavelength used
  - incident beam intensity and detector background
  - details of the incident and scattered beam conditioning (monochromator, slits, collimator, and other optics)
  - incident beam divergence
-. Raw data and corresponding fitted simulation data
-. Graphical plots of experimental and simulated specular reflectivity data for each specimen in terms of reflected intensity vs. omega (incident) angle in a logarithmic scale
-. The analysis (simulation and fitting) results: Mean thickness value and uncertainty for every specimen, expressed down to two places of decimals (see section 8.2)
-. The date of measurements
-. A complete uncertainty budget in accordance with the principles of the ISO Guide to the Expression of Uncertainty in Measurement [8], including degrees of freedom for every component and calculation of the coverage factor. Such an analysis is a prerequisite to be considered in the calculation of the Comparison Reference Value(CRV).
-. Signature and title of the laboratory representative

References

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[8] ISO/IEC Guide 98-3:2008, Uncertainty of measurement-Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995), 2008

A1. Detailed list of participants

Institute (Acronym)	Country/ Economic Region	Contact person	Address	Telephone	e-mail
National Institute of Metrology (NIM)	China	Huifang Gao (Lingling Ren)	National Institute of Metrology (NIM), Center for Advanced Measurement of Science (Room 2019/Building 5), No.18, Beisanhuan Donglu, Chaoyang District, Beijing 100029, China	+86 10 64526513	gaohf@nim.ac.cn (renll@nim.ac.cn) Mobile: +86 13717873748
Center for Measurement Standards (CMS)	Chinese Taipei	Guo-Dung Chen (Fang-Hsin Lin)	Center for Measurement Standards (CMS), Industrial Technology Research Institute, Bldg. 16, No. 321, Sec. 2, Kuang Fu Rd. 300044, Hsinchu City, Chinese Taipei	+886 3 5743753	Eric_chen@itri.org.tw (itriA40317@itri.org.tw) +886-3-5743744
National Metrology Institute of Japan (NMIJ)	Japan	Yasushi Azuma	Research Institute for Material and Chemical Measurement, National Metrology Institute of Japan (NMIJ), AIST, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, 305-8565 Japan	+81 29 861 2251	azuma.y@aist.go.jp
Korea Research Institute of Standards and Science (KRISS)	Korea, The republic of	Chang Soo Kim	Korea Research Institute of Standards and Science (KRISS), 267 Gajeong-Ro, Yuseong-Gu, Daejeon 34113, Rep. of Korea	+82 42 868 5323	kimcs@kriss.re.kr Mobile: +82 10 5545 5323

A2. Specimen delivery sequence and time schedule

Institute	Country/ Economic Region	Start date	Time for measurements and delivery
KRISS(Pilot)	Korea	Mar. 28, 2022	2 weeks
NIM	China	Apr. 11, 2022	3 weeks
KRISS	Korea	May. 02, 2022	1 weeks
CMS	Chinese Taipei	May. 09, 2022	3 weeks
KRISS	Korea	May. 30, 2022	1 weeks
NMIJ(Co-pilot)	Japan	Jun. 06, 2022	3 weeks
KRISS	Korea	Jun. 27, 2022	2 weeks

-End-