The Report of the 1st & 2nd International MEIS RRT with nm HfO_2 thin films and multilayer HfO_2 delta layers

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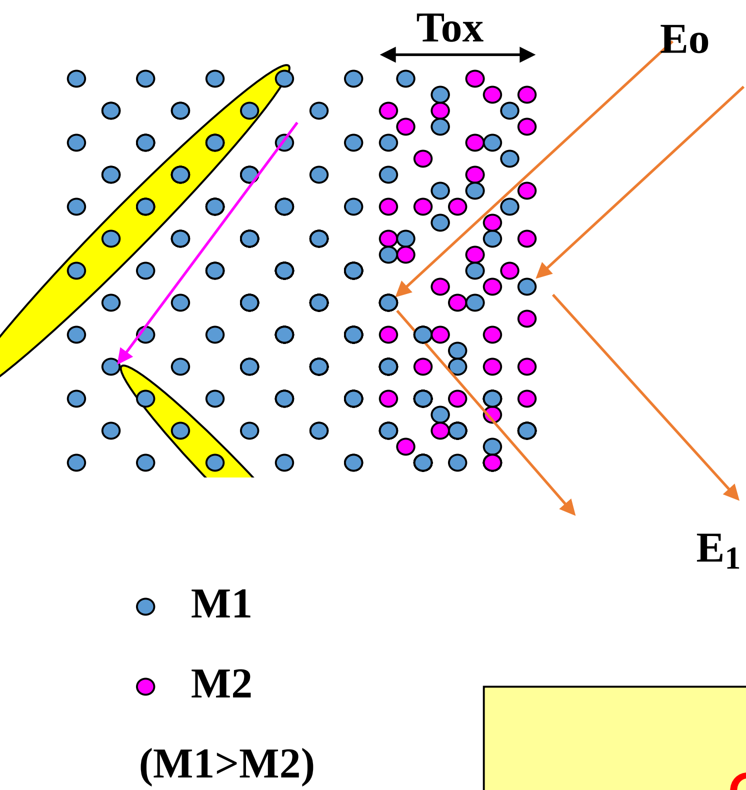
ISO/TC201 Surface Chemical Analysis/SC4 Depth Profiling
/SG1 (Non-destructive depth profiling using ion scattering)
Reported in 2015, October 16, Seattle
To be reported in 2016, October 14, Seoul

Medium Energy Ion Scattering (MEIS)

100~400 keV, H^+, He^+



$$\frac{E_1}{E_0} = \left[\frac{\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_1 \cos\theta}{M_2 + M_1} \right]^2$$: kinematic factor

ds/dΩ: quasi-Coulomb scattering cross section

dE/dx: electronic stopping

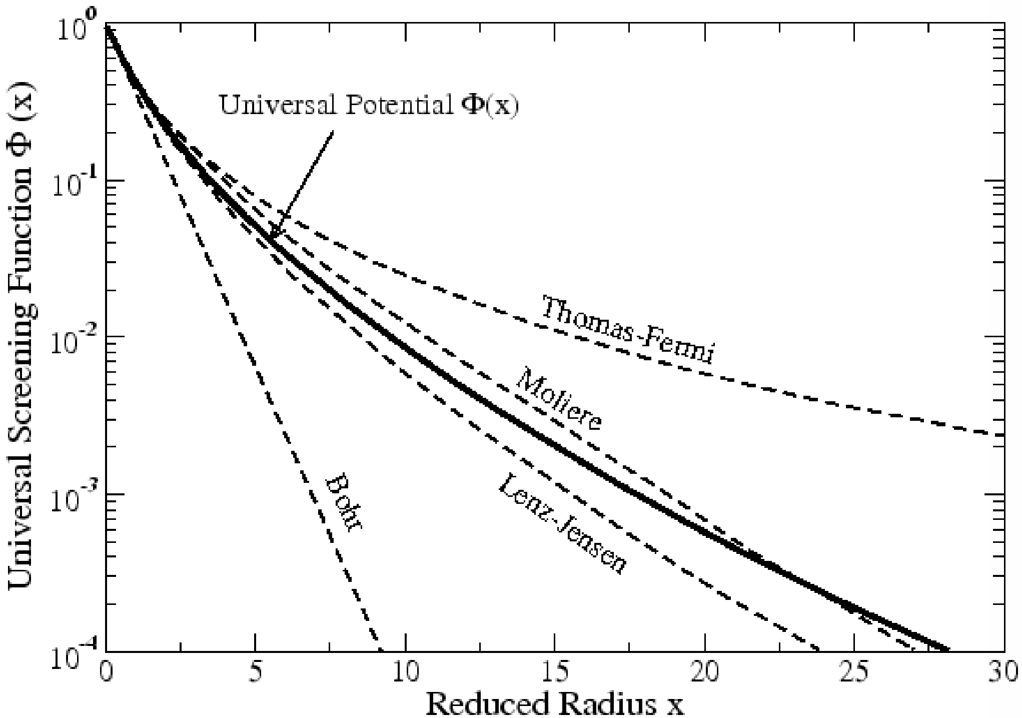
Non-destructive & Quantitative
Compositional and Structural Depth Profiling

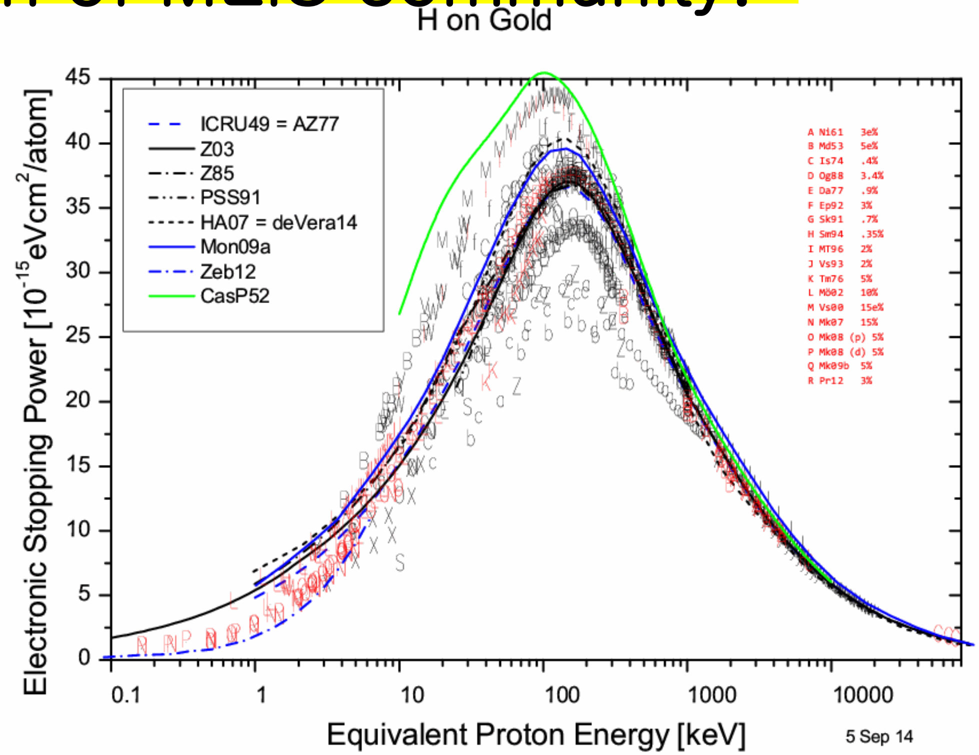
with atomic layer depth resolution down to ~ 10 nm
without any sample preparation
widely used for nm thin films (gate oxides) and nanoparticles

Summary of MEIS techniques used currently

Name	Energy Analyzer Type	Remarks	Major Users
TEA-MEIS	Entrance Slit + Toroidal electrostatic energy analyzer	Developed ~1980 By FOM most widely used.	IBM, Rutgers, Western Univ., UFRGS, KIST, Huddersfield (7)
HR-RBS	Entrance Slit + Magnetic sector energy analyzer	Developed ~ 2000 by Kyoto U.	Kyoto Univ., IBM-Fishkill, Samsung, SK (10)
TOF-MEIS	No slit Time-of-flight energy analyzer Detection of ions and neutrals	Developed ~ 2010 by KRISS/KMAC	DGIST, KMAC (2)

Are we doing all right ?
Do we generate reproducible & reliable results ?
>> critical for the growth of MEIS community.





Are the scattering cross sections ds/dΩ accurate enough for the MEIS energy range ?

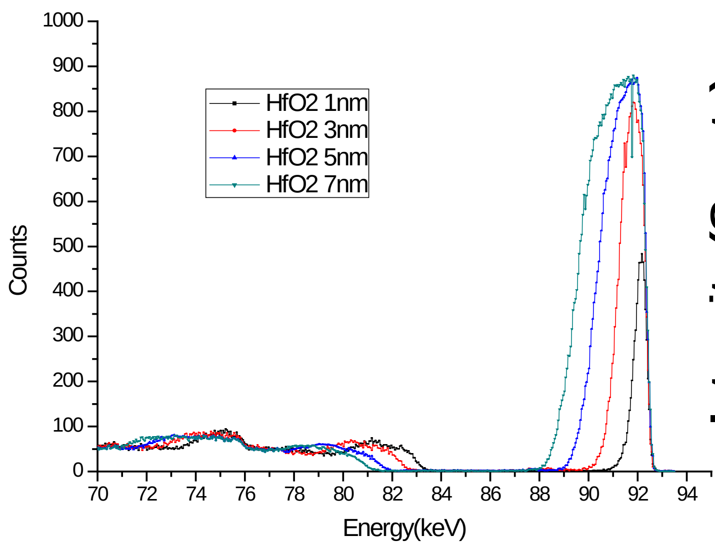
How about the electronic stopping power dE/dx and the electronic straggling ??

12 Participants of the 1st international MEIS RRT & analysis conditions

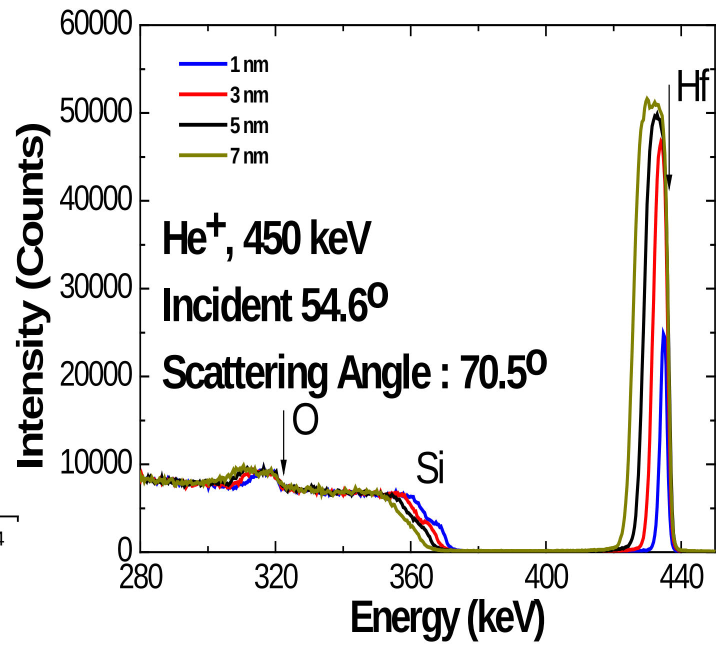
	A (DGIST)	B (KMAC)	C (SAMSUNG electronics)	D (SAMSUNG ADVANCED)	E (IF – UFRGS)	F (SK)	G (KIST)	H (Gustafsson)	I(Kyoto univ)	J (IBM– East Fishkill)	K(Western University)	IBM
Equipment	TOF-MEIS	TOF-MEIS	HRBS	HRBS V500	TEA-MEIS	HRBS V500	TEA-MEIS	TEA-MEIS	HRRBS	HRRBS	TEA-MEIS	TEA-MEIS
Ion species	He+	He+	He+	He+	H+	He+	H+	H^+	He+		H+	H+
Energy	80 keV	100 keV	499keV	450 keV	100 keV	300 keV	100 keV	100 (keV)	400(keV)	400(keV)	94.1keV	100keV
Current	0.15 nA	0.2 nA		30 nA	20 nA	25 nA	50~70 nA	5 (nA)	70nA	144nm	20nA	
Incident angle	45°	45°		54.6°	0°	45°	0°	5°	30.3°	45°	45°	54.74
Scattering angle	89~91°	130°	78.3°	70.5°	120°	58~64°	125.25°	133°	74.7°	80.8°	135°	90
Ion dose (Coulomb)		2E-6 C	1E15 C	2E-5 C	1E-4 C	20 nC	1.69E-16 C		70 μCx5 spectra	120000nC	45μC	1E-6 C
Beam radius	20 μm	0.12 mm		1 mm	1 mm	1 mm	1 X 0.5 mm	1 x 0.1(mm	2x2mm	2x3mm	1x0.15mm	0.1x1.0
Analysis time	30 min	160min		60min	90min	45min	240min	240/each min	~17min.	14min	4.5Hors	
HfOx density	9.68 g/cm^3	9.68 g/cm^3	8.1 g/cm^3	9.68 g/cm^3			9.69 g/cm^3	9.69 g/cm^3	9.68 g/cm^3	9.68 g/cm^3	9.68 g/cm^3	9.68 g/cm^3
SiOx density	2.1977 g/cm^3	2.1977 g/cm^3	2.2 g/cm^3	2.33 g/cm^3			2.1977 g/cm^3	2.1977 g/cm^3	2.1977 g/cm^3	2.1977 g/cm^3	2.2 g/cm^3	2.1977 g/cm^3
Interatomic potential								Moliere	Moliere	Universal	Moliere	Moliere
Stopping power	Anderson-Ziegler	Anderson-Ziegler		TRIM code				Anderson-Ziegler	Anderson-Ziegler	Anderson-Ziegler	SRIM2k	ZBL
Electronic straggling	Chu	Chu		Yang				Lindhard Sharff	Yang	Yang	Bohr	Chu
Neutralization correction								Marion and Young	Marion and Young	Marion and Young	Energy dependent	empirical

Typical MEIS spectra of nm HfO2/nm SiO2 thin films

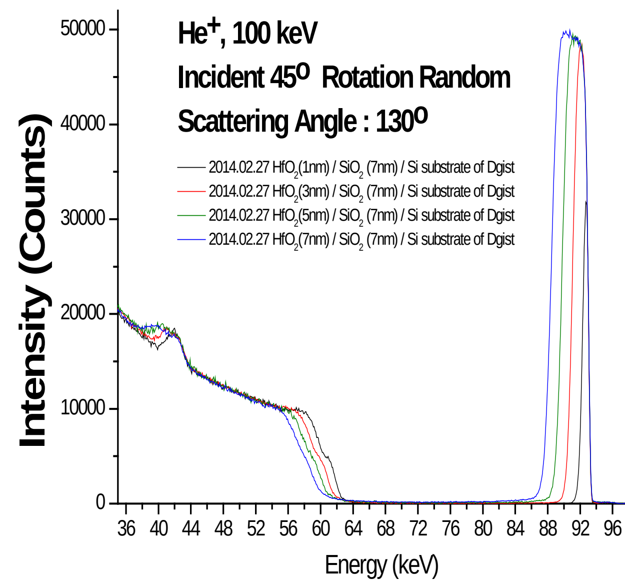
TEA-MEIS (100 keV H+)



HRBS (300~500 keV He+)

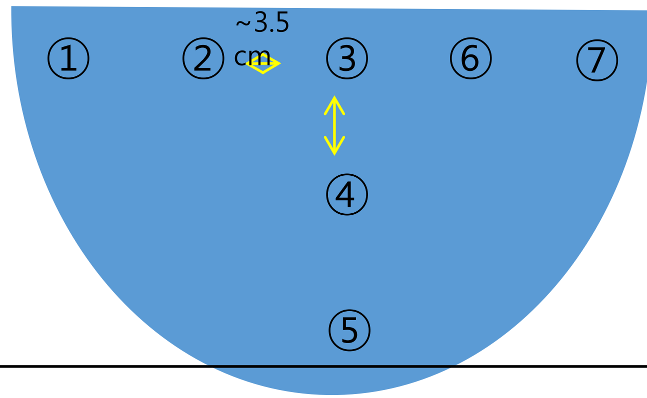


TOF-MEIS (100 keV He+)



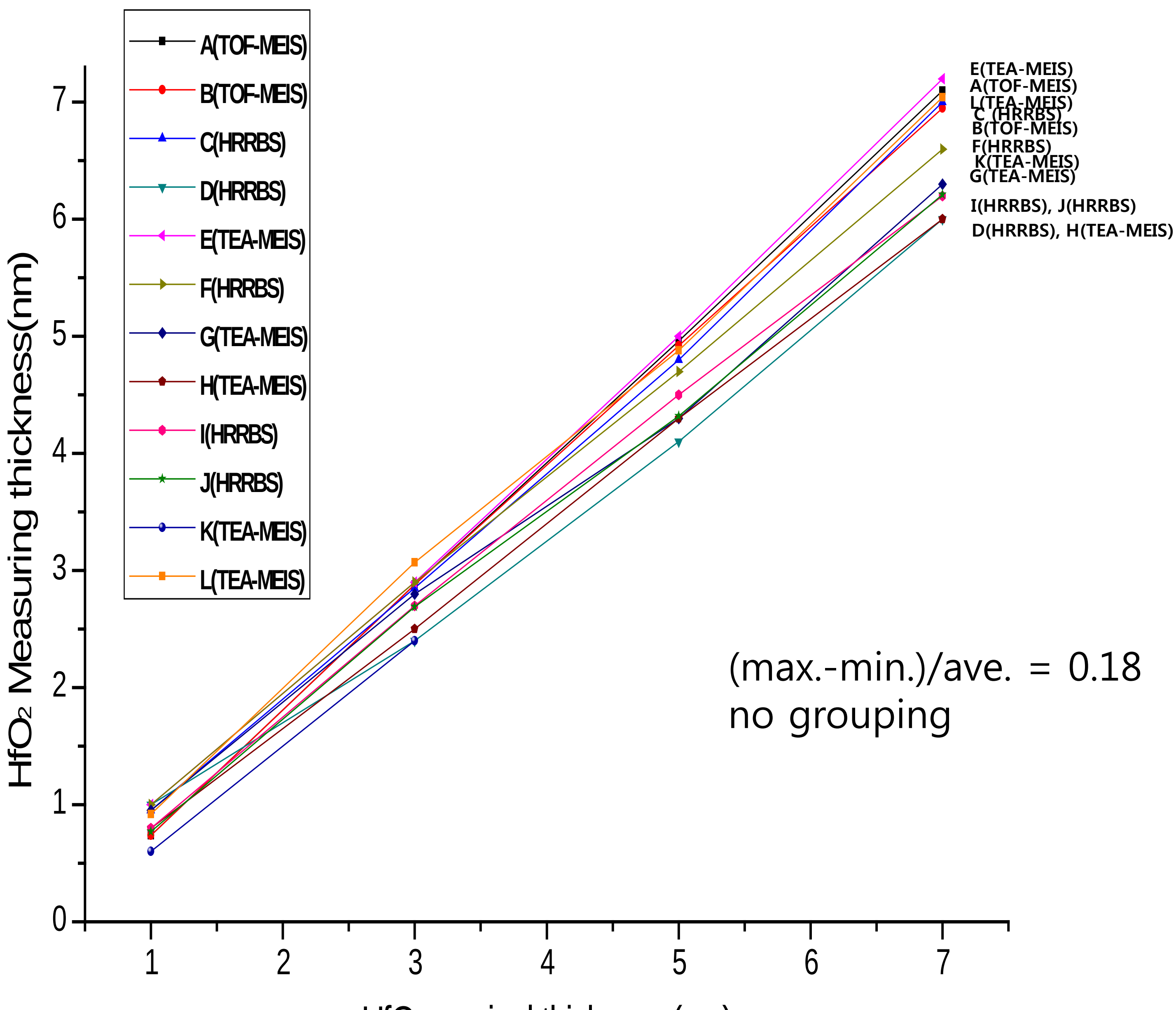
MEIS RRT with 1~7 nm HfO2/7nm SiO2/Si Thin Films Homogeneity Test by Ellipsometry

- sequential measurements of 7 spots according to the number given below with 3.5 mm intervals
- 5 measurements for each spot showed **the homogeneity of 0.3~0.5%**



half wafer	average_MSE	average_Total Thickness (Å)	std.dev
1	1.394	90.866	0.301 (0.33%)
2	1.284	108.668	0.318 (0.27%)
3	1.229	126.584	0.545 (0.41%)
4	1.346	145.016	0.721 (0.52%)

Results Summary of the international MEIS RRT



(max.-min.)/ave. = 0.18
no grouping

	1nm	3nm	5nm	7nm
A	0.74 nm	2.88 nm	4.96 nm	7.1 nm
B	0.74 nm	2.88 nm	4.92 nm	6.95 nm
C	0.95 nm	2.85	4.8 nm	7 nm
D	1 nm	2.4 nm	4.1 nm	6.0 nm
E	1 nm	2.9 nm	5 nm	7.2 nm
F	1 nm	2.9 nm	4.7 nm	6.6 nm
G	0.95 nm	2.8 nm	4.3 nm	6.3 nm
H	0.8 nm	2.5 nm	4.3 nm	6.0 nm
I	0.8 nm	2.7 nm	4.5 nm	6.2 nm
J	0.77 nm	2.69 nm	4.32 nm	6.21 nm
K	0.75 nm	2.6 nm	4.5 nm	6.3 nm
L	0.92	3.07	4.88	7.04

Possible Causes of the Dispersion in the RRT

1. The definition of the thickness of HfO_2 layer
   #1: converting the areal density of Hf into HfO_2 thickness with the bulk density of HfO_2
   #2: the position of 50% of the Hf plateau concentration
   #3: others ??

2. Inconsistency of analysis parameters such as interatomic potential, stopping power, straggling for the ion energy region (from 80 keV to 450 keV)

3. Neutralization & its correction

>> Simulations for the areal density of Hf with the same simulation program by the same person will be tried.

RRT Re-analysis by Wonja Min

Won Ja Min, K-MAC , 2015.8.19.

Simulations by SimNRA program
(random only, dual scattering included)

Anderson cross section

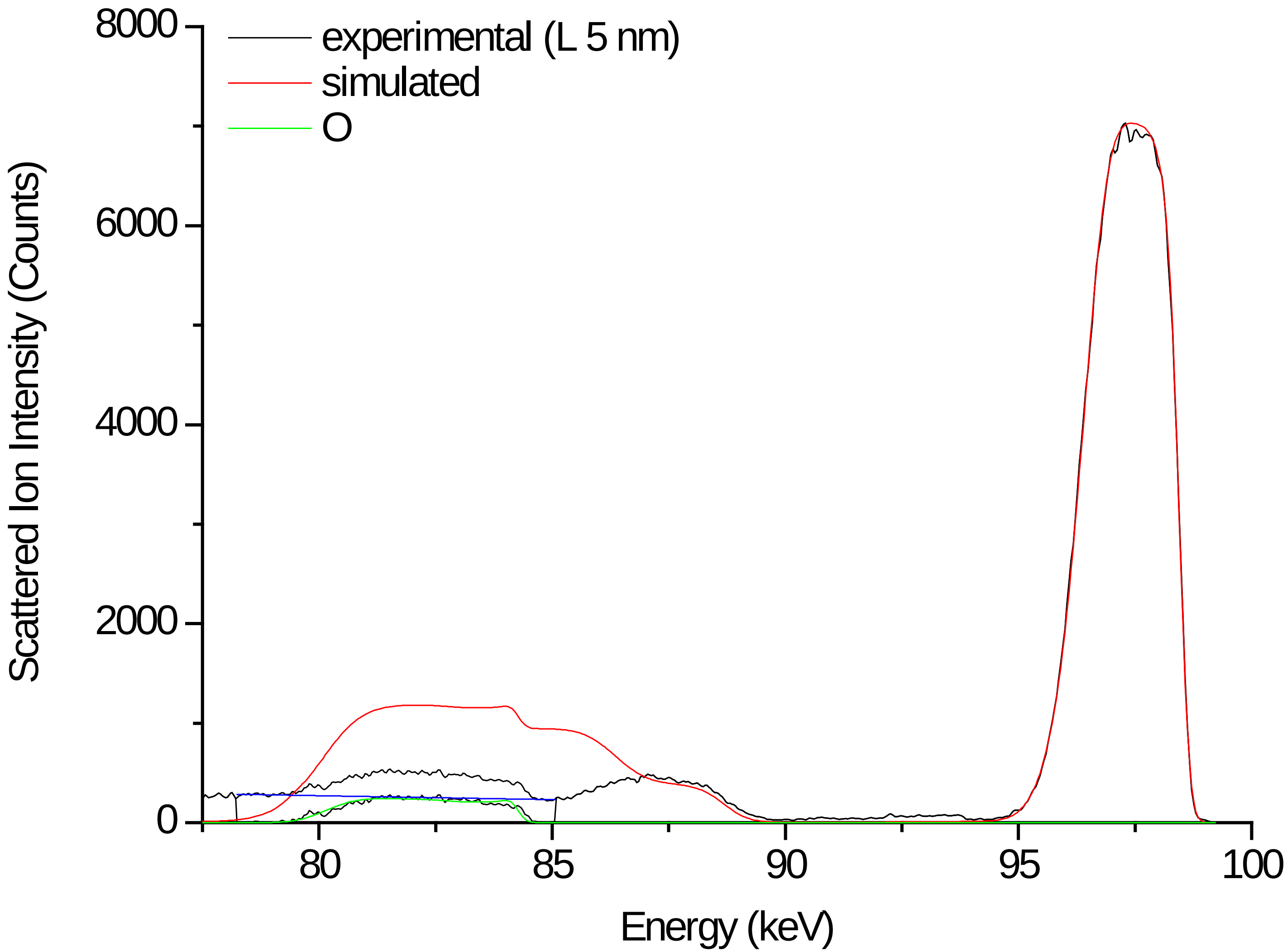
AZ stopping

Chu straggling

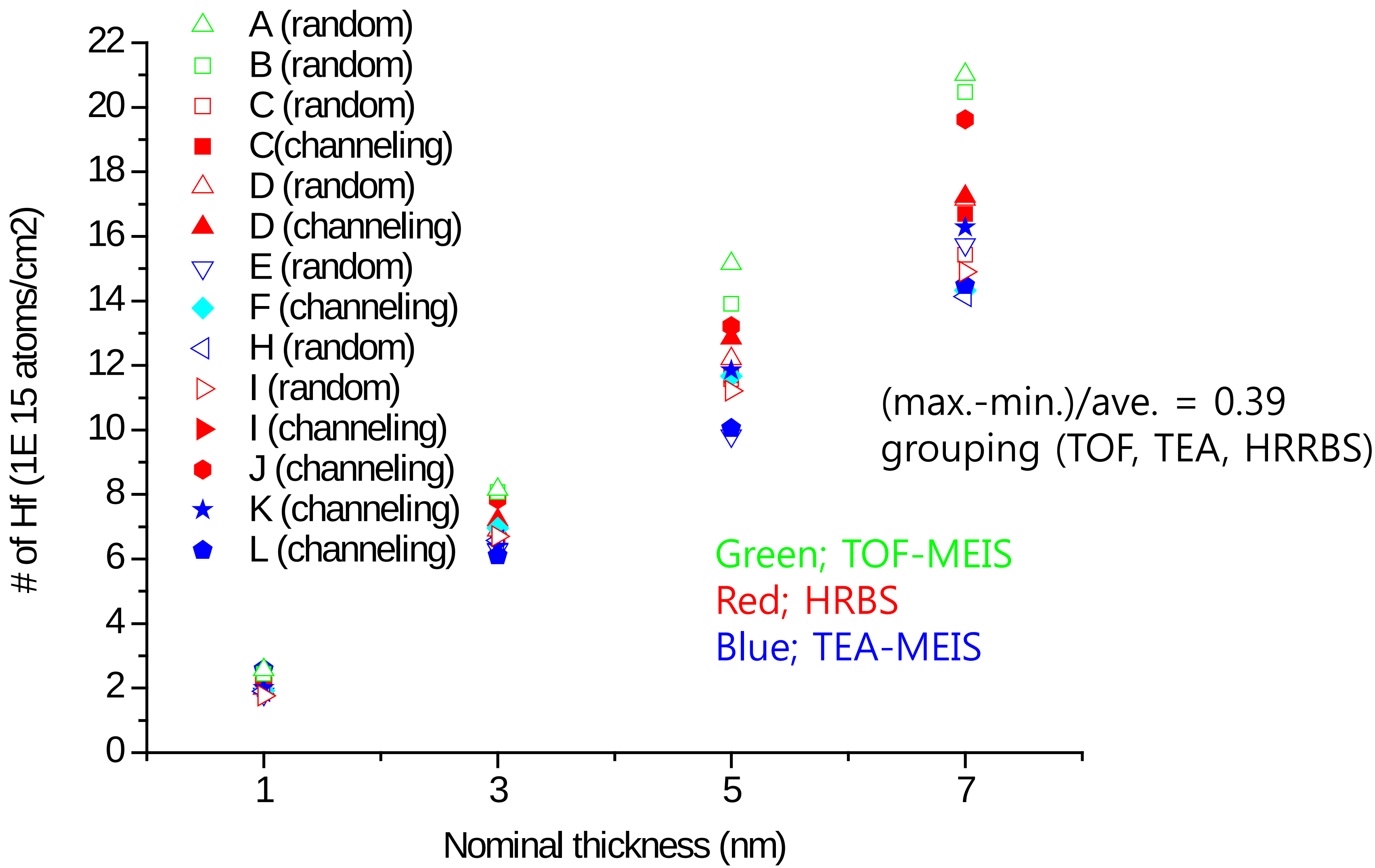
The low background between Si and Hf peak was subtracted to choose the optimum simulation fitting

The background around the O peak was fitted with a polynomial function, which was subtracted from the total intensity. The background subtracted O peak was compared with the simulated O elemental peak in green.

5 nm (TEA-MEIS)


experimental (L 5 nm)
simulated
O
Scattered Ion Intensity (Counts)
0
2000
4000
6000
8000
Energy (keV)
80
85
90
95
100

Hf areal density Recalculated by Dr. Min using reported MEIS spectra

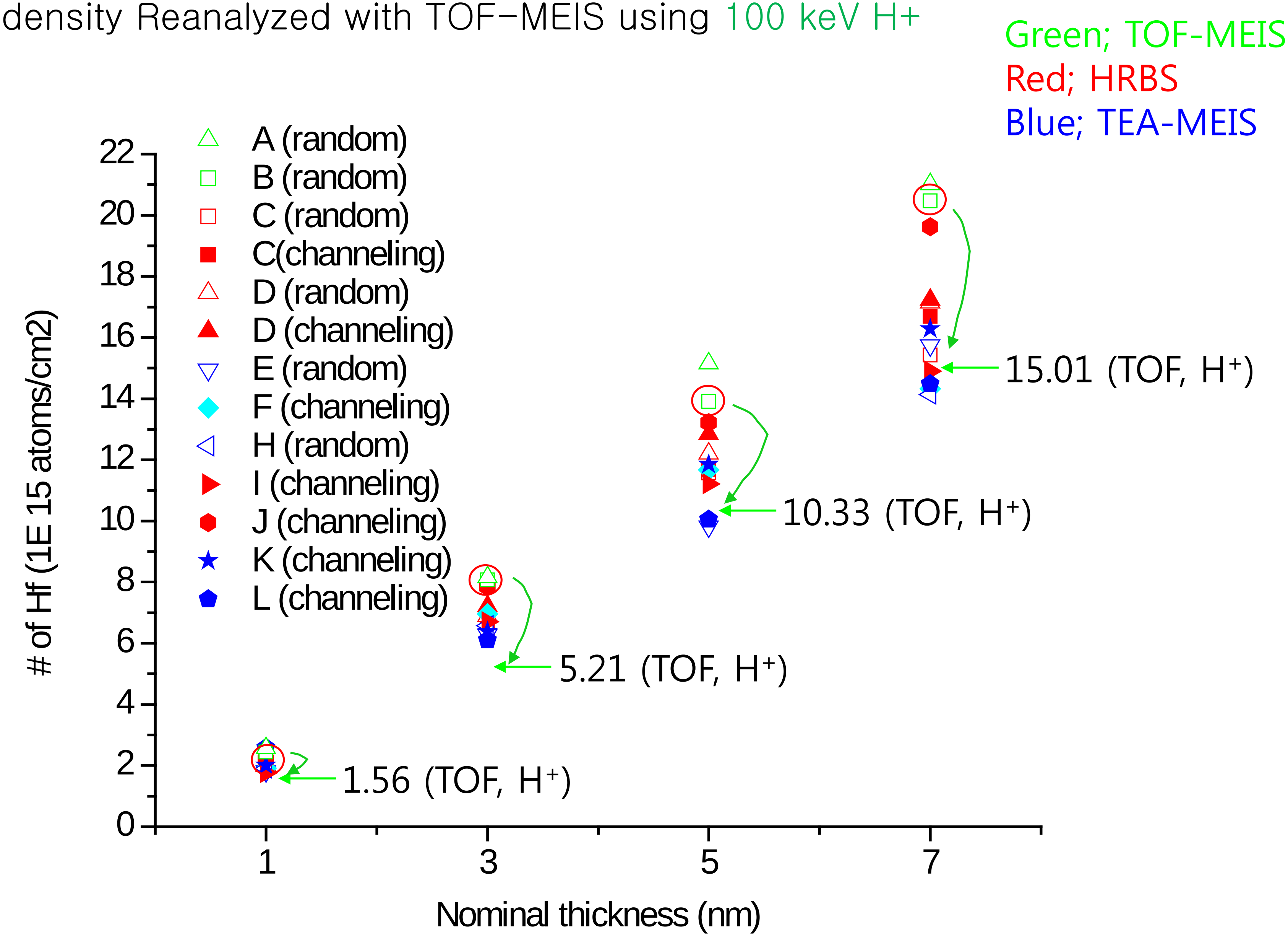


Possible Causes of the RRT Scattered Results

Inconsistency of analysis parameters such as interatomic potential, stopping power, straggling for the ion energy region (from 80 keV to 450 keV)

>> 100 keV H+ instead of 100 keV He+ was tried.

Hf areal density Reanalyzed with TOF-MEIS using 100 keV H+



Conclusions and Action Plans to Resolve Possible Causes of the MEIS RRT Discrepancies.

1. interatomic potential problems

   : for 100 keV He+, SimNRA (Anderson cross section, AZ stopping) does not work.

   : possible systematic errors between 100 keV H+ and 300 keV He+

   C #1: adequate interatomic potentials for the MEIS range should be investigated.

   C #2: possible systematic errors of electronic stopping power should be investigated (industrial demands)

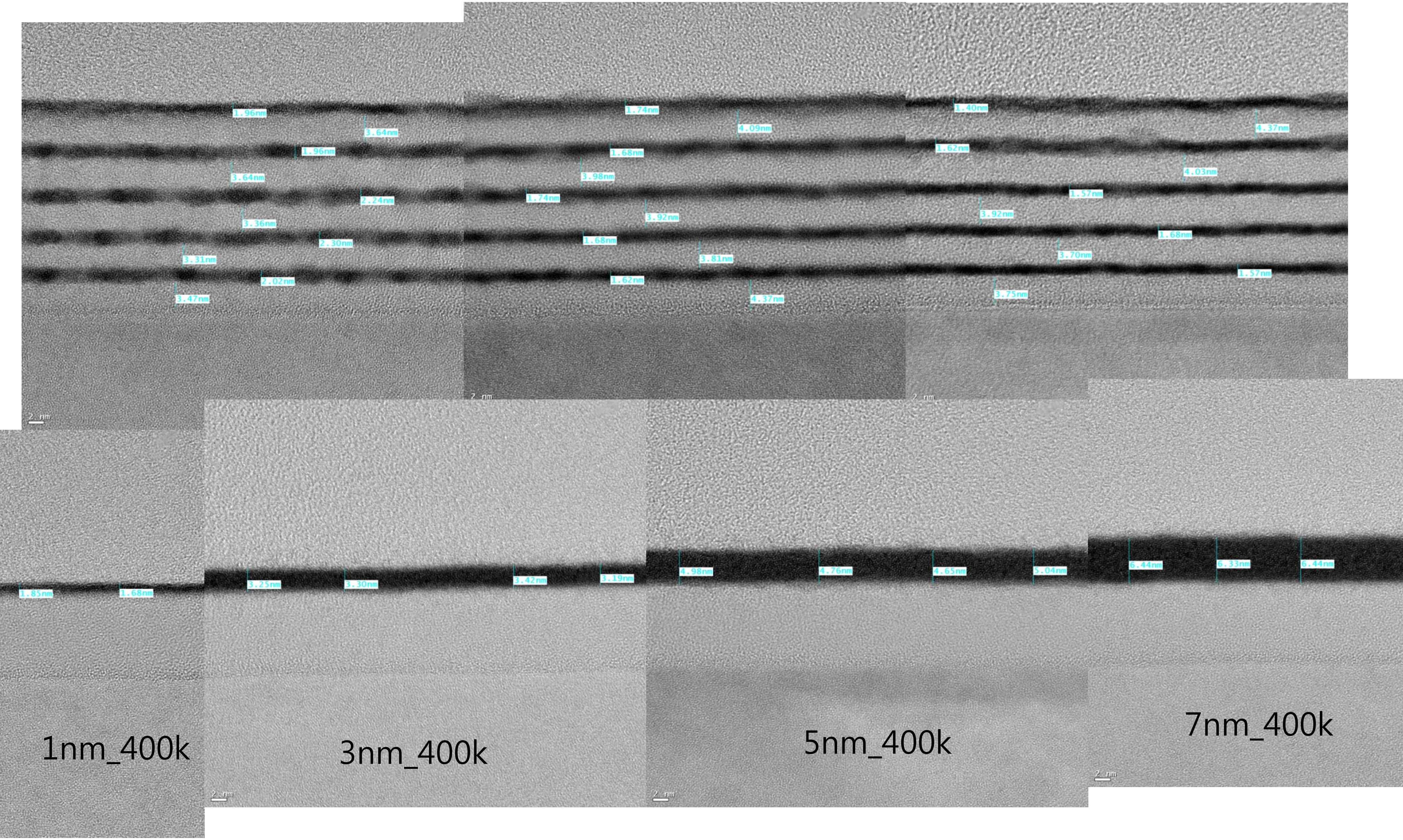
   AP #2: 2nd int. RRT with 1~7 nm HfO2 on 15 nm SiO2 & multiple delta (1 nm) HfO2/10 nm SiO2 layer can be tried.

2. background control and correction

   C #1: instrumental improvement for minimum background is required (option or manufacturer's work)

   C #2: consistent background measurement and correction can be asked in the 2nd RRT.

TEM images of 2nd int. RRT samples with 1, 3, 5, 7 nm HfO2 on 15 nm SiO2 & multiple delta (1 nm) HfO2/10 nm SiO2 layer



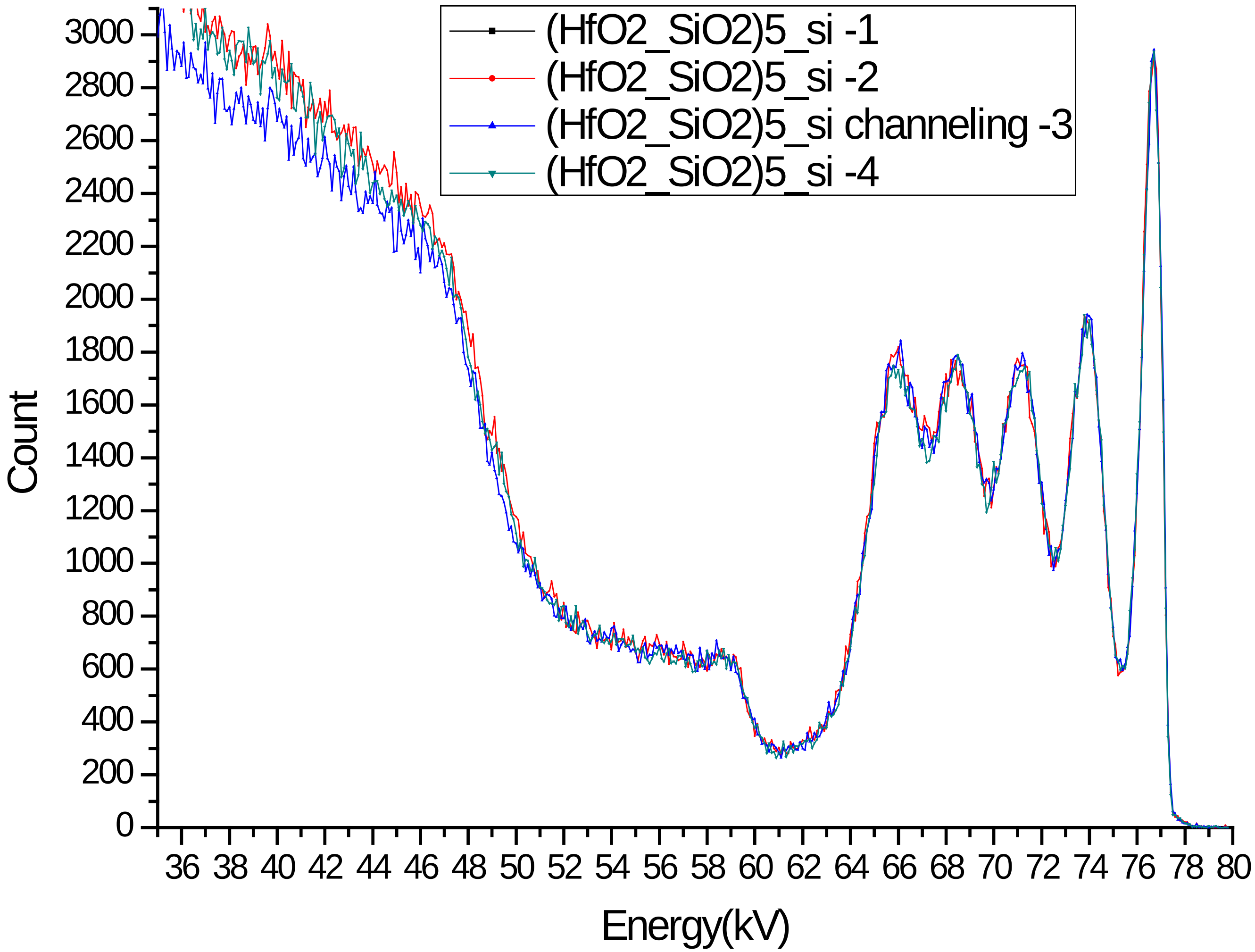
Summary of TEM analysis : TEM cannot be regarded to be accurate.
TEM thickness is just TEM thickness.

		thickness(nm)	
		average	standard deviation
1.96,1.74,1.4	1st HfO_2	1.70	0.28
3.64,4.09,4.37	1st SiO_2	4.03	0.37
1.96,1.68,1.62	2nd HfO_2	1.75	0.18
3.64,3.98,4.03	2nd SiO_2	3.88	0.21
2.24,1.74,1.57	3rd HfO_2	1.85	0.35
3.36,3.92,3.92	3rd SiO_2	3.73	0.32
2.3,1.68,1.68	4th HfO_2	1.89	0.36
3.31,3.81,3.7	4th SiO_2	3.61	0.26
2.02,1.62,1.57	5th HfO_2	1.74	0.25
3.47,4.37,3.75	5th SiO_2	3.86	0.46

		thickness(nm)	
		average	standard deviation
1.62,1.85,1.68	1nm HfO_2	1.72	0.12
3.25,3.3,3.42,3.19	3nm HfO_2	3.29	0.10
4.98,4.76,4.65,5.04	5nm HfO_2	4.86	0.18
6.44,6.33,6.44,6.33	7nm HfO_2	6.39	0.06

80 keV He+, Scattering angle 89° ~ 91°

(HfO2/SiO2)5/Si multi layer : HfO2 1nm, SiO2 5nm



2nd RRT hafnia thin film thickness: PowerMEIS analyses

I. Alencar, T. Avila, R.C. Fadanelli, P.L. Grande, M. Hatori, A. Hentz, L. Magnum, G.G. Marmitt, G. Onzi, M.A. Sortica, M.C. Sulzbach, H. Trombini

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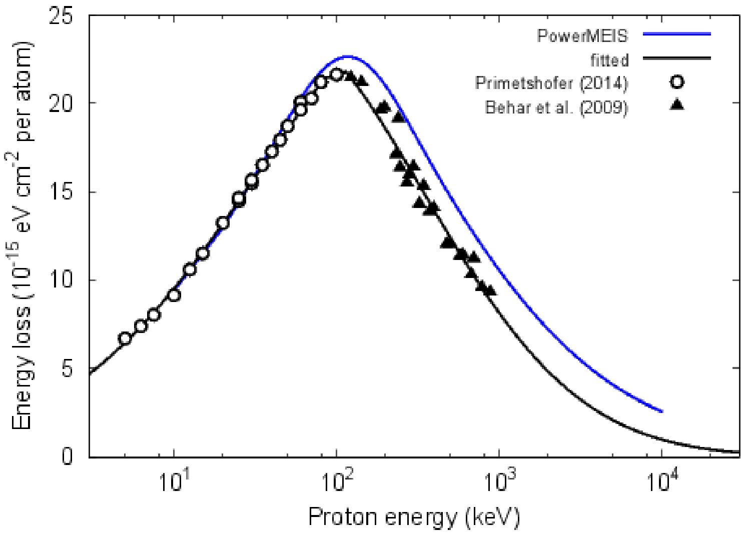
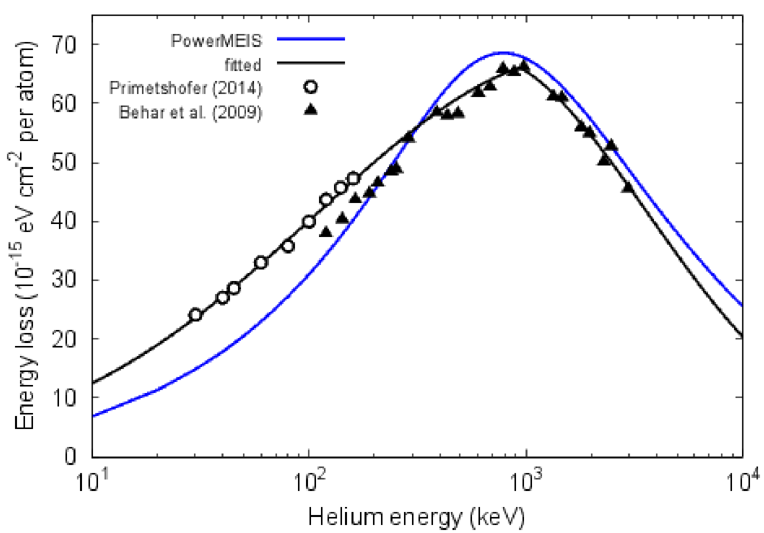
Energy loss in hafnia

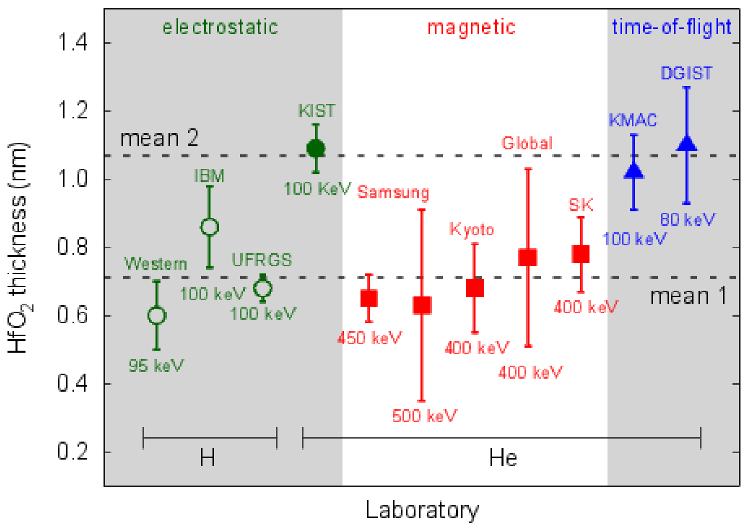


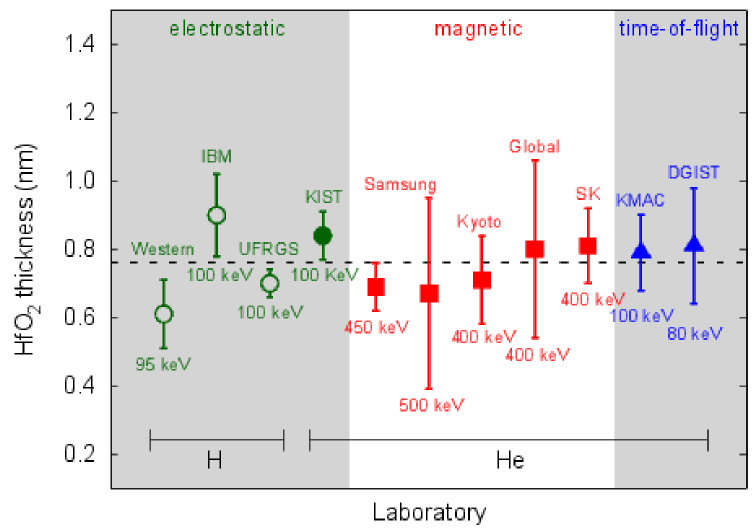


SRIM95 (PowerMEIS)
Log normal function (fitted)

Behar et al., PRA 80 (2009) 062901
Primetshofer, PRA 89 (2014) 032711

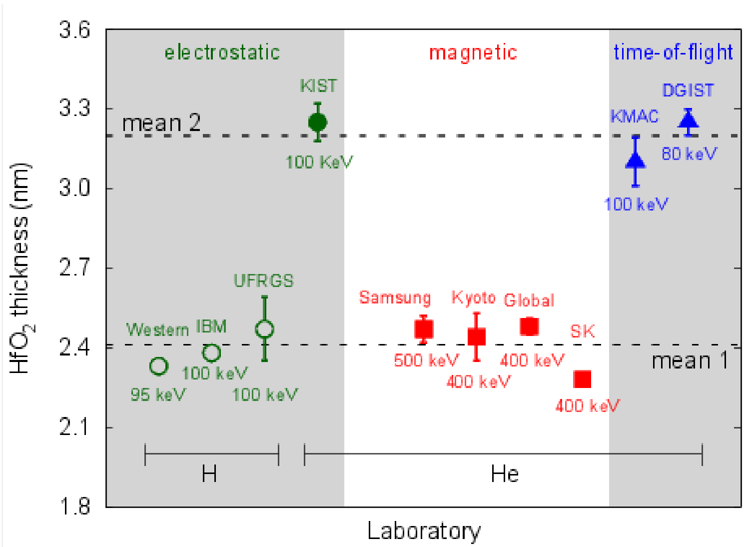
Nominal thickness 1 nm

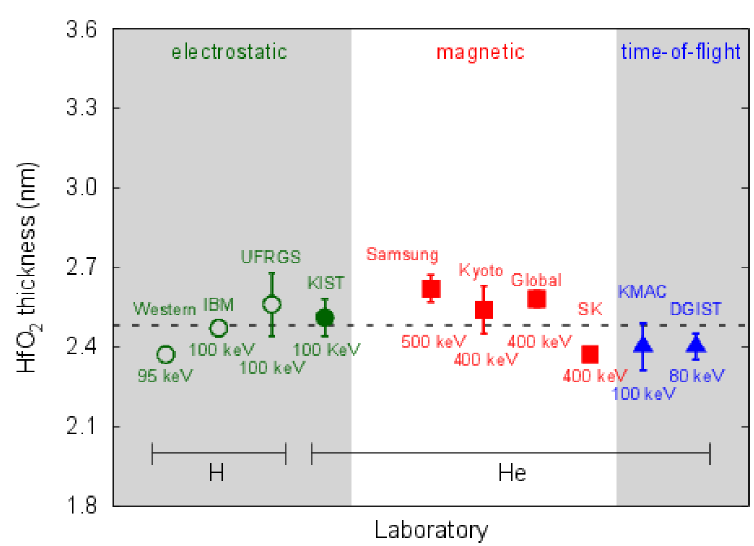




mean	0.76 nm
standard deviation	0.09 nm
maximum difference	0.29 nm

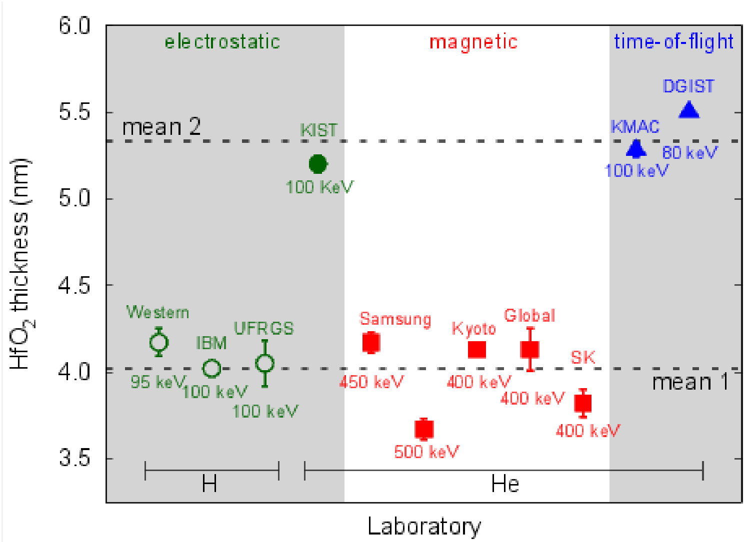
Nominal thickness 3 nm

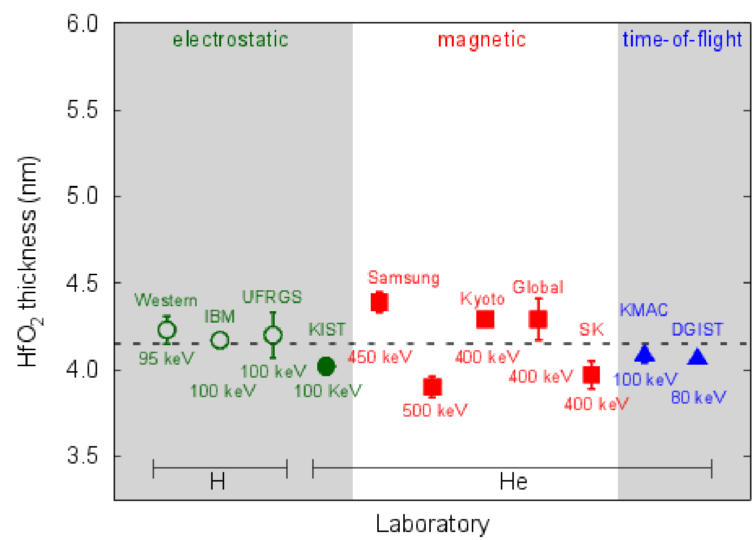




mean	2.48 nm
standard deviation	0.09 nm
maximum difference	0.25 nm

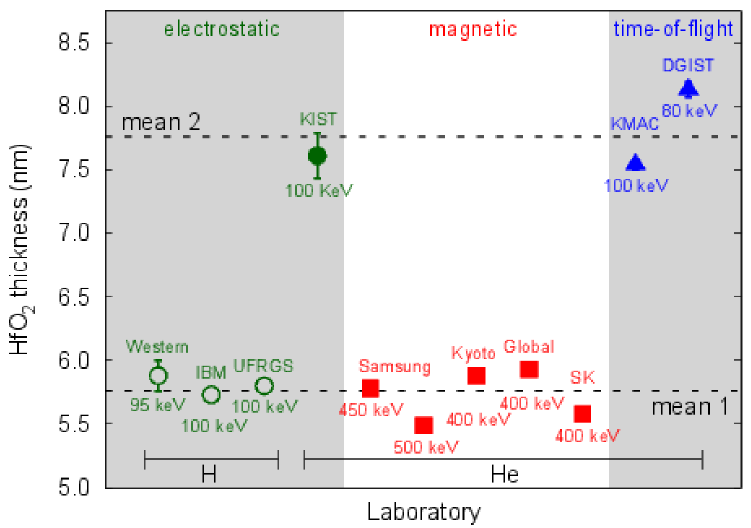
Nominal thickness 5 nm

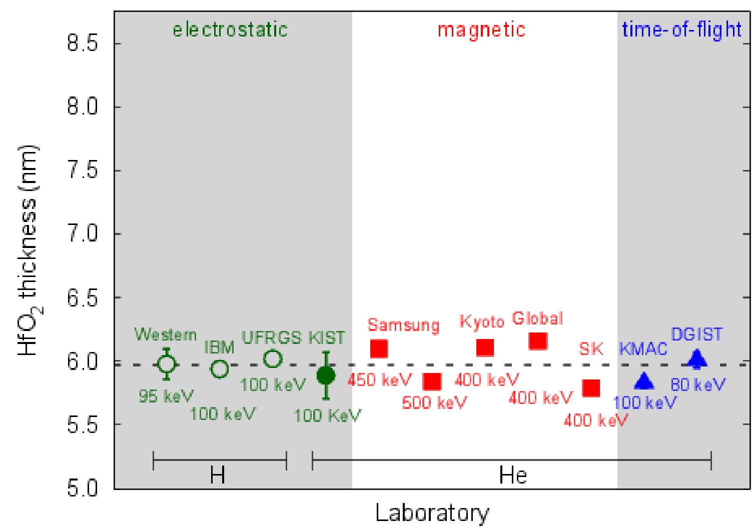




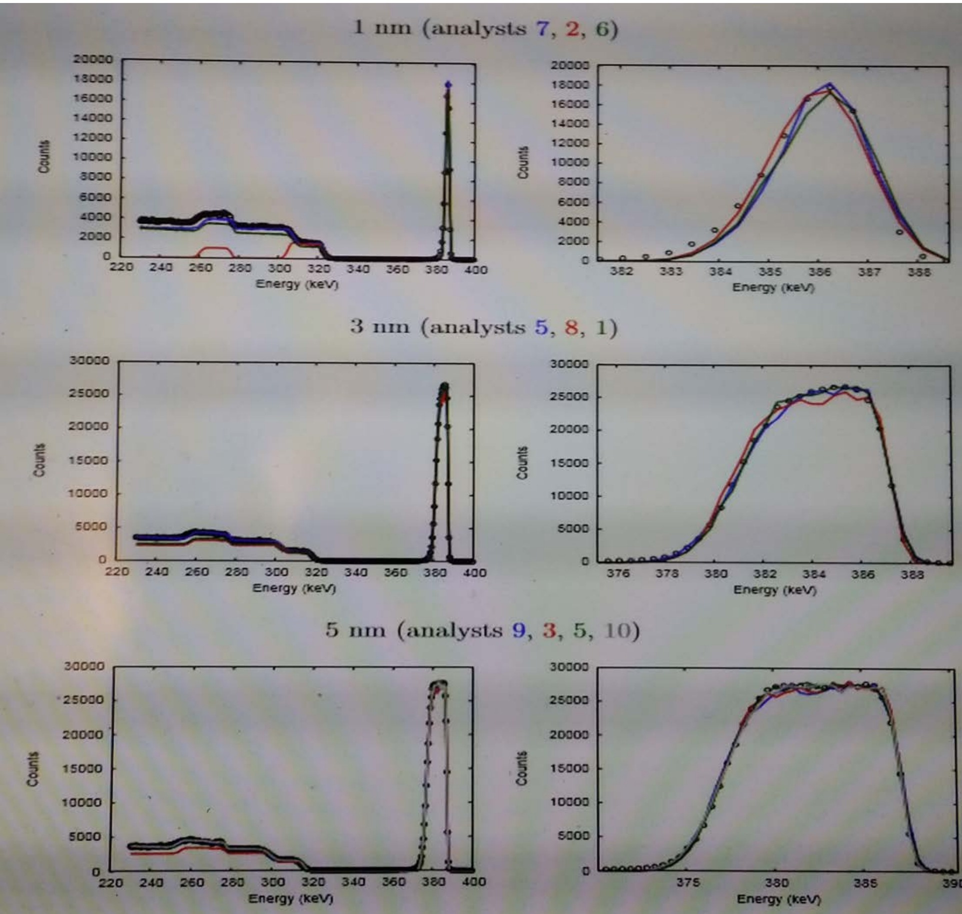
mean	4.15 nm
standard deviation	0.15 nm
maximum difference	0.49 nm

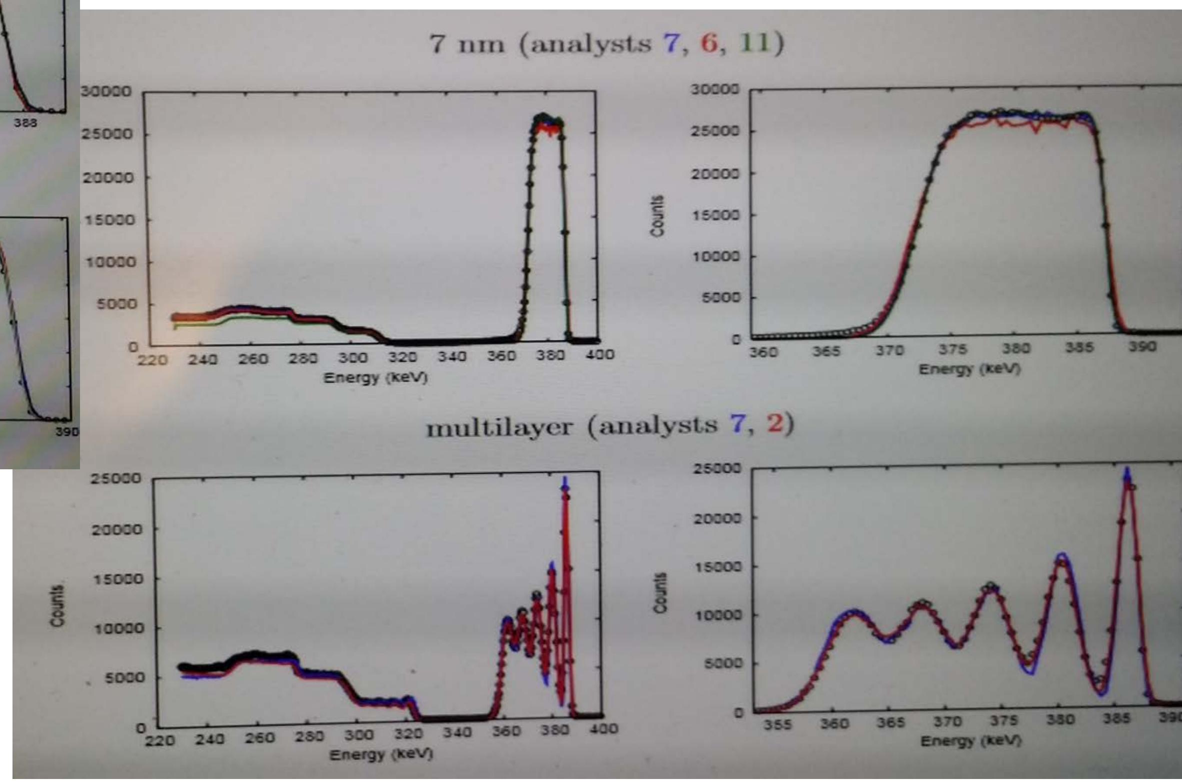
Nominal thickness 7 nm

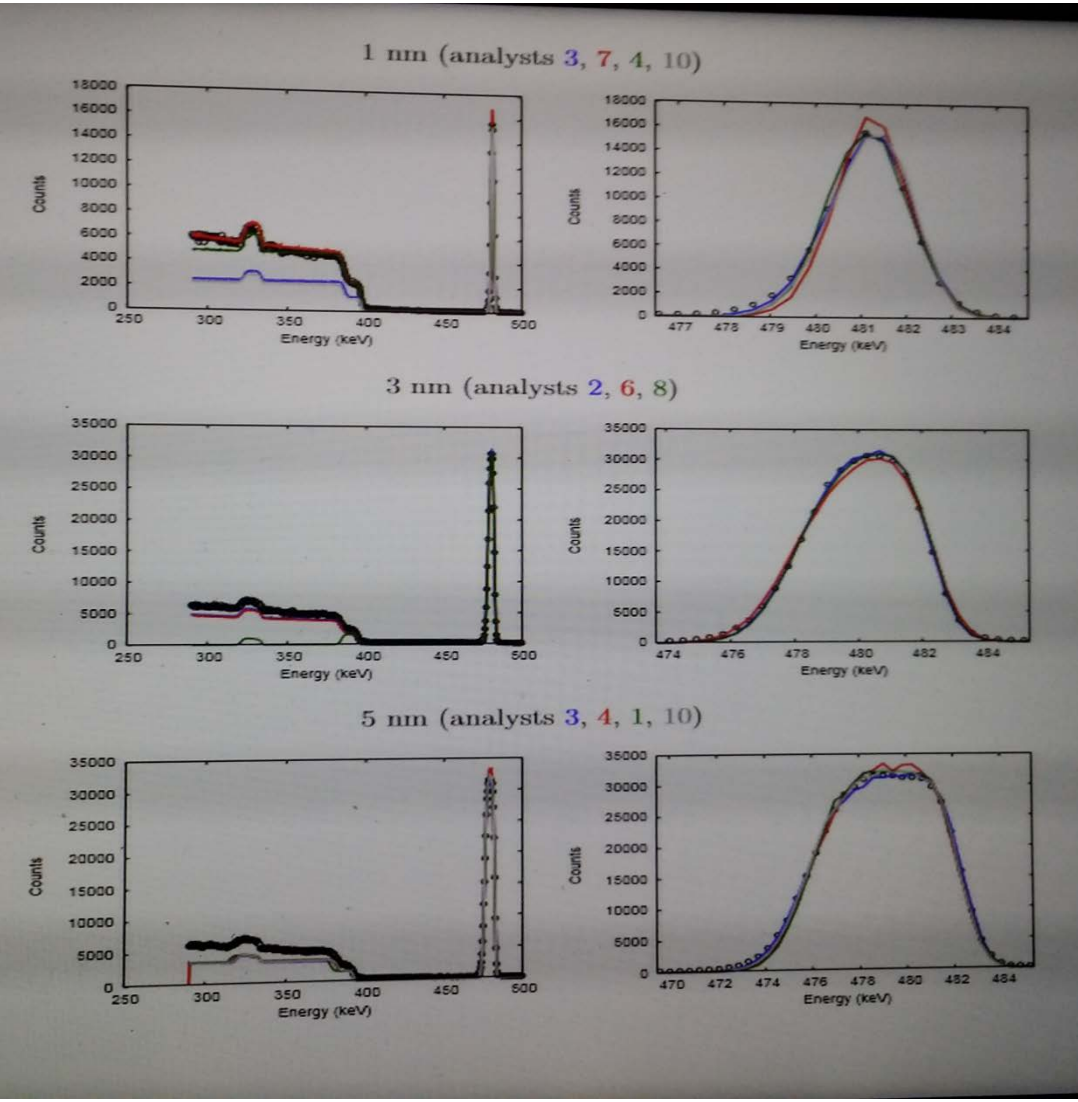


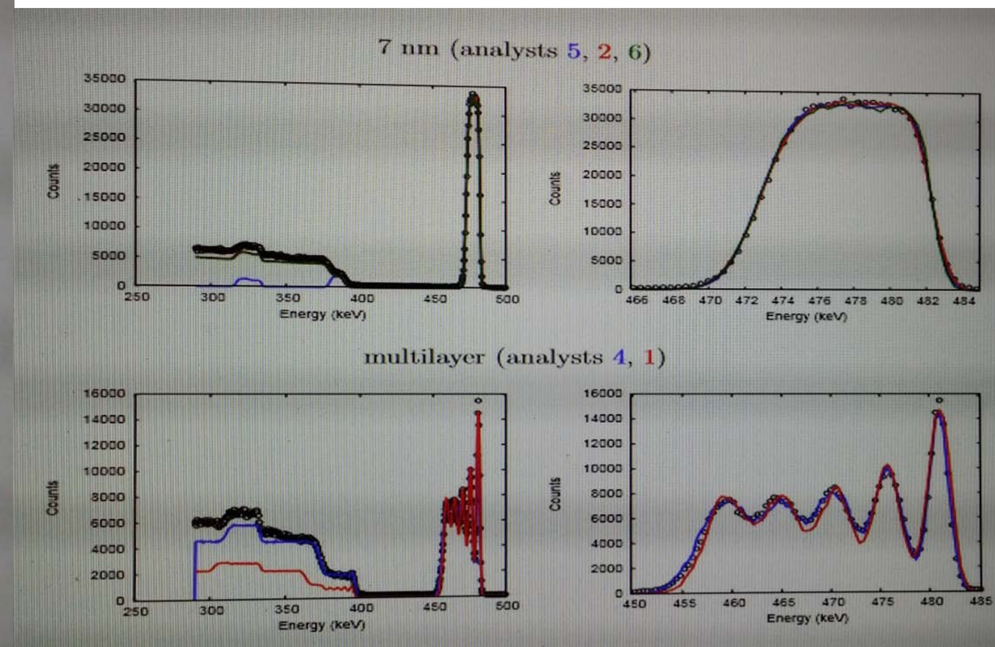


mean	5.97 nm
standard deviation	0.12 nm
maximum difference	0.37 nm


1 nm (analysts 7, 2, 6)
Counts
Energy (keV)
3 nm (analysts 5, 8, 1)
Counts
Energy (keV)
5 nm (analysts 9, 3, 5, 10)
Counts
Energy (keV)


7 nm (analysts 7, 6, 11)
Counts
Energy (keV)
multilayer (analysts 7, 2)
Counts
Energy (keV)


1 nm (analysts 3, 7, 4, 10)
3 nm (analysts 2, 6, 8)
5 nm (analysts 3, 4, 1, 10)
Counts
Energy (keV)


7 nm (analysts 5, 2, 6)
multilayer (analysts 4, 1)
Counts
Energy (keV)


Star Butterfly
MISO
THE BEST!!
Pedro & DaeWon

Preliminary Discussions on the 2nd RRT results

1. Wonderful results (DaeWon) with better fitting electronic stopping powers (Log normal function by Pedro).

2. Little problems in applying MeV interatomic potentials to the MEIS range (Pedro).

3. 15 nm SiO2 layer was not used as a reference as in the 1st RRT but as a guide. (Errors in SiO2 layer were 5~10 % by Pedro)

1. Wonderful but tested only for HfO2 >> try 1~2 other materials (RRT or bilateral?)

2. Simulate again with SiO2 as a reference layer with accurate electronic stopping powers estimated from the multiple delta layers

3. How to generalize it for all the other elements & compounds ?

No Conclusions but open discussions