

Exploring the Limits of Low Voltage EPMA of Coated Samples

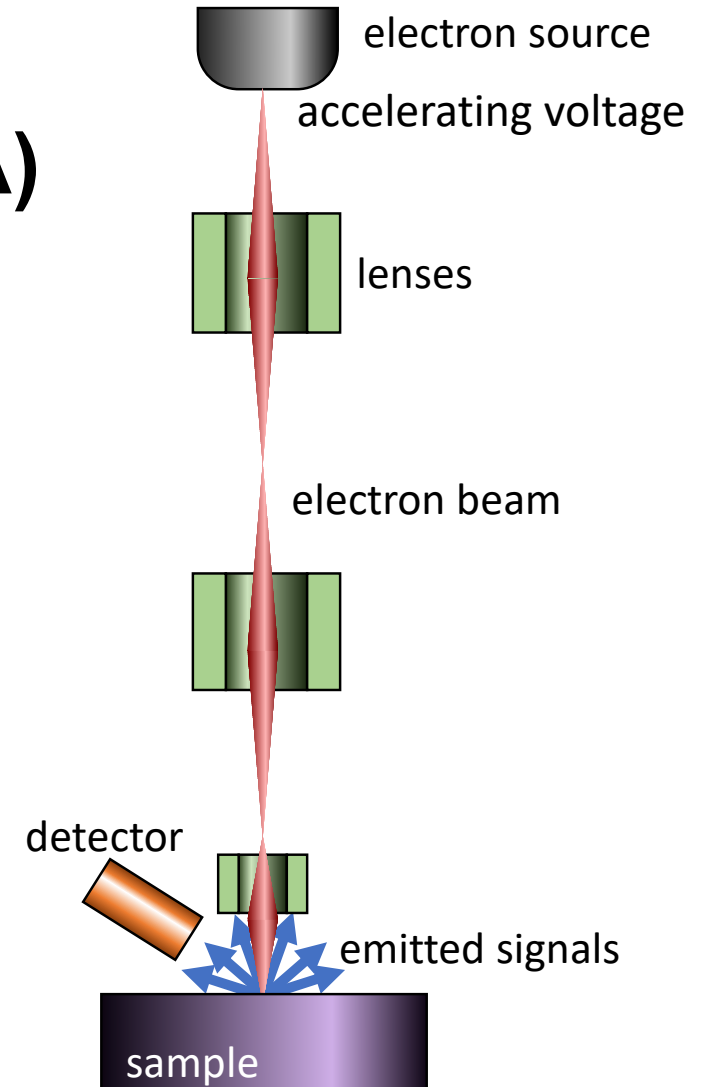
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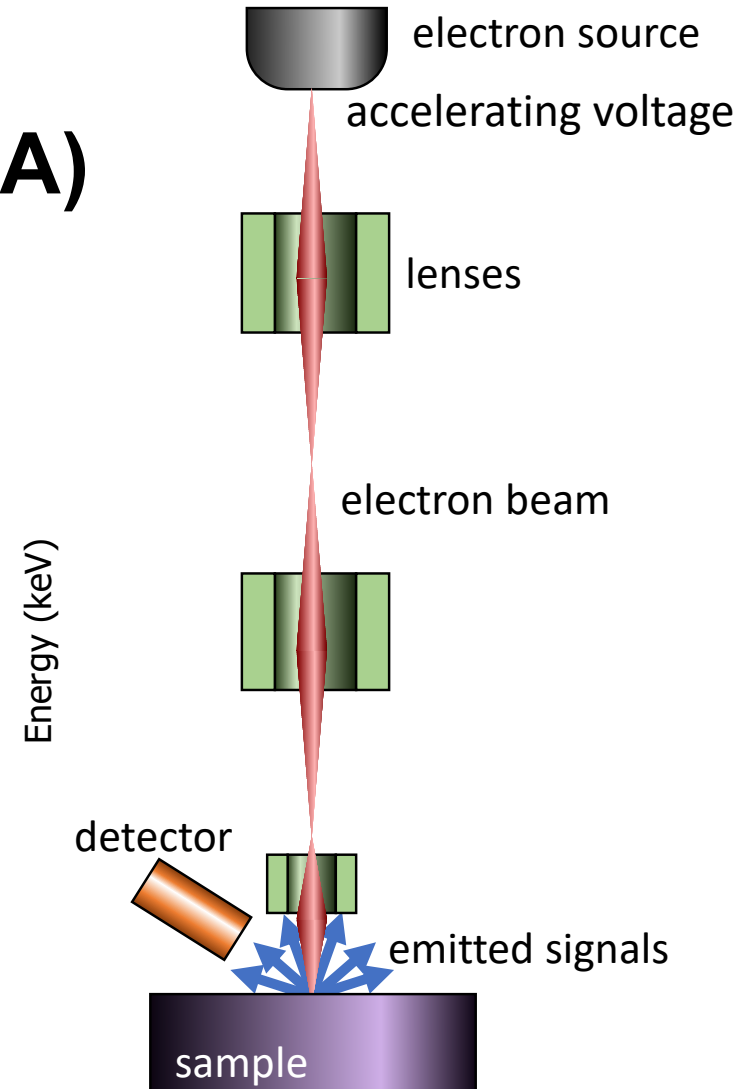
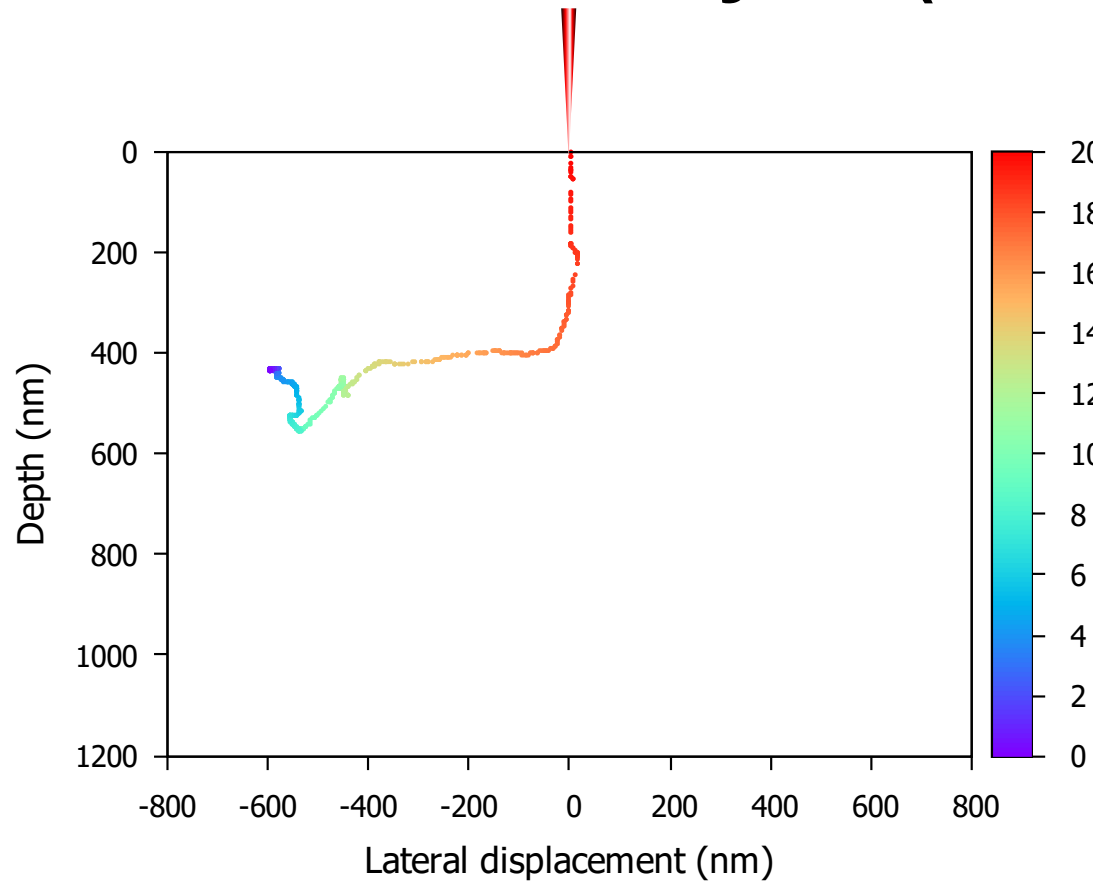
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A Micro-guide to Electron Probe Microanalysis (EPMA)



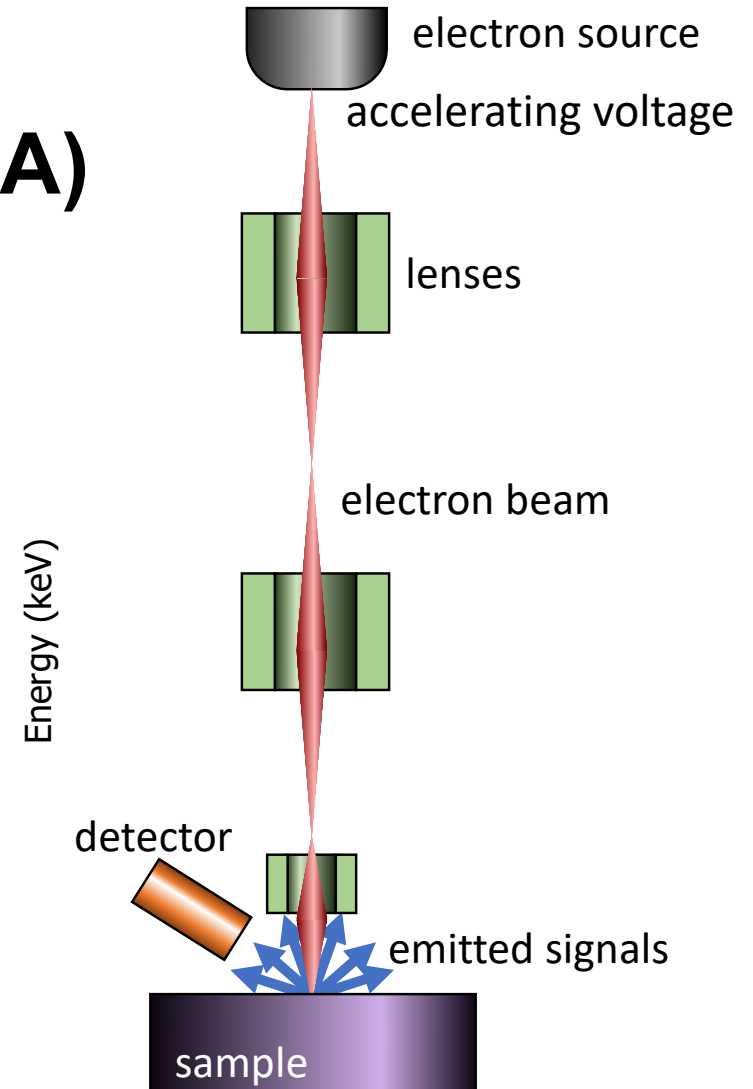
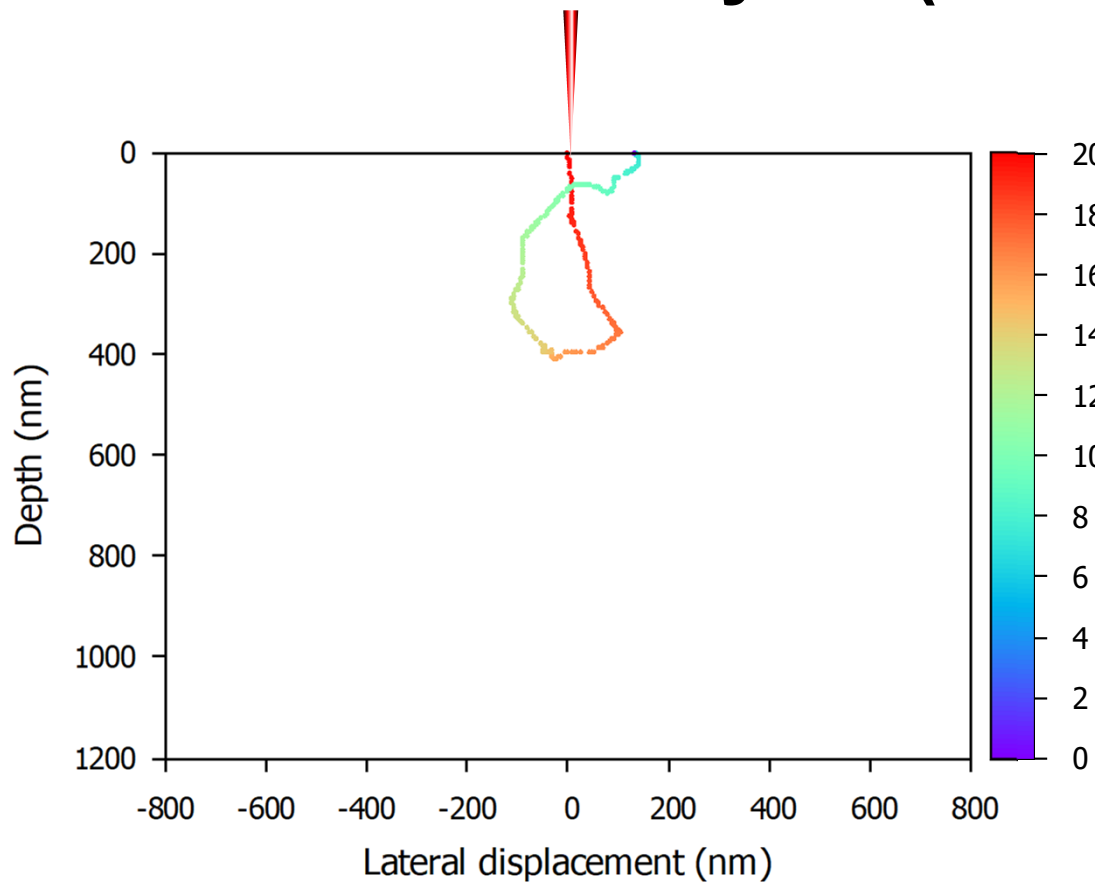
From Matthews 2020, "FEG-EPMA of Nuclear Materials", University of Bristol

A Micro-guide to Electron Probe Microanalysis (EPMA)



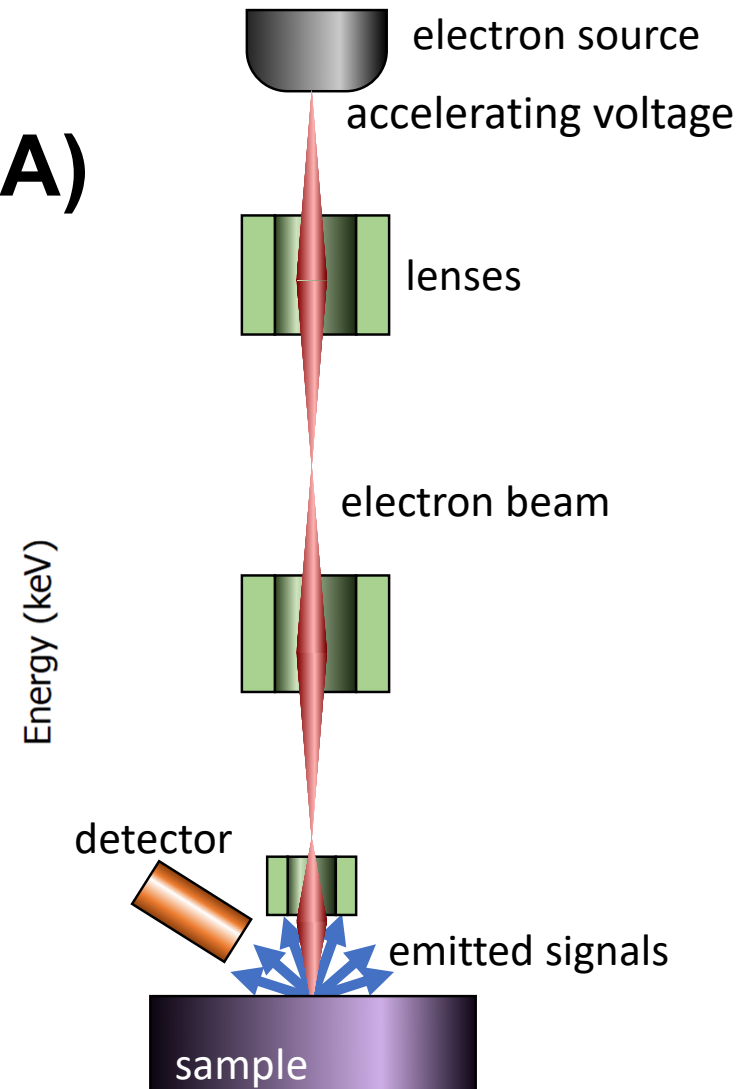
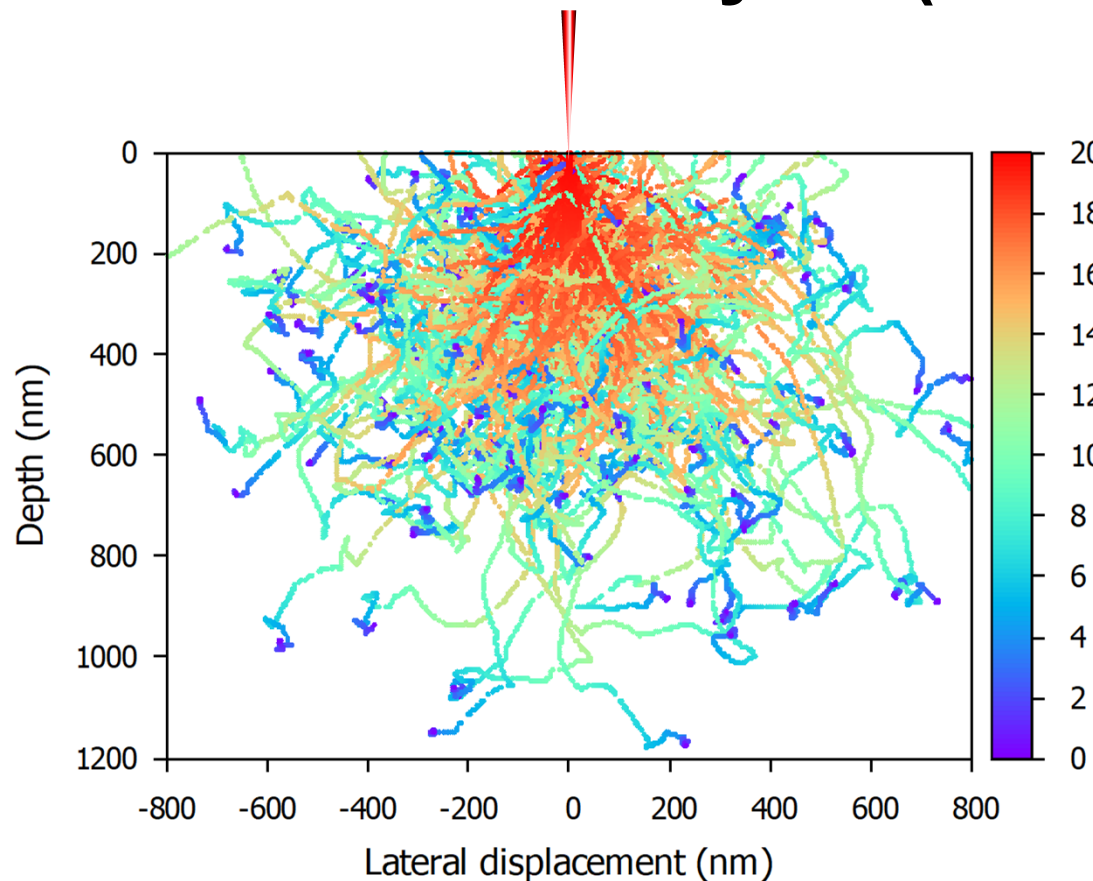
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A Micro-guide to Electron Probe Microanalysis (EPMA)



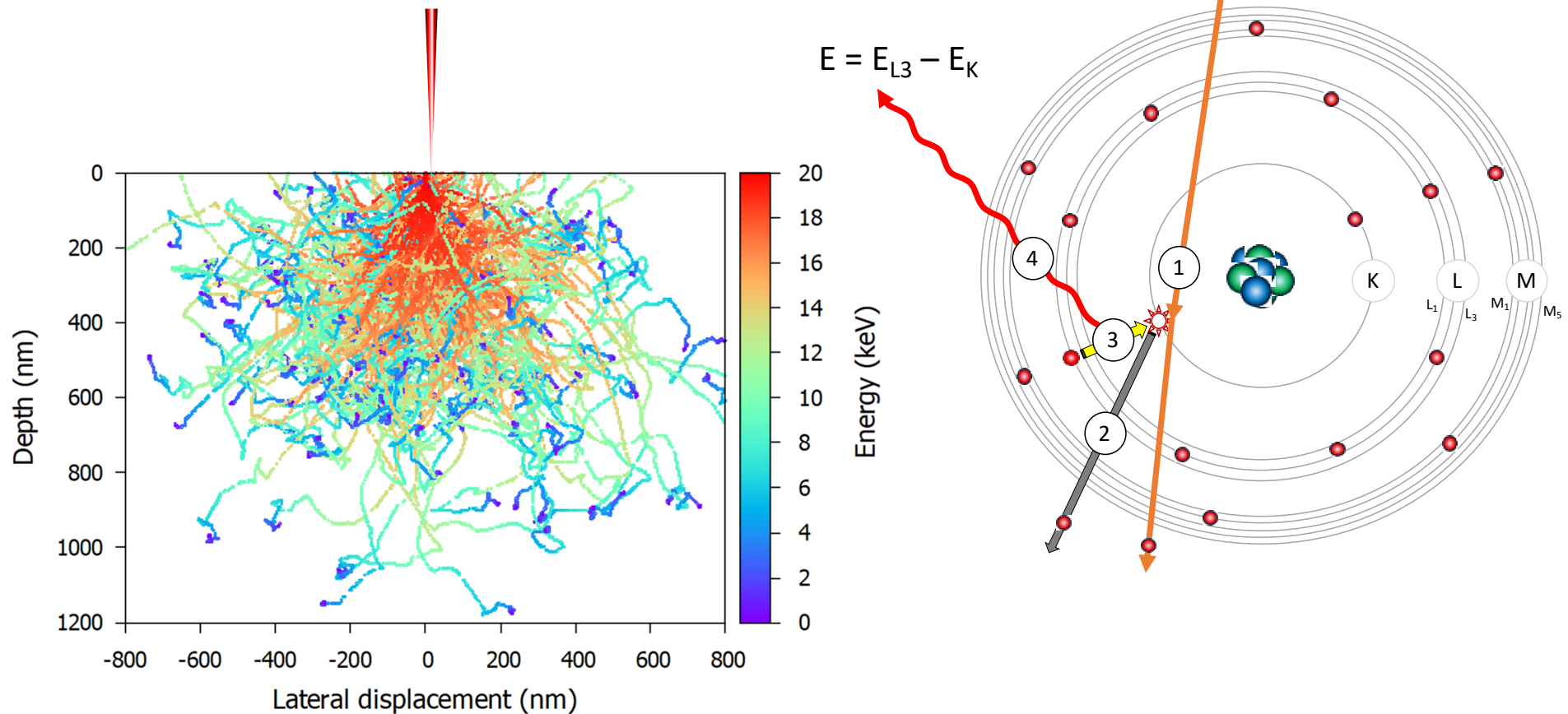
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A Micro-guide to Electron Probe Microanalysis (EPMA)



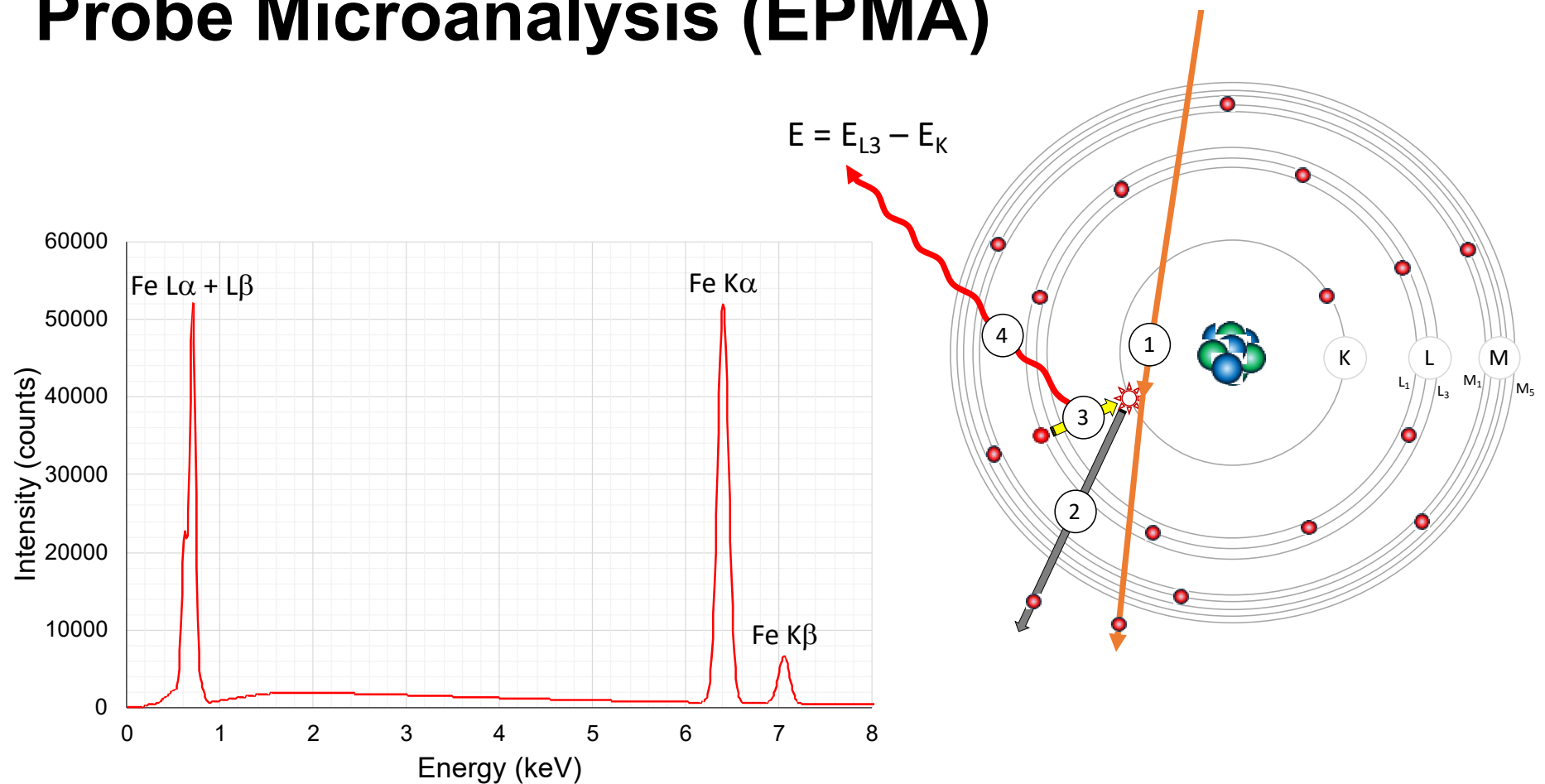
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A Micro-guide to Electron Probe Microanalysis (EPMA)



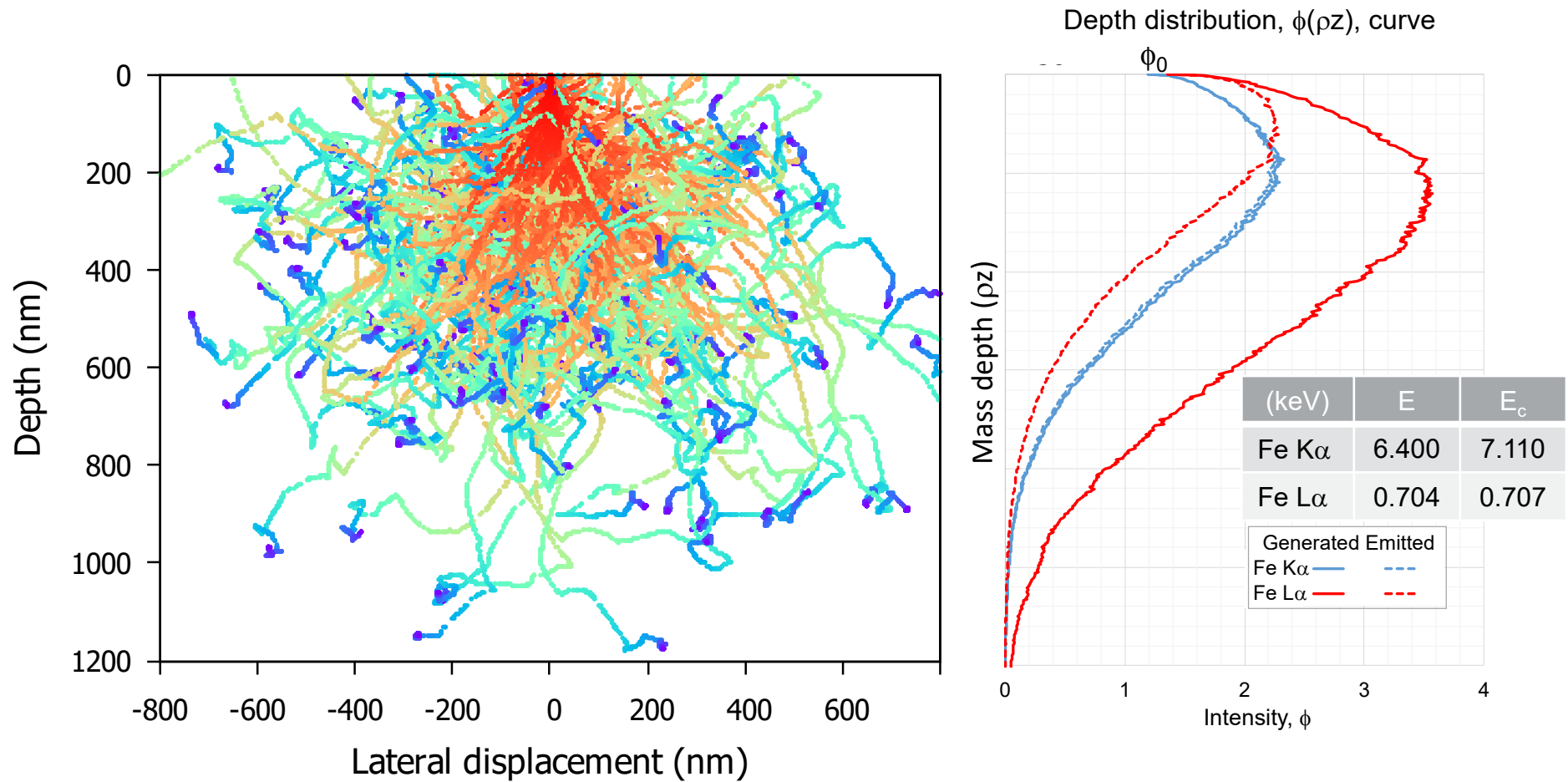
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A Micro-guide to Electron Probe Microanalysis (EPMA)

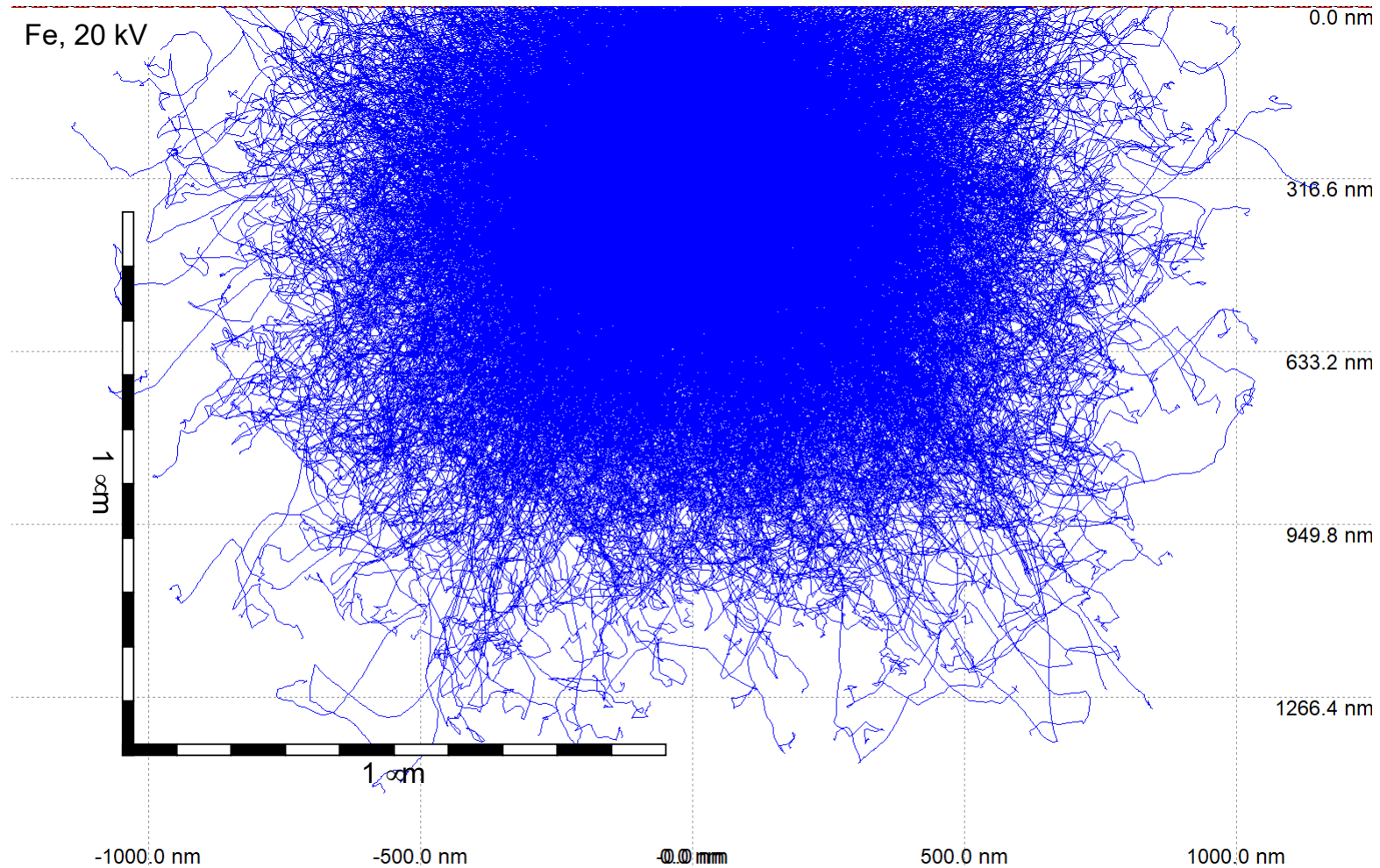


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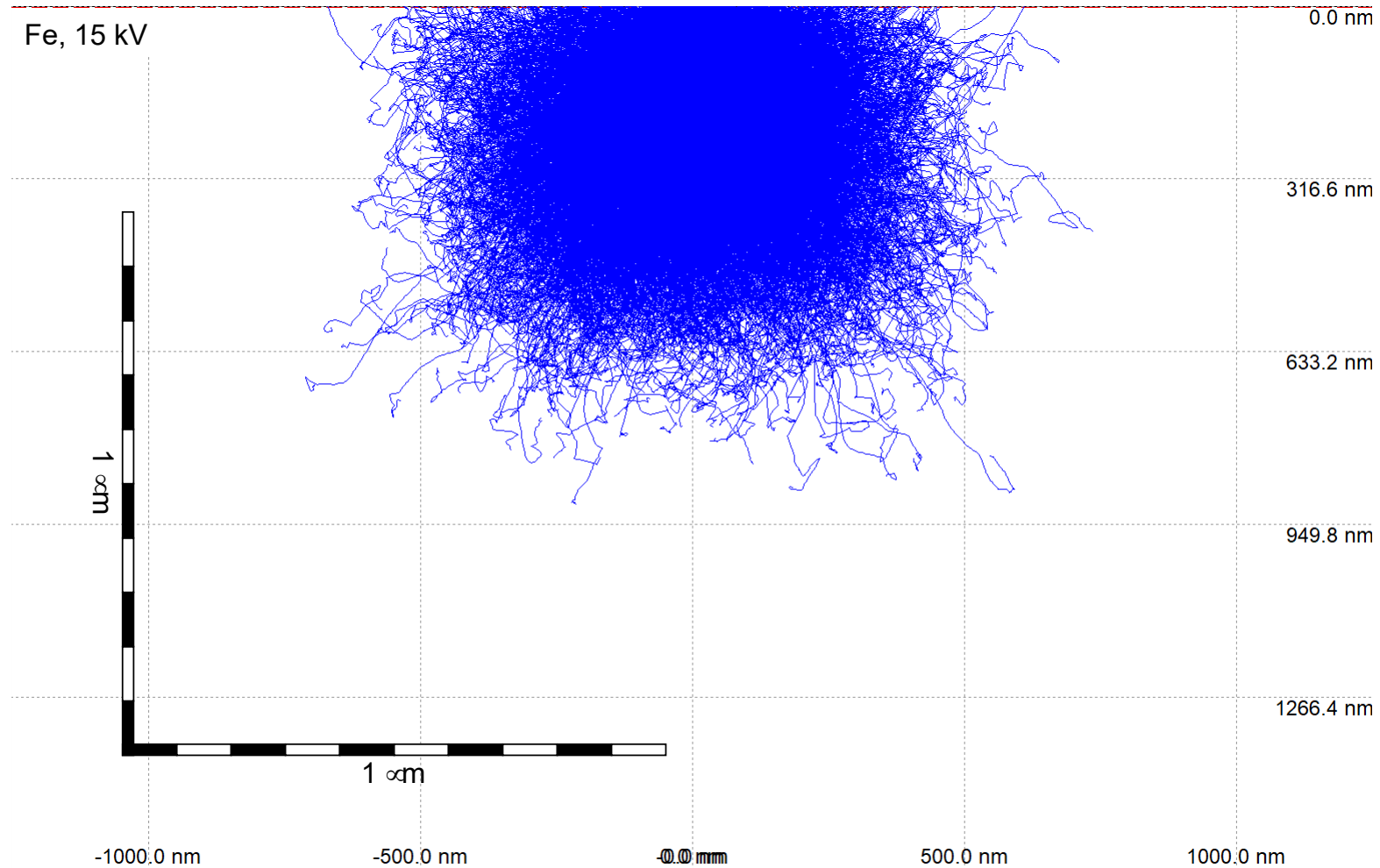
X-ray Depth Distributions, $\phi(\rho z)$ curves



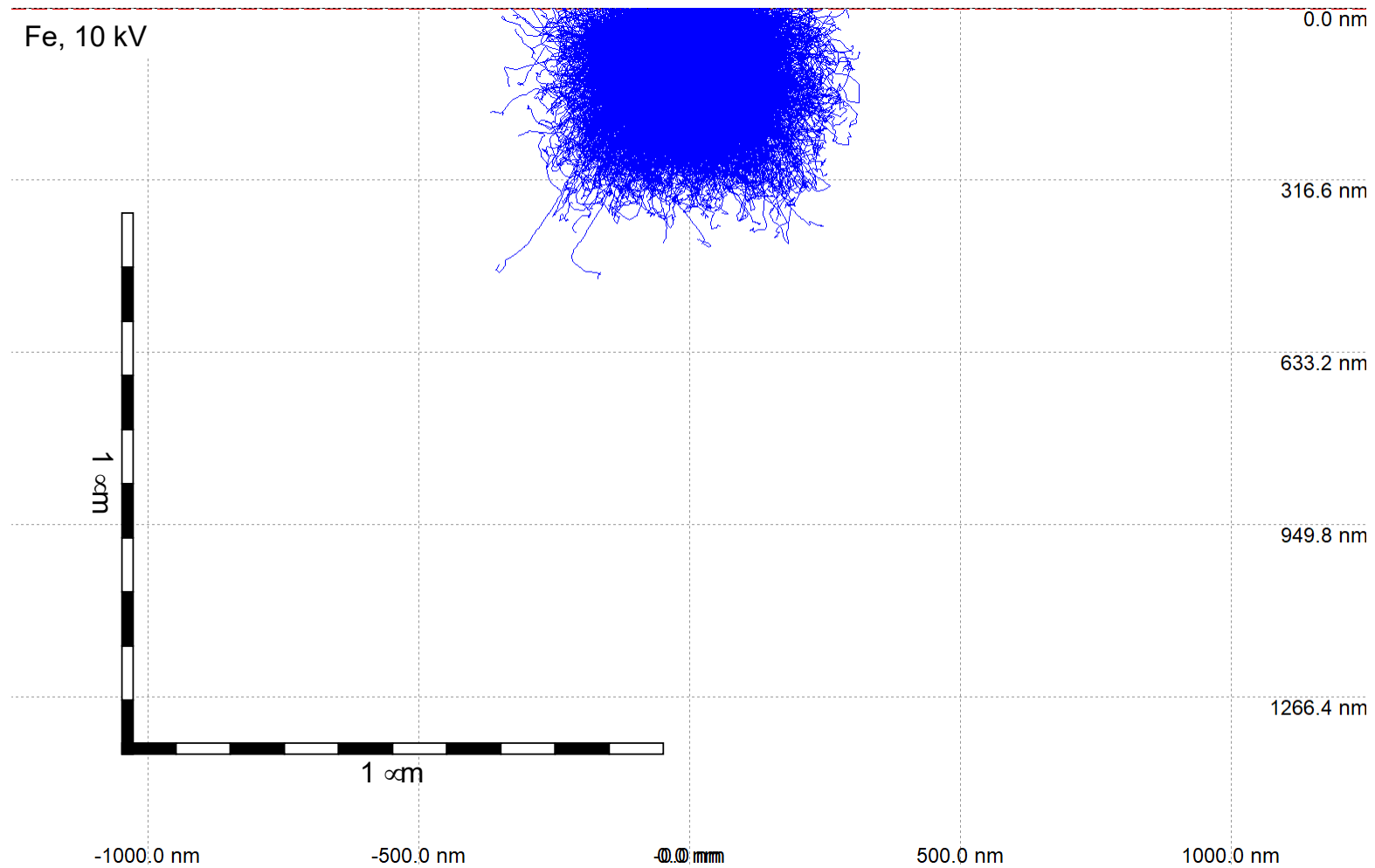
Influence of Accelerating Voltage



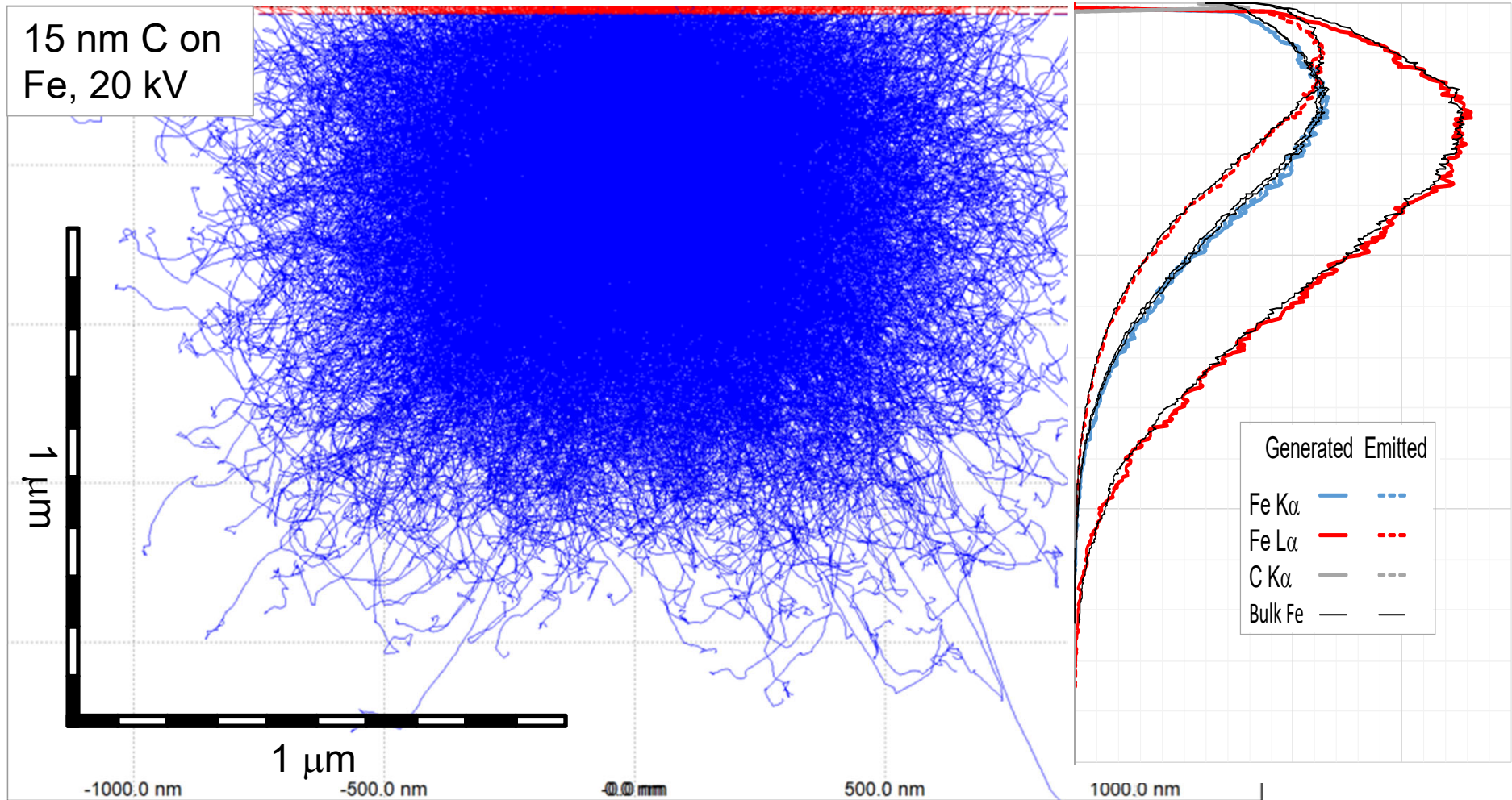
Influence of Accelerating Voltage



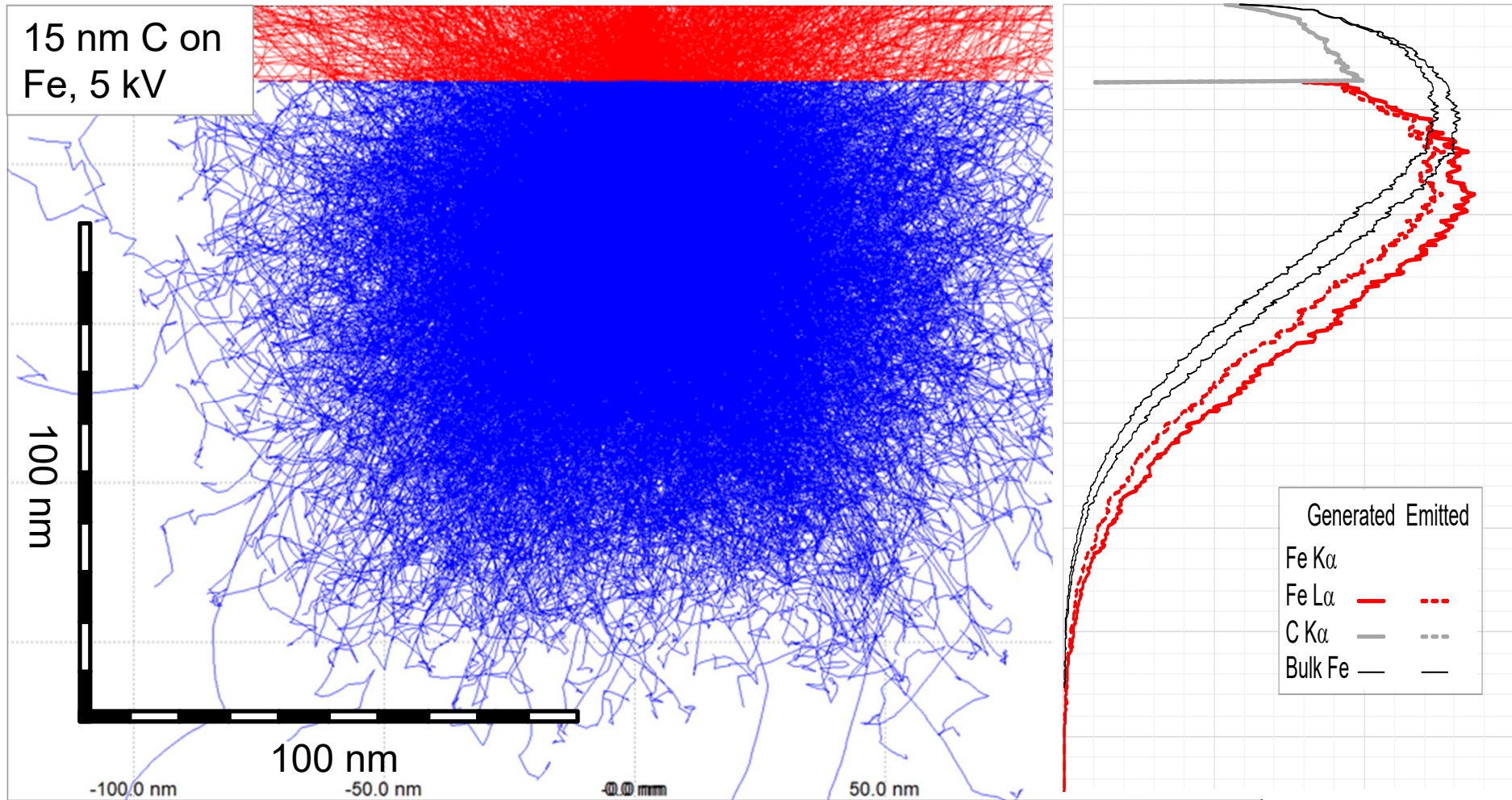
Influence of Accelerating Voltage



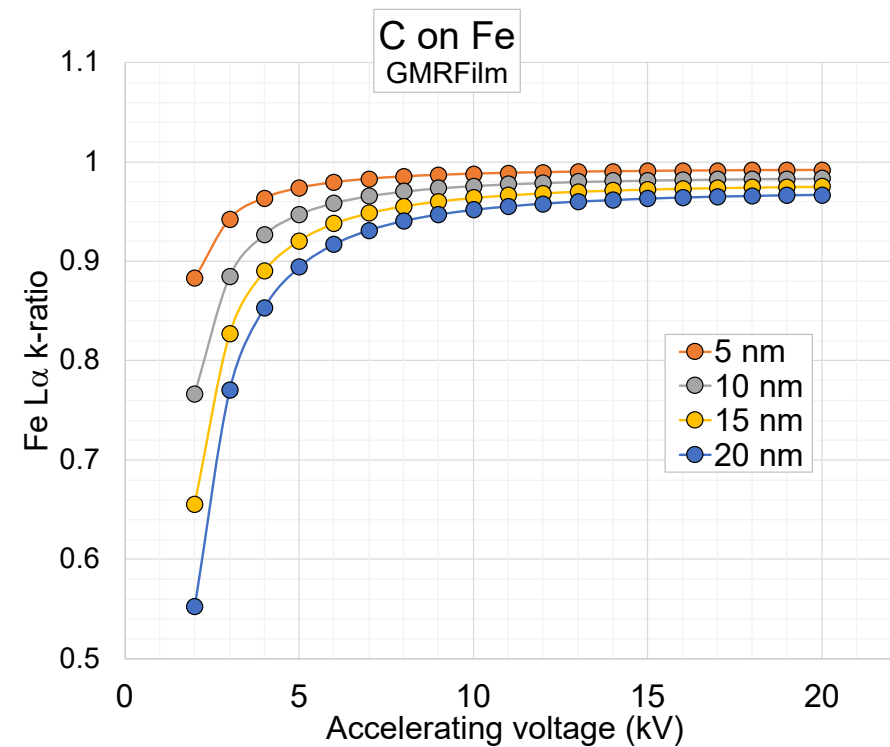
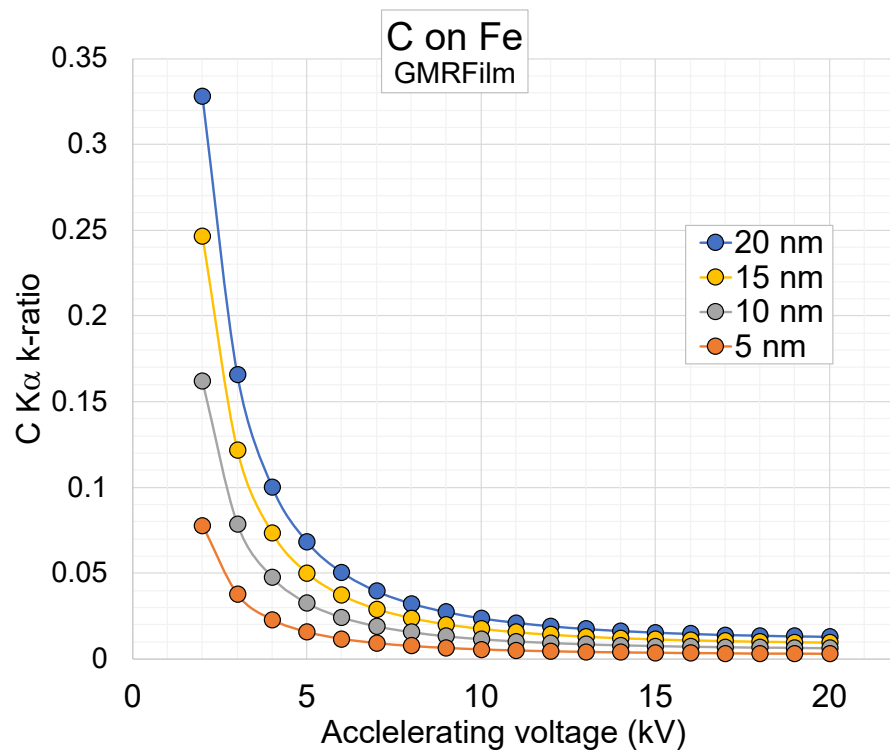
Surface Films



Surface Films



Effect on emitted intensities



Tools – Surface layer(s) and/or substrate

■ Monte Carlo

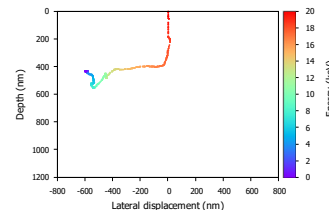
■ Statistical

- Includes noise

■ ‘Accurate’ physics model

■ Slow (10’s of s – hrs)

■ e.g. DTSA-II, Casino, PENELOPE/PENEPMA



■ Algorithm

■ Quantification equations

- No noise

■ ~‘Accurate’ physics model

- Optimised from ‘real’ samples

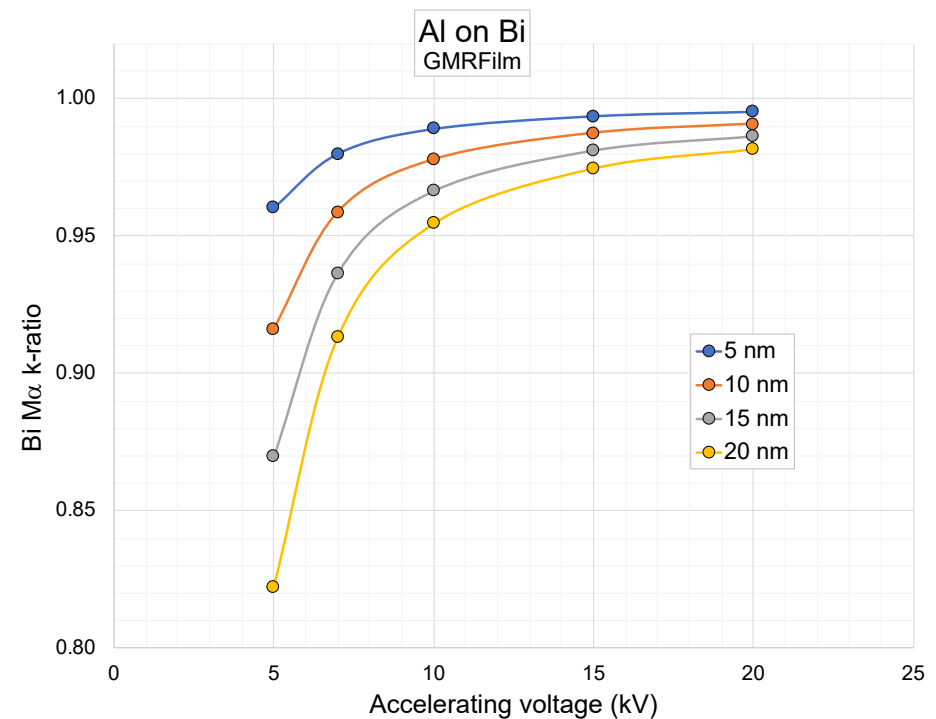
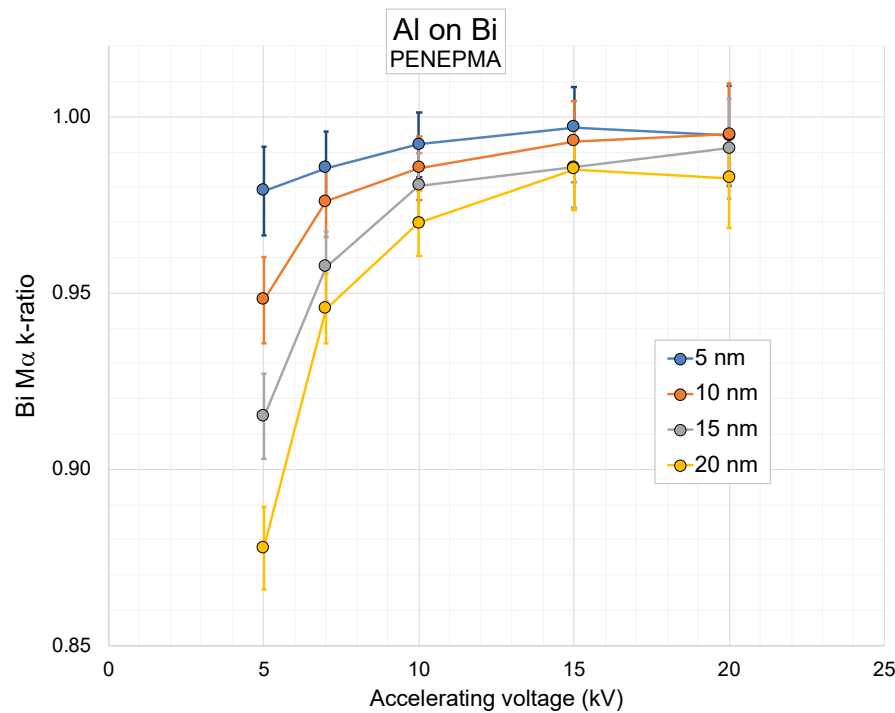
■ Fast (1 – 2s)

■ e.g. GMRFilm, BadgerFilm

Tools – Surface layer(s) and/or substrate

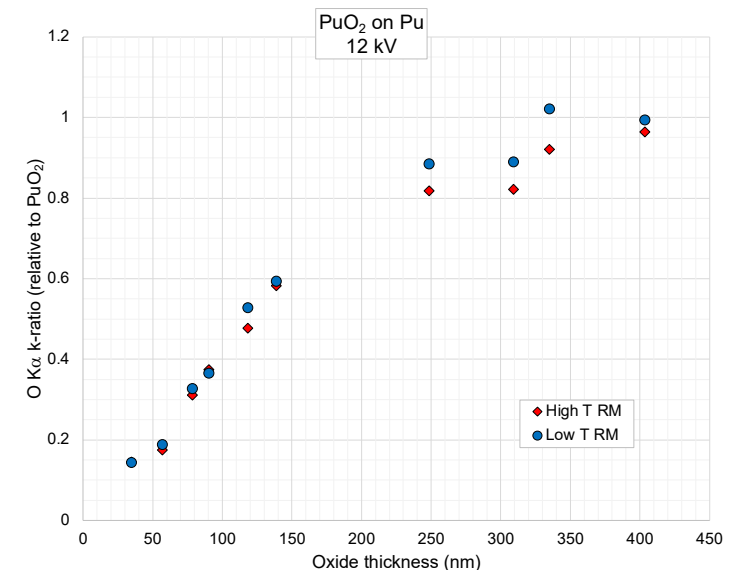
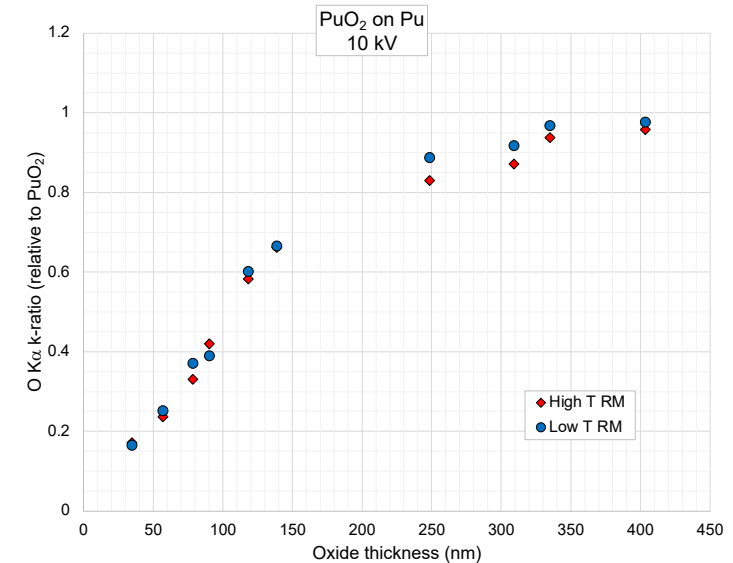
- Monte Carlo

- Algorithm



PuO₂ on Pu

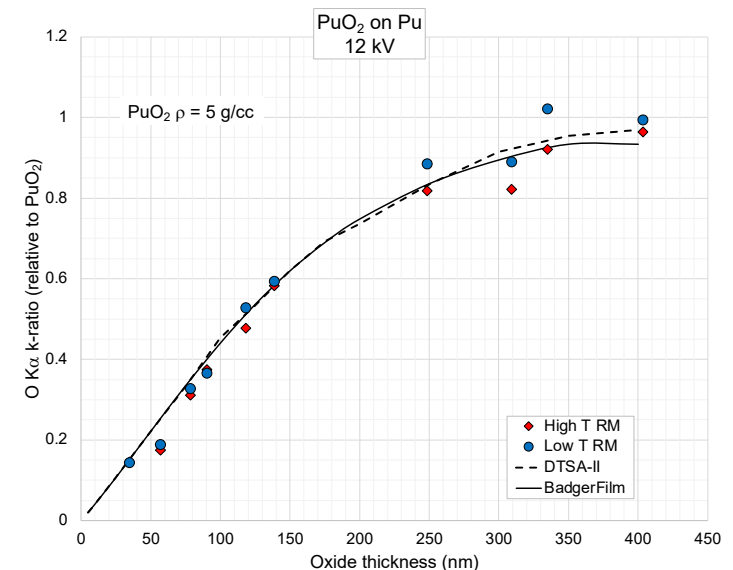
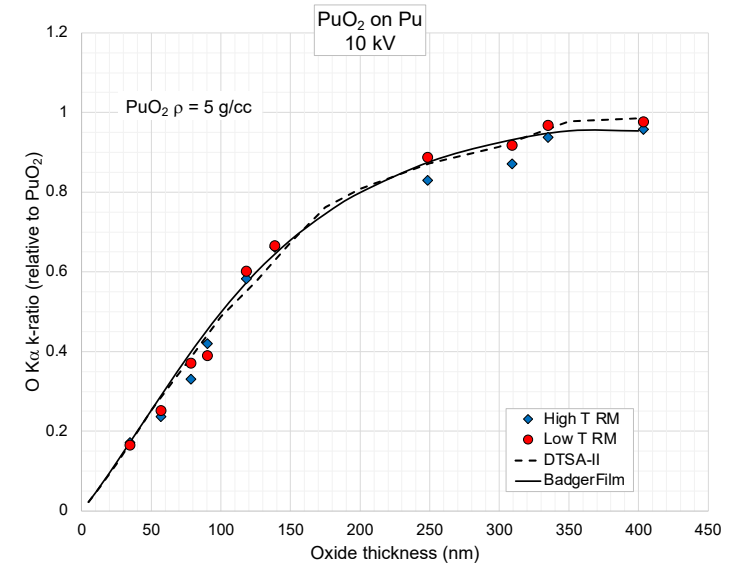
- 10 oxidised Pu metal samples
- EPMA measurements of O K α (relative to bulk PuO₂ RM) at 10kV and 12kV
 - ‘High’ and ‘low’ T versions of the RM)
- FIB sectioning for ‘geometric’ thickness



Stanford, J.A. et al, *Journal of Nuclear Materials* 530 (2020) 15168

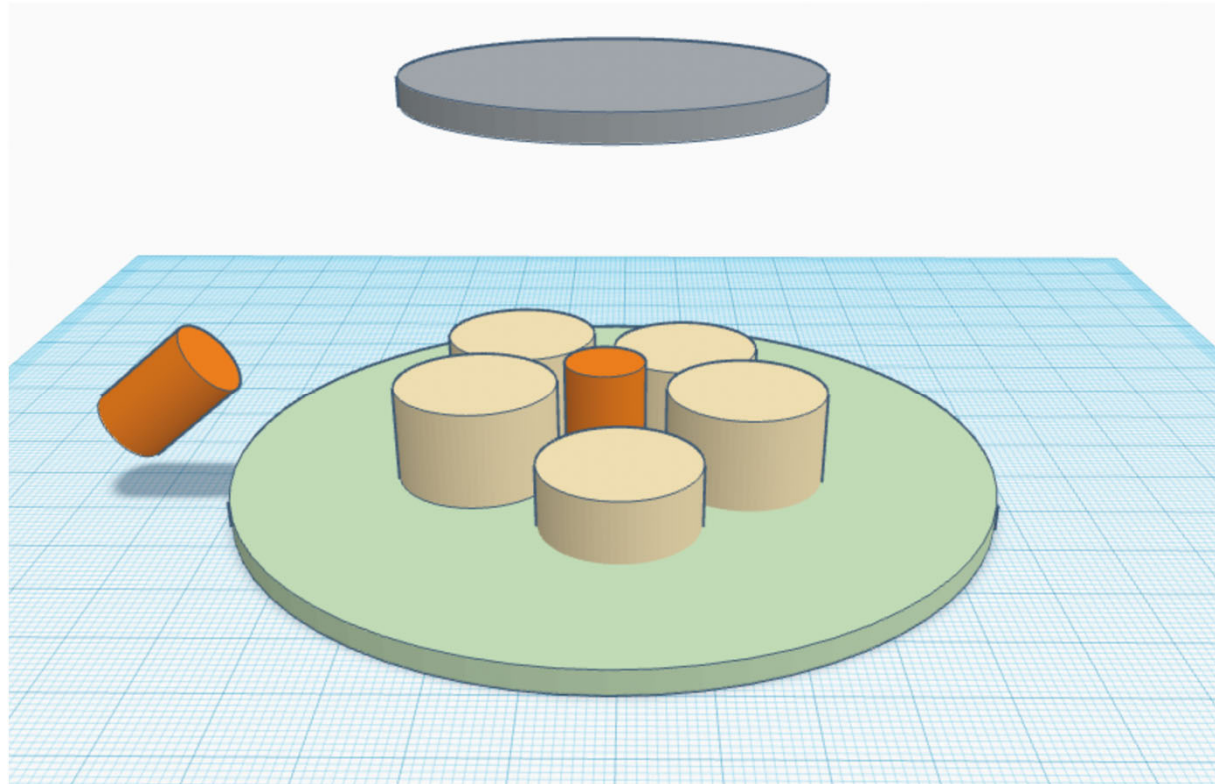
PuO₂ on Pu

- 10 oxidised Pu metal samples
- EPMA measurements of O K α (relative to bulk PuO₂ RM) at 10kV and 12kV
 - ‘High’ and ‘low’ T versions of the RM)
- FIB sectioning for ‘geometric’ thickness
- Model the data
 - Assume PuO₂ density of 5 g/cc



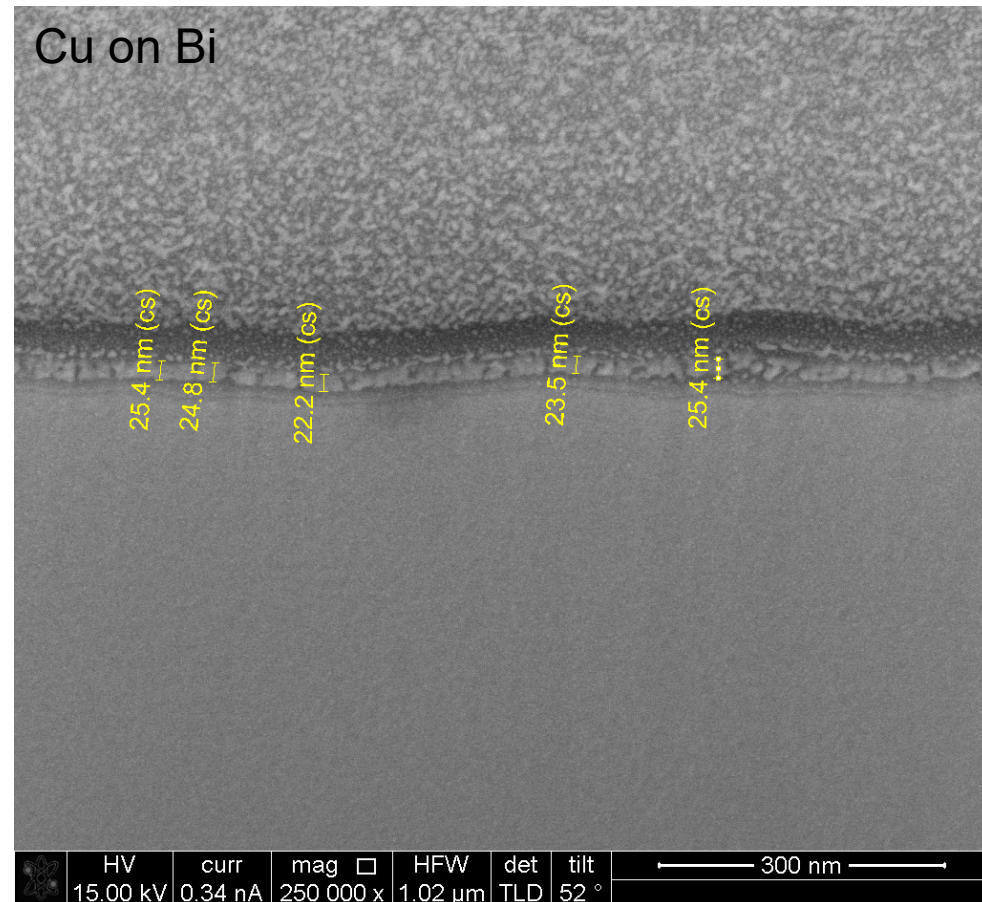
Coating accuracy

- In-coater Film Thickness Monitor (FTM)
 - Side or central position
 - Highly precise
 - Å-level
 - Accurate?



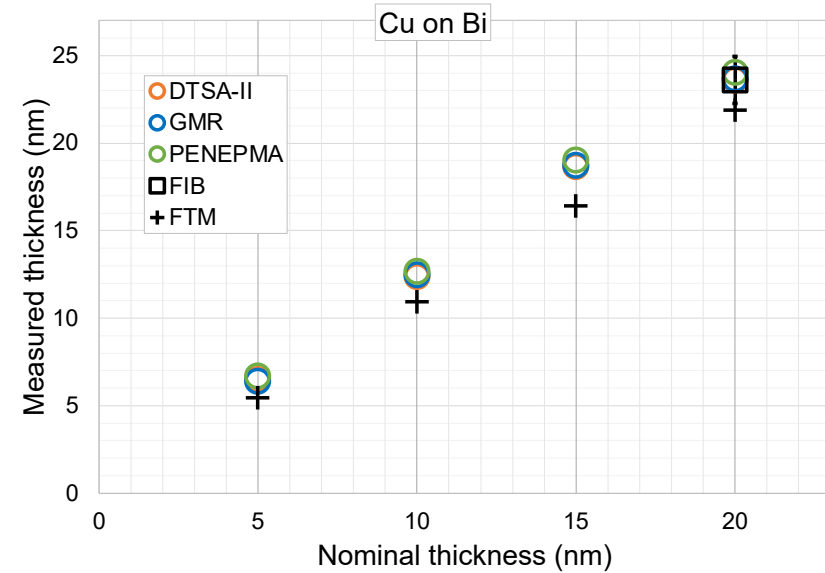
Coating accuracy

- Sputter coated Cu on Bi
 - Nominally 5, 10, 15 and 20nm thicknesses
 - Film thickness monitor (FTM) co-located with samples
 - Assume bulk Cu density
- Determine thicknesses
 - FIB (direct measure)
 - GMRFilm (EPMA + calc)
 - DTSA-II (EPMA + calc)
 - PENEPMA (EPMA + calc)



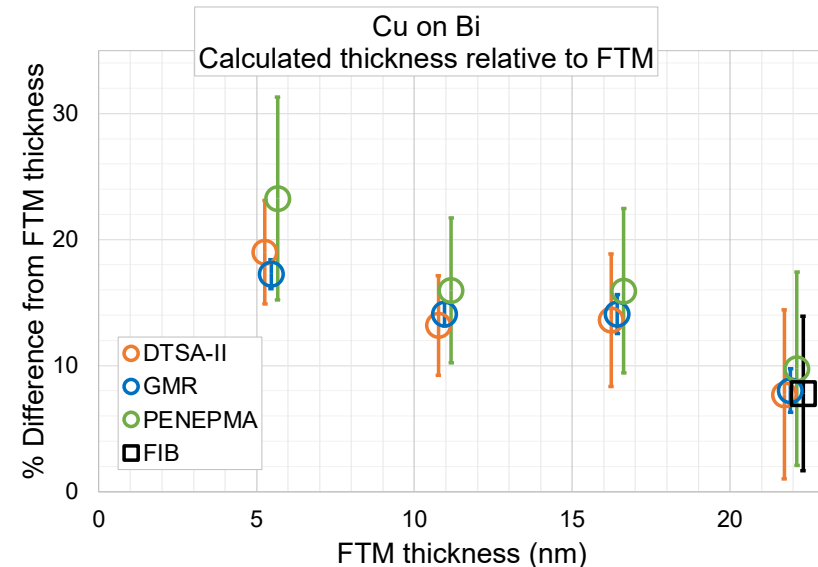
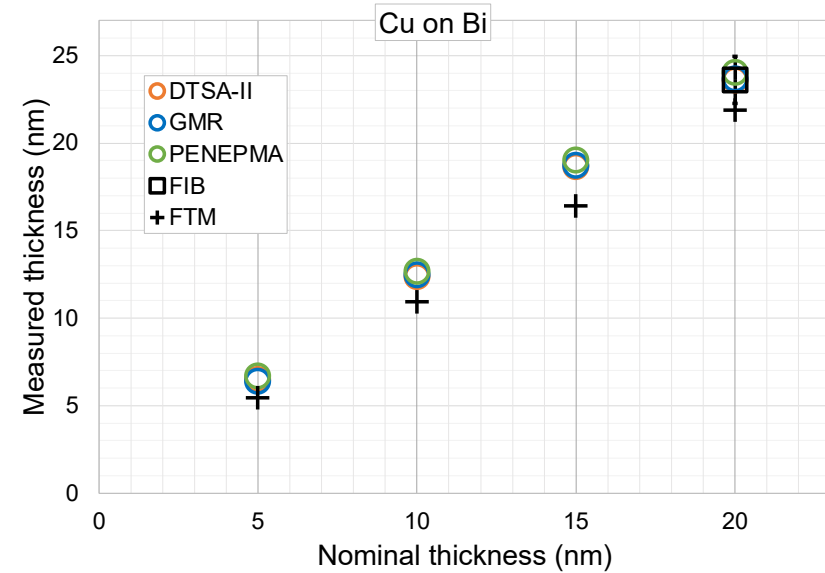
Coating accuracy

- EPMA + model calculated values consistent
 - Agree with FIB
 - Disagree with FTM



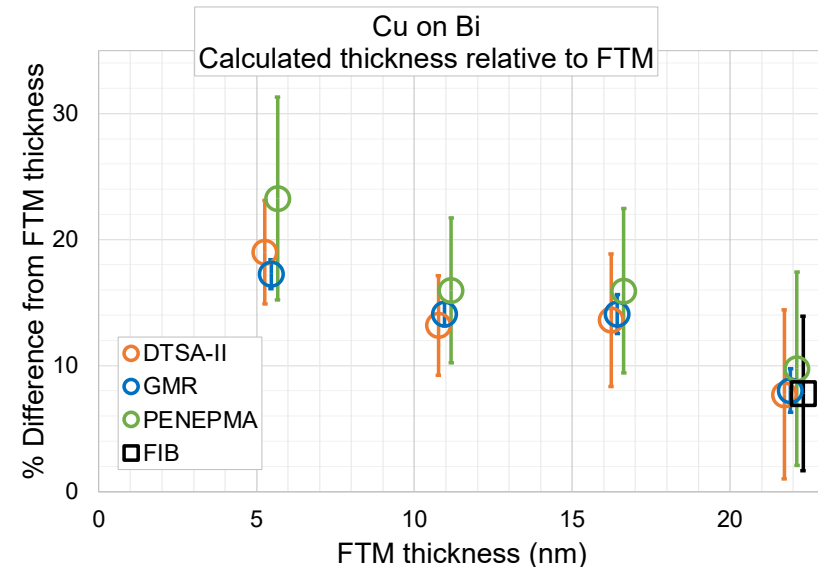
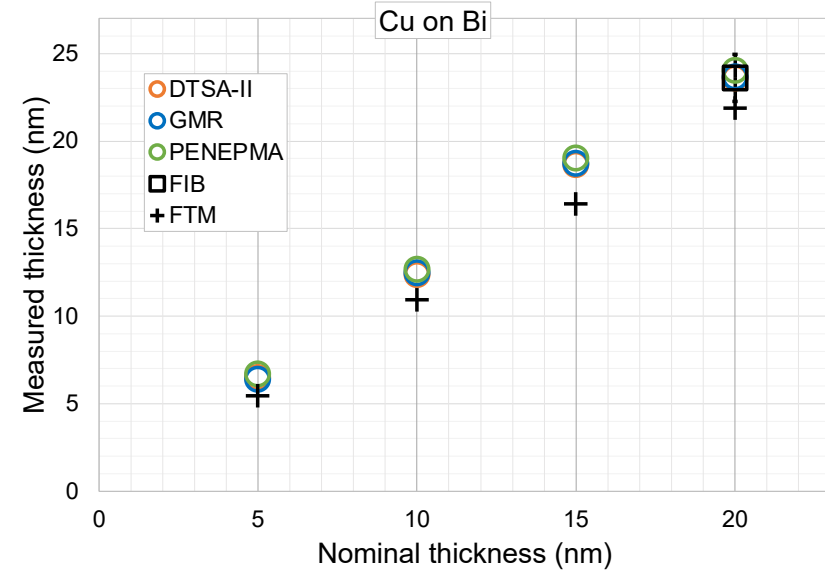
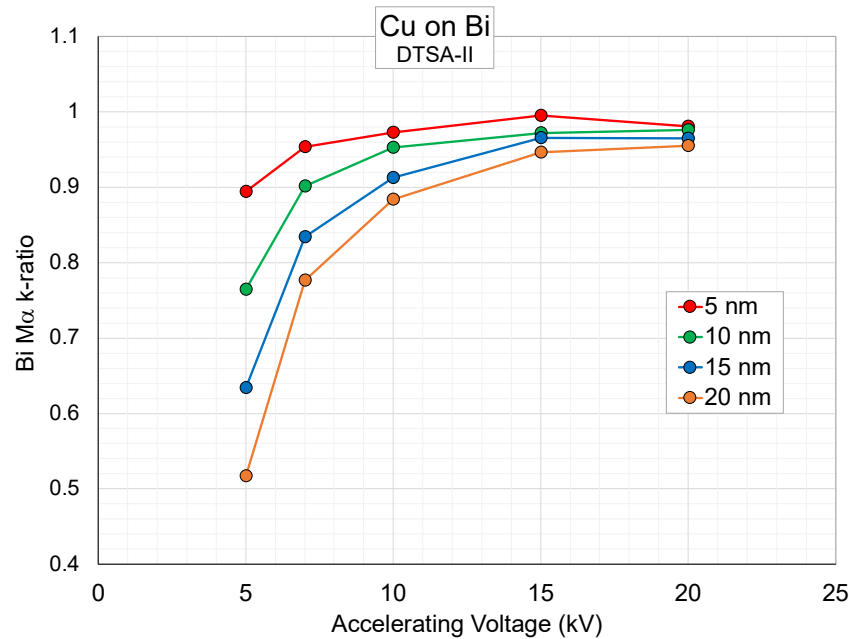
Coating accuracy

- EPMA + model calculated values consistent
 - Agree with FIB
 - Disagree with FTM by 10 – 20%



Coating accuracy

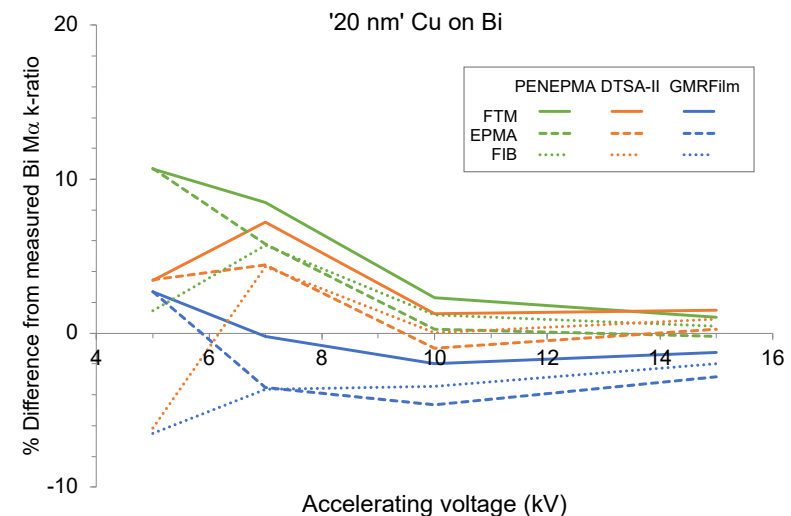
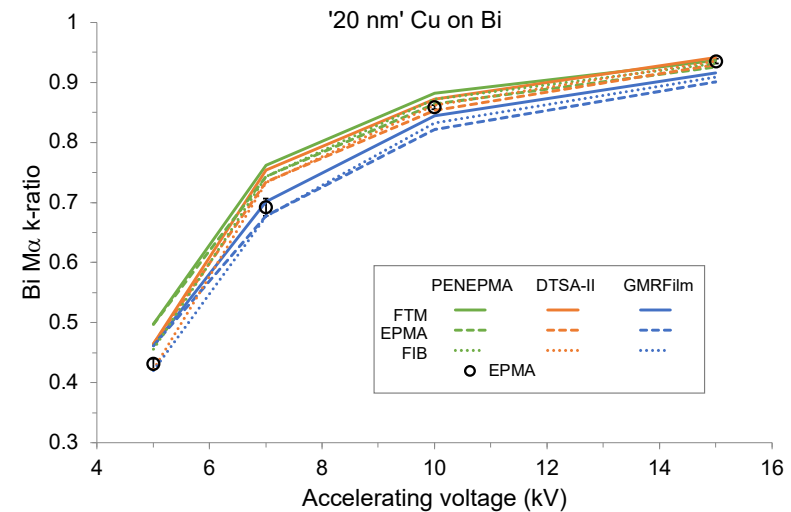
- EPMA measured values consistent
 - Agree with FIB
 - Disagree with FTM by 10 – 20%



Substrate Quantification

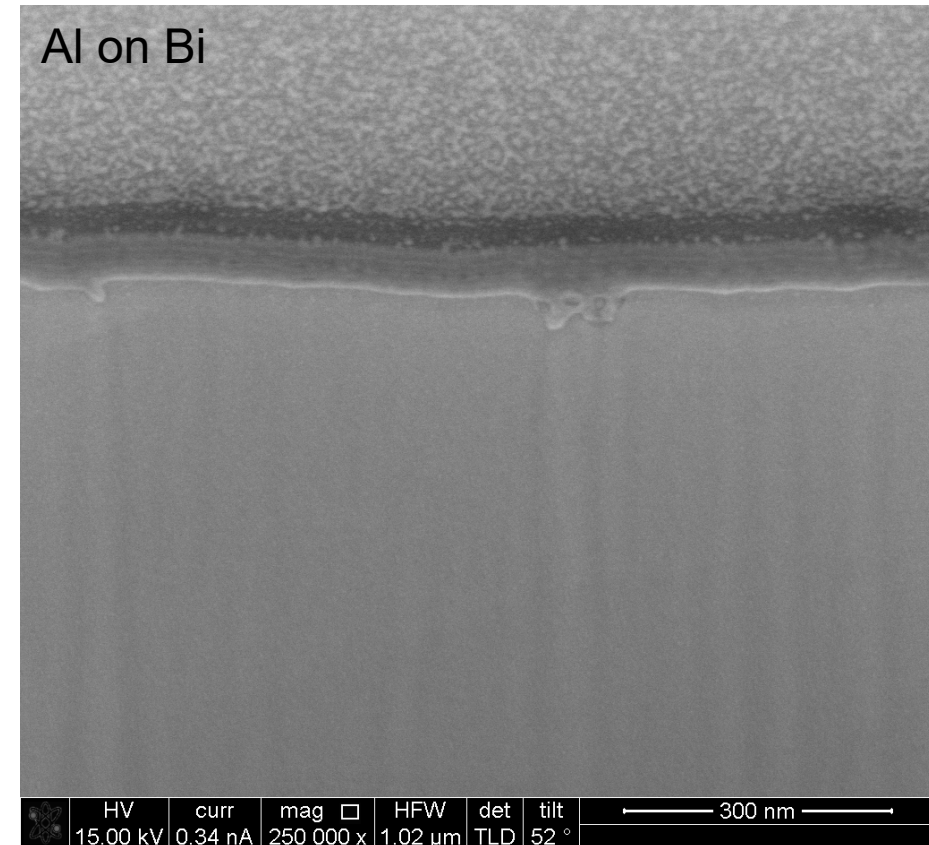
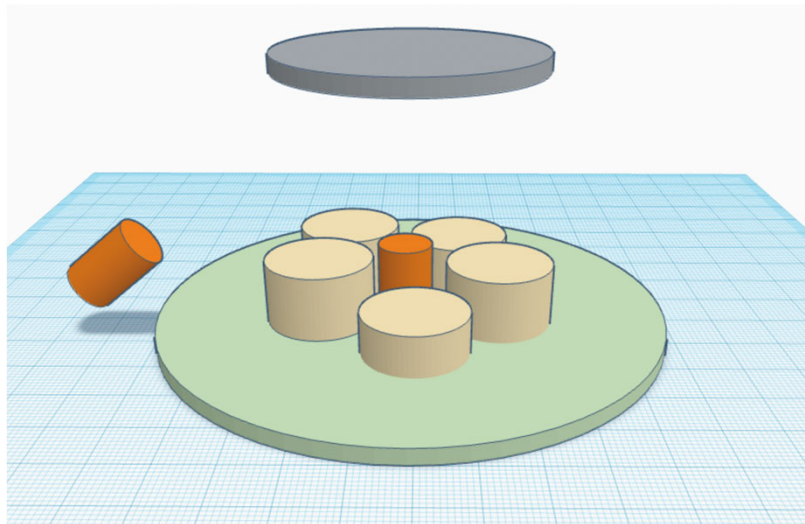
Cu on Bi

- Calculated vs measured k-ratios
 - Removes any effect of quantification routine used
- Absolute fit looks good
- No model better at all kV
- Relative errors increase as kV decreases
 - >10 kV, $<\pm 5\%$
 - <10 kV, $\pm 5 - 10\%$



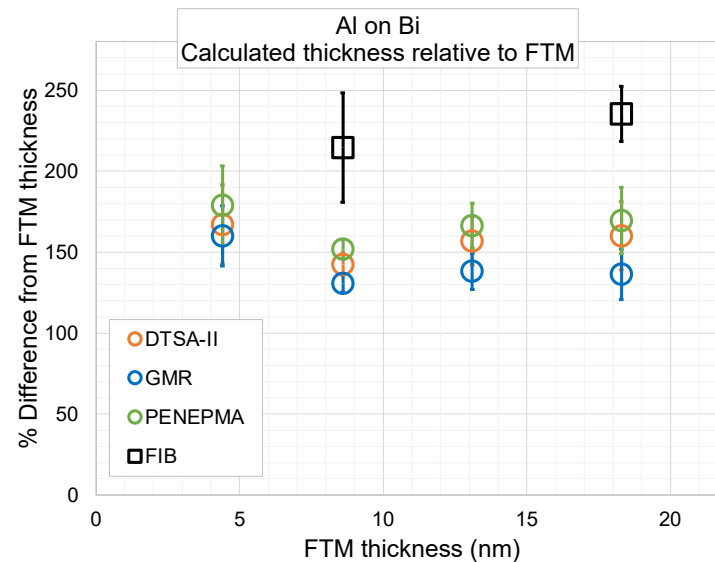
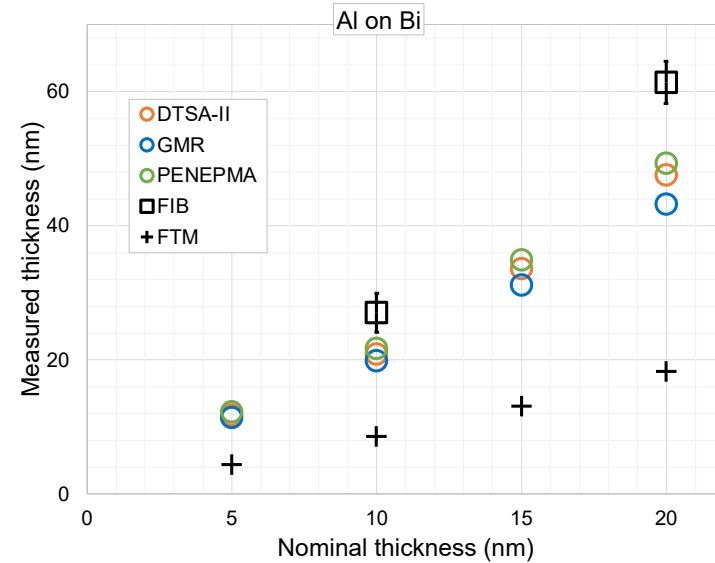
Coating accuracy

- Sputter coated Al on Bi
 - Nominally 5, 10, 15 and 20nm thicknesses
 - Film thickness monitor (FTM) side-located
 - Assume bulk Al density



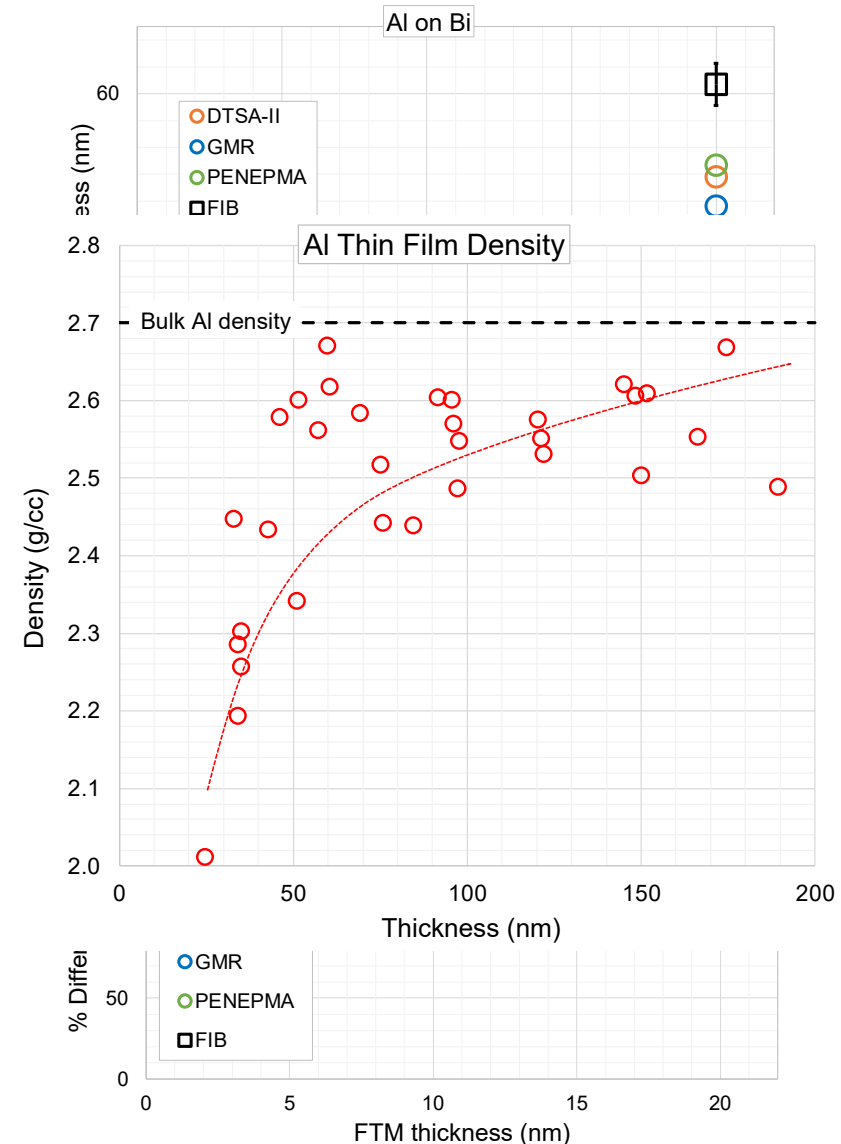
Coating accuracy

- EPMA measured values consistent
 - Disagree with FIB by ~50%
 - Disagree with FTM by ~150%



Coating accuracy

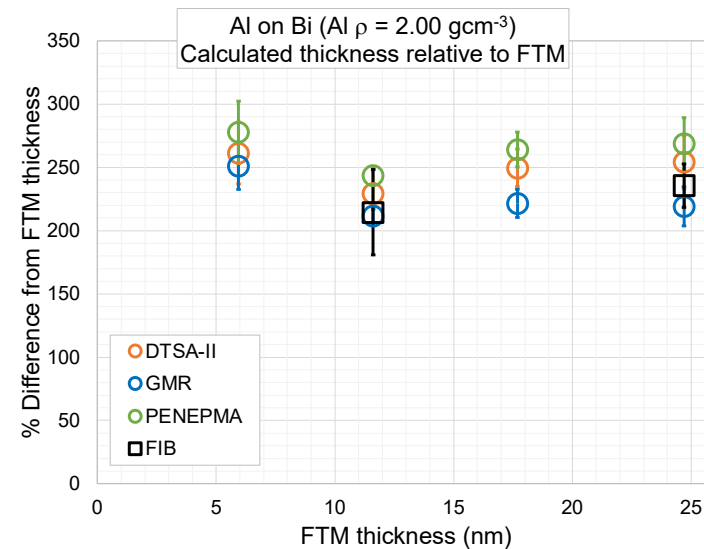
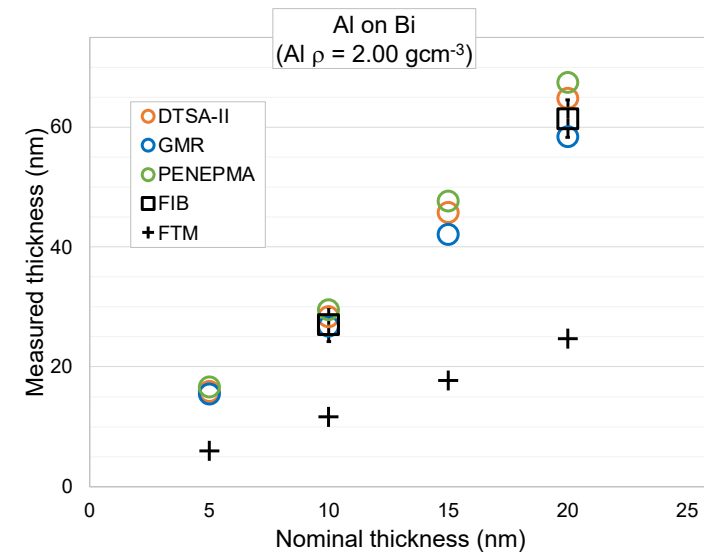
- FIB measures thickness, t_c
- FTM and EPMA models measure mass thickness, $fn(\rho_c)$
- Thin film $\rho \leq$ bulk ρ
 - Hartman (1965): Al $\rho = fn(t_c)$
 - 2.5 g/cm³ for $t_c = 50$ nm
 - 2.0 g/cm³ for $t_c = 25$ nm



Hartman, T.E. (1965) Density of Evaporated Aluminium Films. *J. Vac. Sci. Technol.* **2**(5), 239

Coating accuracy

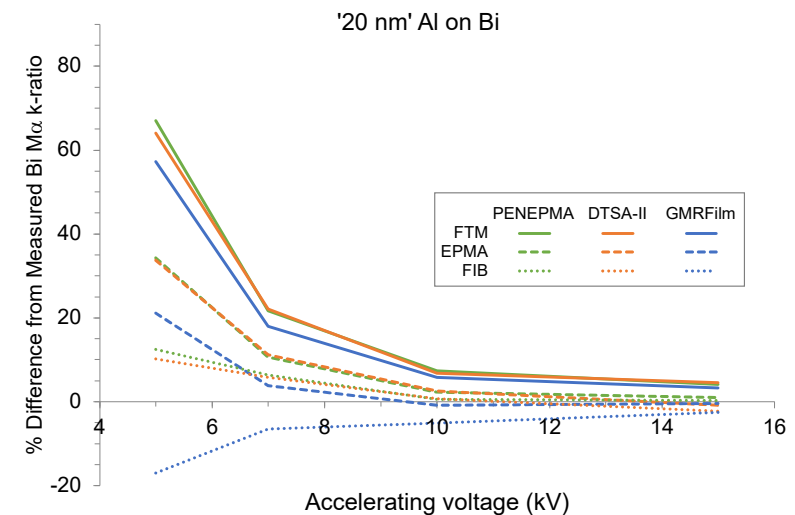
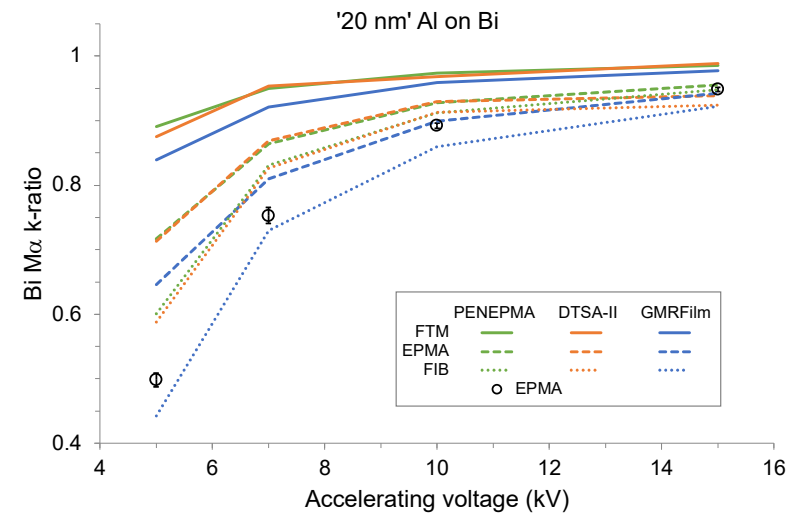
- Reduce Al density to 2.0 g/cm^{-3}
- EPMA re-calculated values consistent
 - Agree with FIB
 - Disagree with adjusted FTM by $\sim 250\%$



Substrate Quantification

Al on Bi

- Calculated vs measured k-ratios
 - Corrected for low Al density
- Absolute fit looks poor
- No model better at all kV
- Relative errors increase as kV decreases
 - >10 kV, $\pm 5\%$
 - <10 kV, -20% – +70%



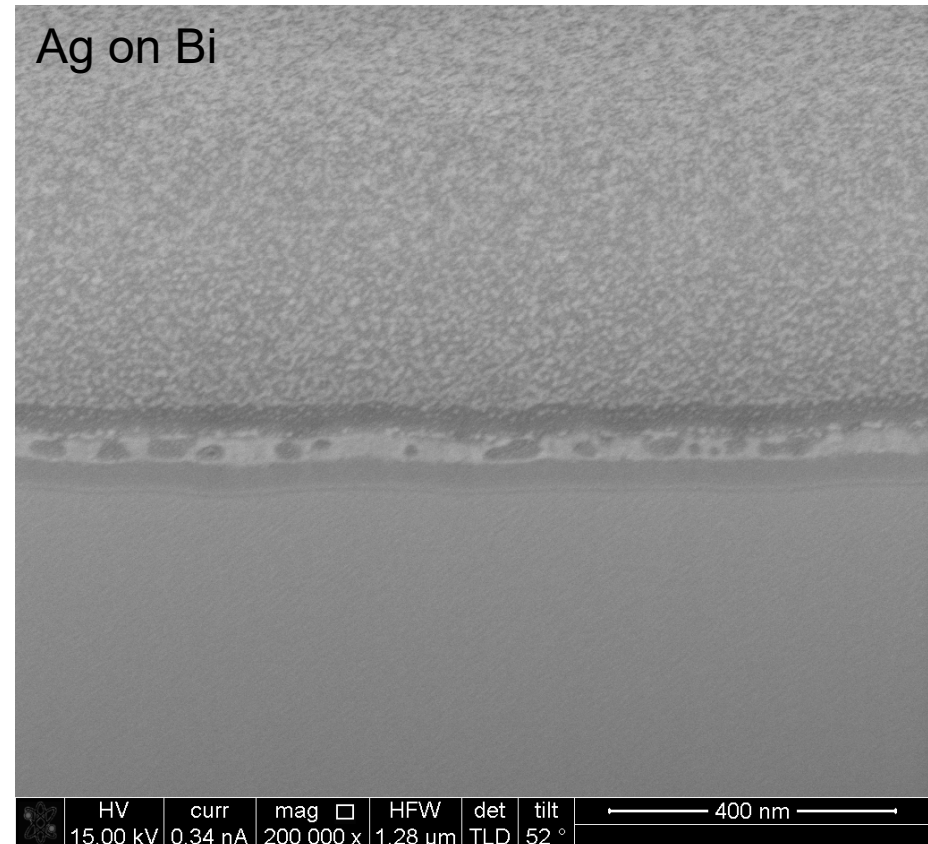
So, how should you measure coating thickness?

- FTM
 - Convenient
 - Highly precise
 - Potentially highly inaccurate!
- FIB
 - Best measure of true 'geometric' thickness
 - Very expensive equipment
 - Slow
 - Need to know coating density
- EPMA
 - Uses same algorithms as quantification
 - Self-corrects for density
 - Uses data already being acquired
 - Extra calculation steps
 - Accuracy decreases appreciably at low kV

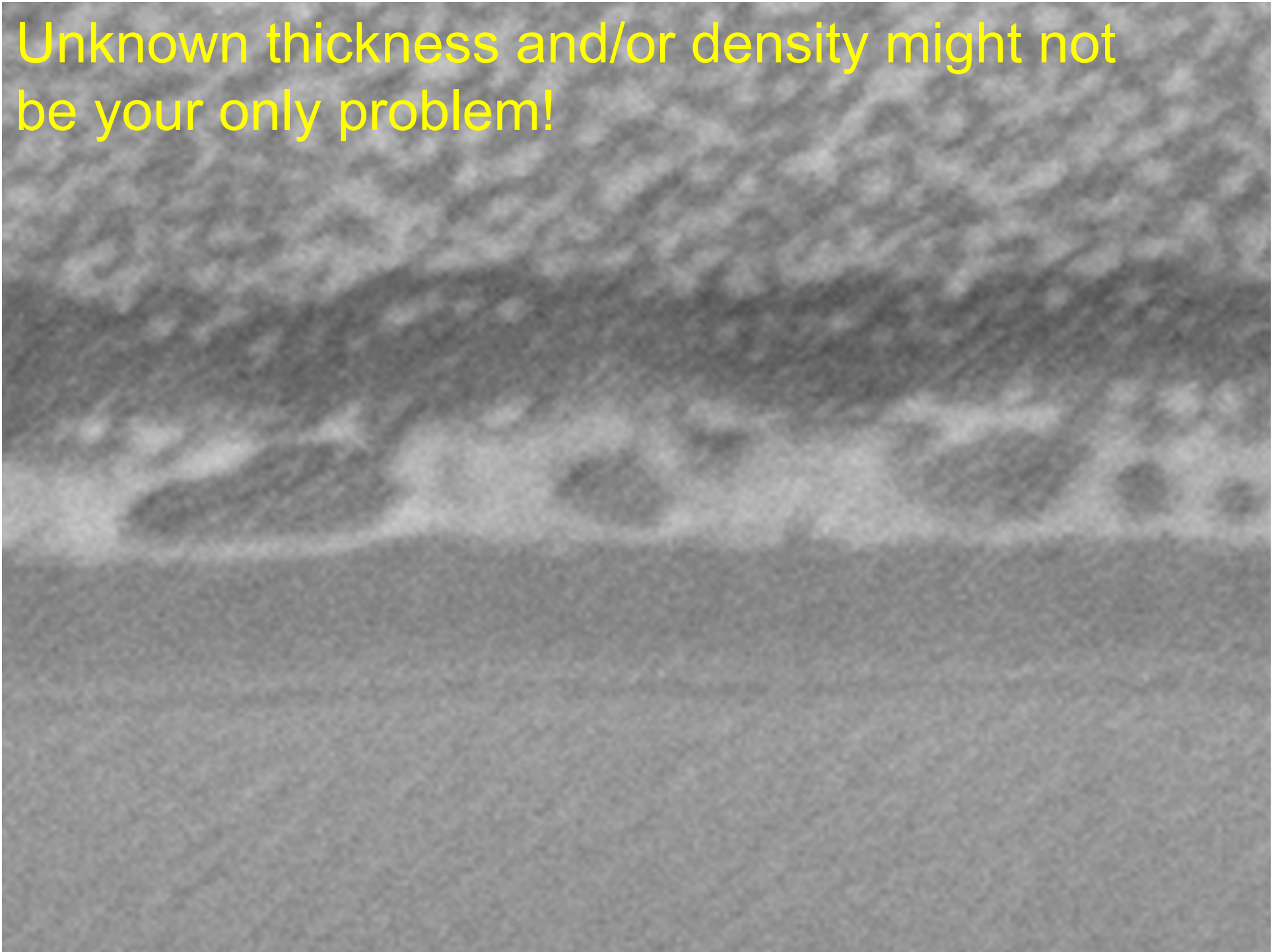
Coating Accuracy

- Ag on Bi
 - Side located FTM

Film Thicknesses (nm)					
		Cu	Ag	Al	C
FTM		21.9	19.7	18.3	20.3
FIB	Mean	23.6	45.7	61.4	21.3
	Std Dev	1.3	4.3	3.1	1.2
GMR	Mean	23.7	39.3	43.3	18.2
	Std Dev	0.4	1.4	2.9	0.7
DTSA-II	Mean	22.8	40.2	47.3	18.8
	Std Dev	1.5	5.9	3.5	1.0



Unknown thickness and/or density might not be your only problem!

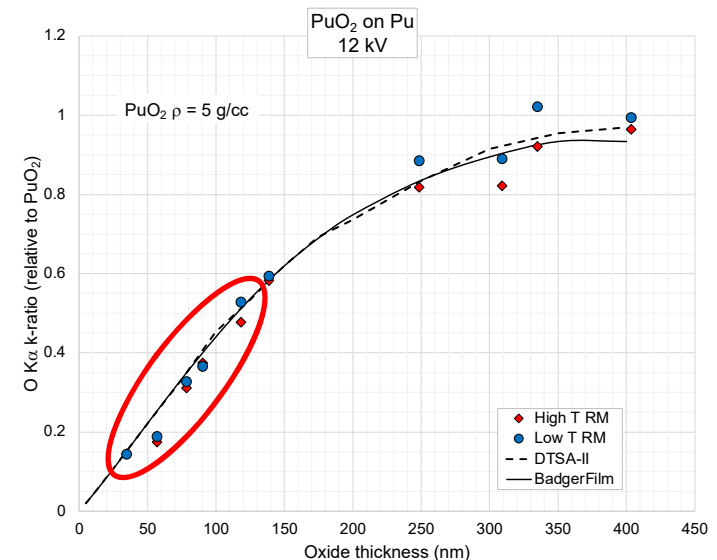
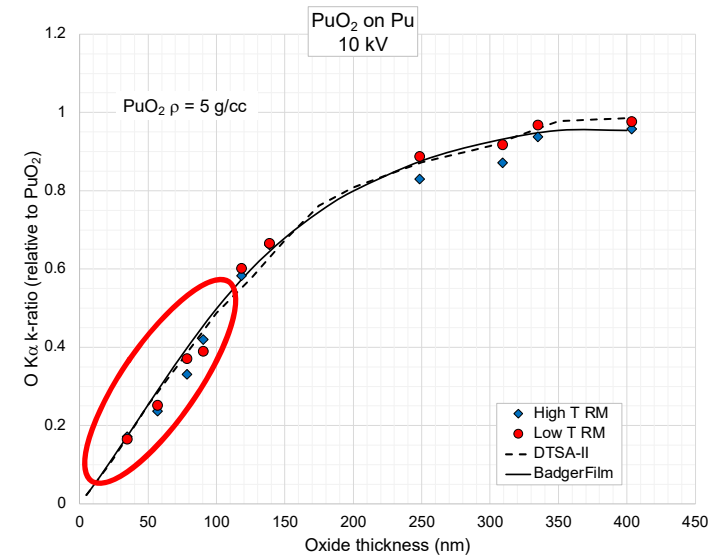


Summary

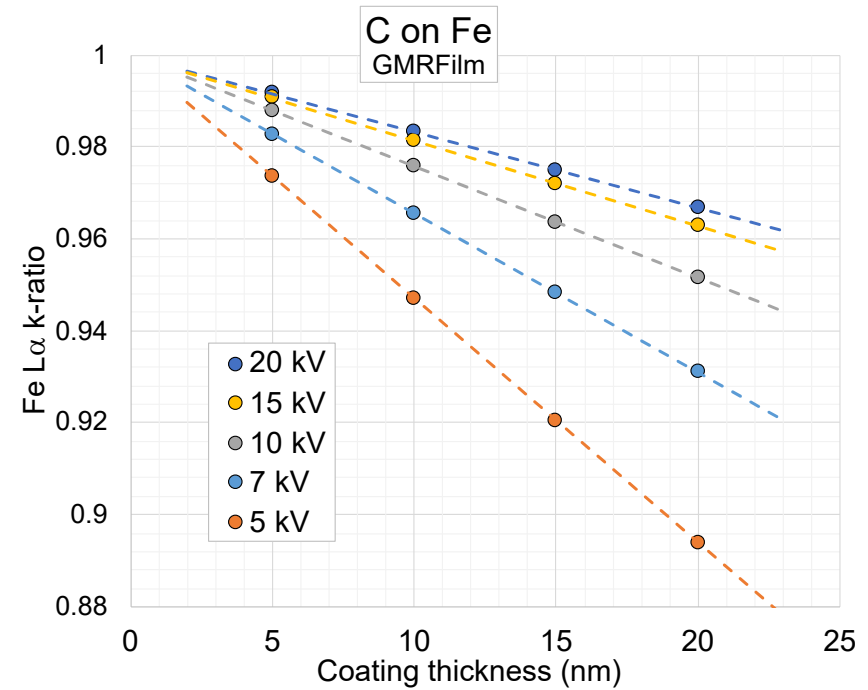
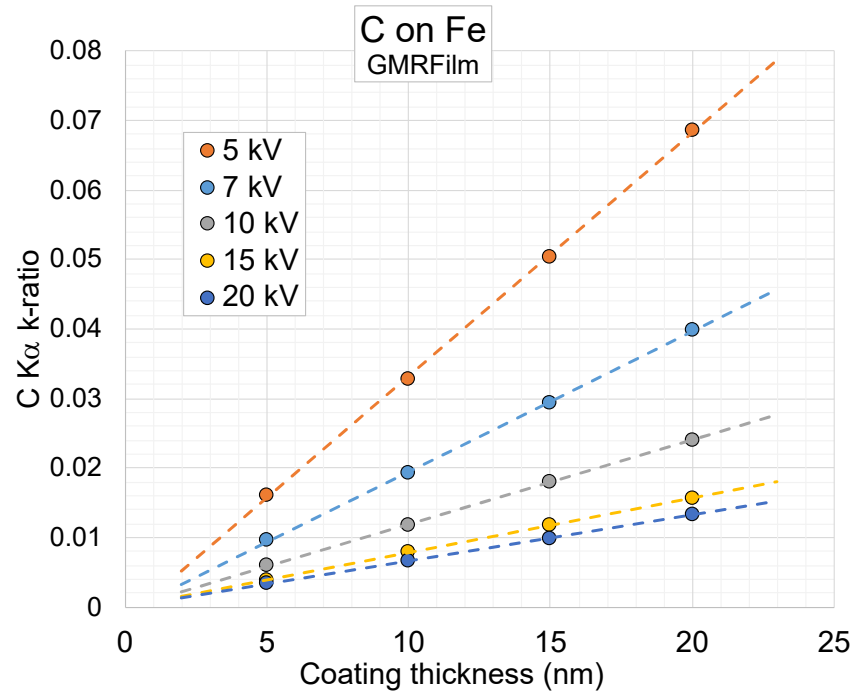
- There are v. good free tools available
 - e.g., BadgerFilm – see next talk!
- Thin Film v. useful BUT be aware that:
 - Errors will increase with decreasing voltage
 - Magnitude of errors can be v. large
 - Low Z coatings on high Z substrates
 - Inaccurate FTM thicknesses

And finally, A Useful Shortcut...

- Model k-ratios vs thicknesses
 - Limit thickness range
 - Fit linear trends
 - $y = mx + c$
 - Use m and c to calculate t from measured k-ratios



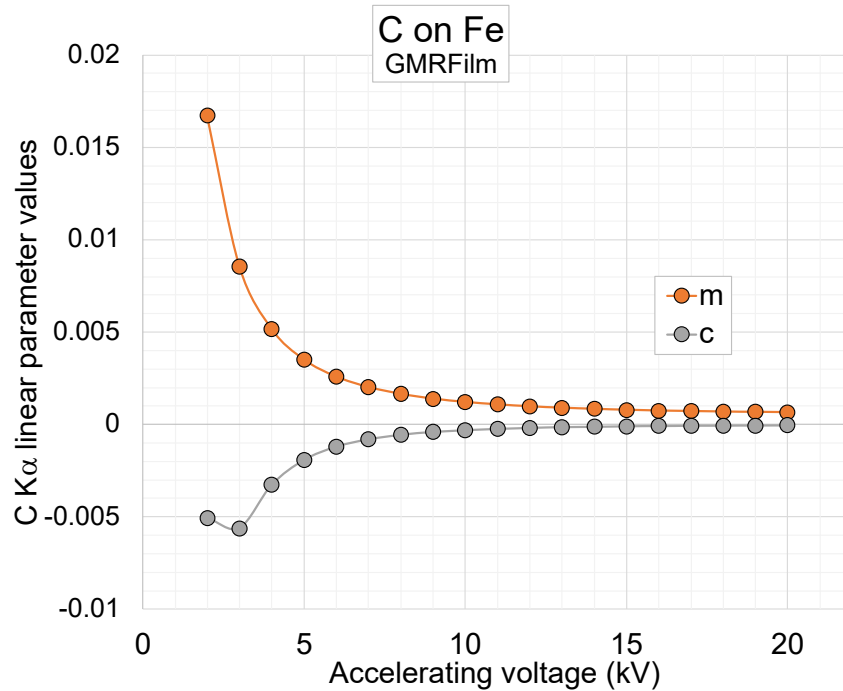
Linear approximation



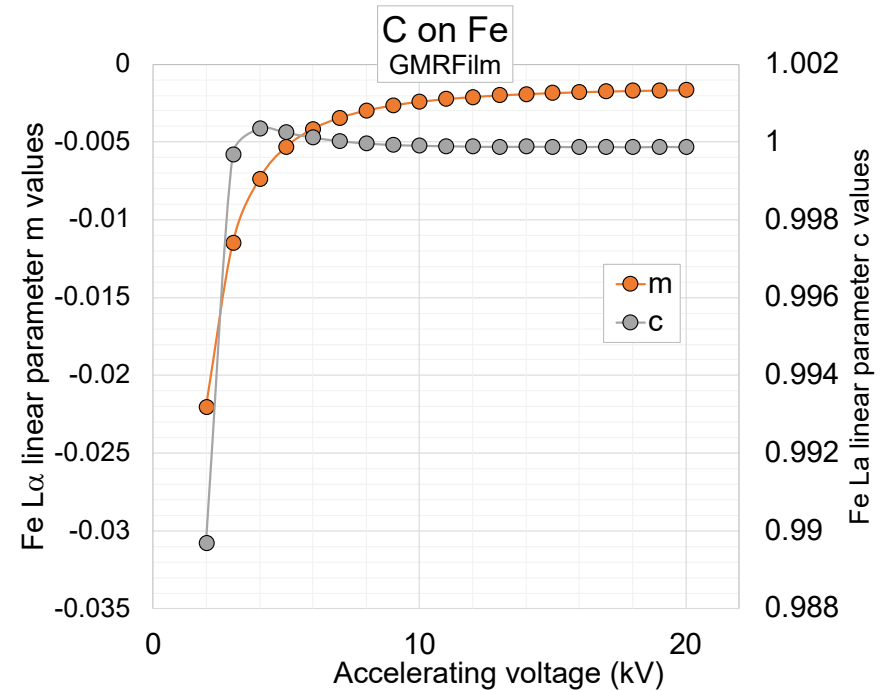
kV	C K α		
	m	c	R ²
5	0.00351	-0.00193	0.99970
7	0.00202	-0.00081	0.99982
10	0.00121	-0.00031	0.99992
15	0.00079	-0.00010	0.99998
20	0.00066	-0.00005	0.99999

kV	Fe L α		
	m	c	R ²
5	-0.00531	1.00025	1.00000
7	-0.00345	1.00003	1.00000
10	-0.00241	0.99991	1.00000
15	-0.00185	0.99988	1.00000
20	-0.00165	0.99988	0.99999

Linear approximation



kV	C K α		
	m	c	R ²
5	0.00351	-0.00193	0.99970
7	0.00202	-0.00081	0.99982
10	0.00121	-0.00031	0.99992
15	0.00079	-0.00010	0.99998
20	0.00066	-0.00005	0.99999



kV	Fe L α		
	m	c	R ²
5	-0.00531	1.00025	1.00000
7	-0.00345	1.00003	1.00000
10	-0.00241	0.99991	1.00000
15	-0.00185	0.99988	1.00000
20	-0.00165	0.99988	0.99999

Linear approximation

