Versatile thickness and composition metrology of graphene and other carbon based materials by SEM/EDX

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Graphene applications & demand for thickness metrology

- **Single-layer graphene (SLG) and multi-layer graphene (MLG) applications**
  - **Microelectronics:**
    - **Field-effect transistor (FET) in RF electronics**
    - **Graphene capacitor for electro-optical modulator**
    - **Infrared detector**
  - **Optical and electrical devices**
    - **Transparent conducting electrode for solar cells and LED displays**
    - **Plasmonic devices**
    - **Chemical and biosensors**
- **Both R&D and industrial manufacturing need a versatile metrology technique for SLG and MLG thickness measurements**
  - **Good throughput**
  - **Less thickness limitation**
  - **Substrate independent**
  - **Large and small lateral dimensions**

Limitations of traditional graphene-thickness metrology

- **Raman 2D band intensity and shape**
  - Applicable to less than six layers of graphene
  - Efficient on silicon substrate with thick silicon film due to optical enhancement effect. But more difficult on substrate such as metals with no optical enhancement.
  - Defect density and substrate interaction affect peak shape and intensity
- **AFM step height**
  - Not applicable to continuous films
  - Difficult for thin layer on rough substrates
  - Very slow
- **Ellipsometry**
  - Difficult on metal substrates because of variations of metal optical constants with metal grain structures
  - Correlation of thin graphene optical constants with thickness.
- **TEM**
  - Destructive
  - Time consuming

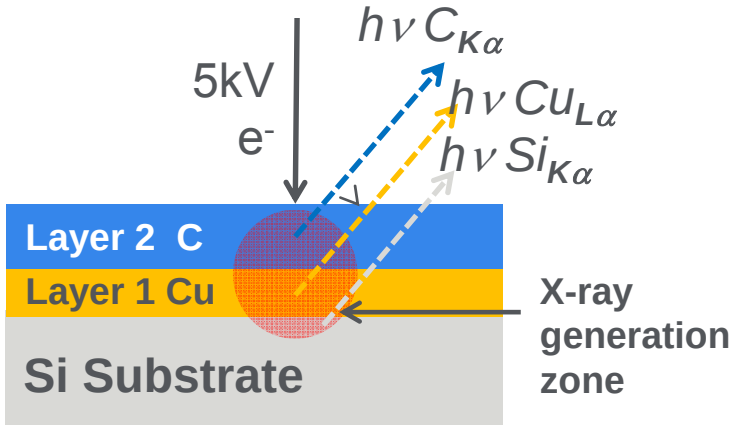
Graphene thickness metrology techniques

- **X-ray photoelectron spectroscopy (XPS)**
  - Has monolayer sensitivity
  - Limited to thicknesses below 100Å because of low electron attenuation length
  - Minimum lateral resolution is 10 to 100µm.
- **X-ray fluorescence spectroscopy (XRF)**
  - Thickness range of several Å to 3µm
  - Needs calibration, but procedure is very simple
  - Minimum lateral resolution is ~100µm
- **SEM-based energy-dispersive X-ray spectroscopy (SEM\EDX)**
  - Has monolayer sensitivity
  - Very large dynamic range for different thickness and spatial resolution; e-beam current range is 0 to 100nA (Schottky field emitter SEM); EDX detector range is 100Kcps to 1Mcps (Si drift detector).
  - Minimum lateral resolution is ~1 µm or better
  - Well developed data-reduction algorithm (ZAF and ϕ–ρ–Z)

- ***All three techniques are non-destructive***
- ***SEM\EDX is the most versatile in terms of thickness range, data reduction algorithm, lateral resolution and throughput***

Principles of SEM/EDX quantification

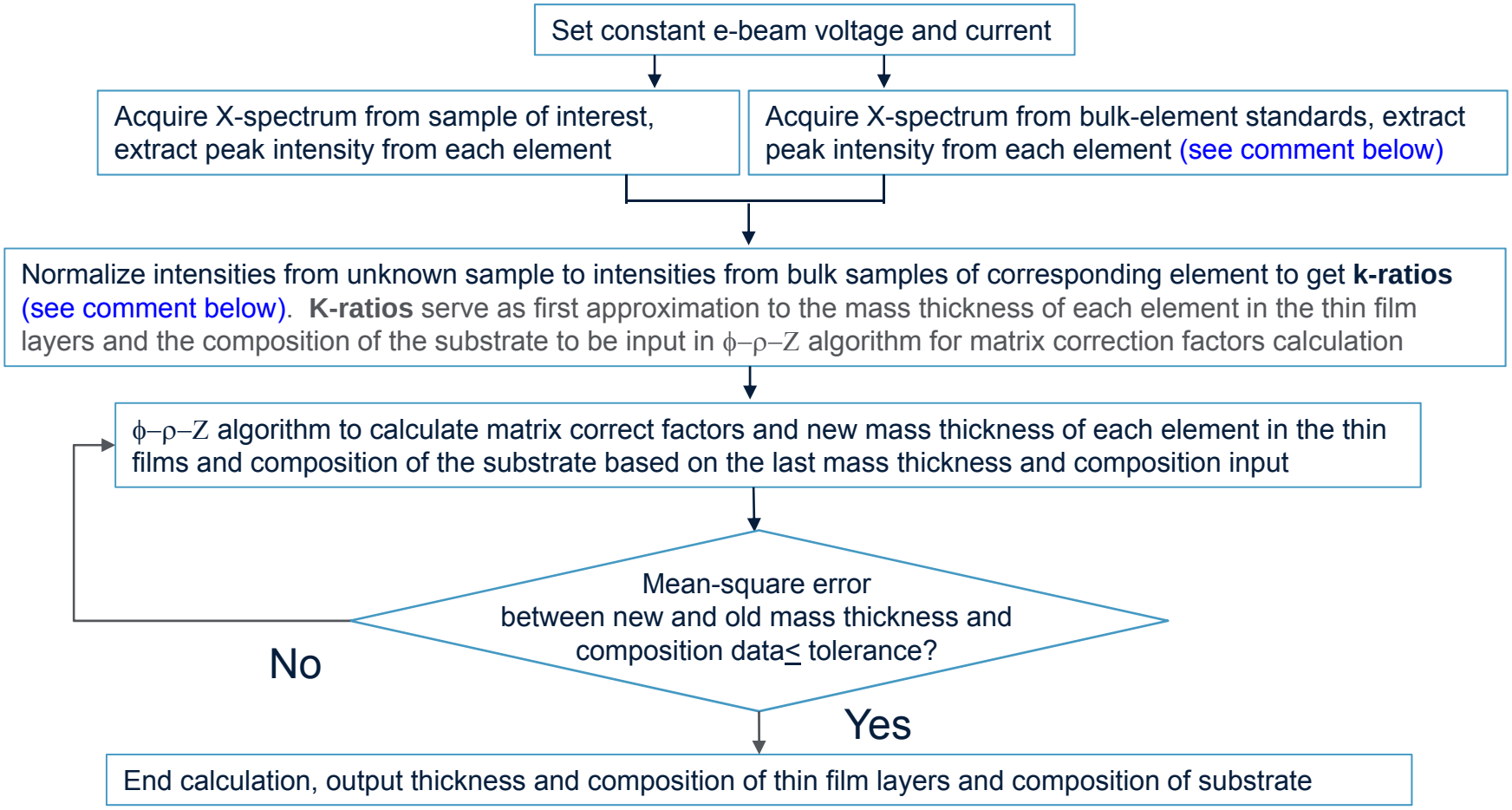
- **Assuming two-layer thin film on substrate for SEM\EDX analysis**
  - **If densities of the two layers of thin film are known, thickness and composition of each layer can be calculated from SEM\EDX spectra by proper control of the experimental environment and using proper data collection procedures and data reduction methodology**



- **X-ray production and detection are affected by the three factors Z, A and F, which are functions of the sample composition, resulting in a linear correction algorithm ZAF**
  - **Z factor (atomic number): trajectories traversed by incident electrons**
    - **Electron stopping-power correction**
    - **Backscattering-effect correction**
  - **A factor (absorption): attenuation of X-rays produced by incident electrons**
    - **Photoelectric effect**
  - **F factor (fluorescence): secondary X-rays produced by fluorescence effect**
    - **Characteristic fluorescence**
    - **Continuum fluorescence**
- **For light elements, a more sophisticated ϕ–ρ–Z algorithm is needed to model the primary X-ray generation and absorption in the sample. Composition and thickness of multi-layer thin films on a substrate can be deduced from SEM\EDX spectra.**

SEM\EDX data reduction - Recursive ZAF or ϕ-ρ-Z calculation

- **Recursive data reduction for general cases of thin films on substrate**



Comment: Most SEM\EDX systems now have a standardless method (built-in bulk element intensity references) to generate k-ratios directly from the X-ray spectrum of the sample. In such cases, the step to acquire X-ray spectrum from bulk-element standards can be eliminated, if the standardless method generated k-ratos are accurate enough.

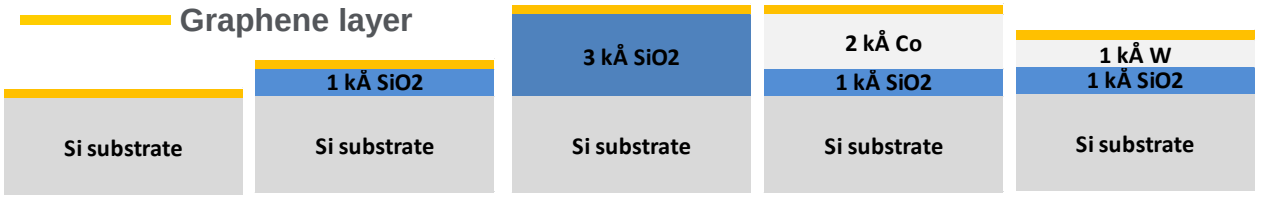
SEM\EDX data reduction – Calibration curve method

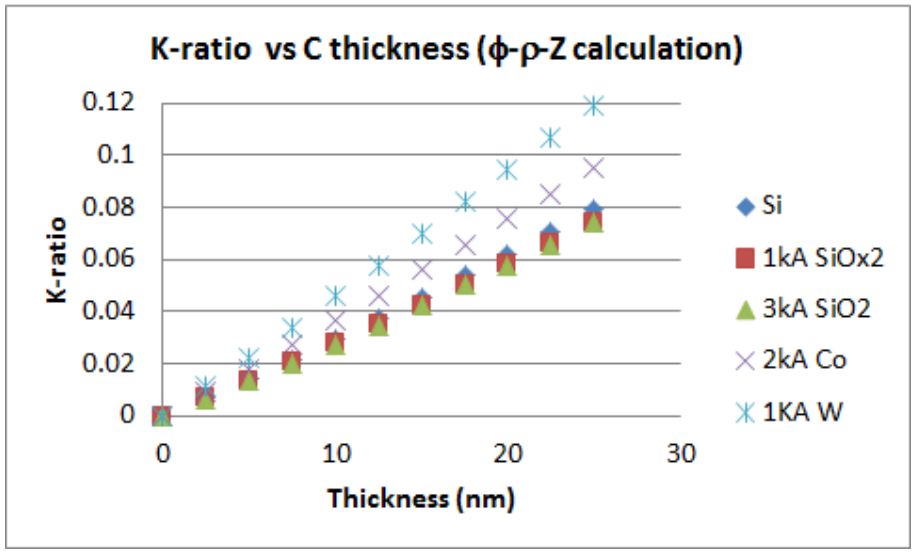
- **Problem:**
  - **In the case of thin graphene layer thickness measurements, the statistical fluctuations of the intensities from underlying thin film layers and substrate can overwhelm the small carbon intensity and lead to erroneous results, if recursive ZAF or $\phi-\rho-Z$ algorithm is used .**
- **Solution:**
  - **Simple carbon X-ray intensity versus thickness calibration curves based on $\phi-\rho-Z$ algorithm calculation can be generated directly for the purpose of measurements**

EDX acquisition conditions:

Acceleration voltage:	5 keV
X-ray take-off angle:	35°
Simulation Algorithm:	$\phi-\rho-Z$

Carbon intensity calculated for thin film systems below:





- **The calculation results showed monotonic increase of carbon signal with thickness of the film as expected.**
- **Carbon signal increases with atomic number of the underlayer due to higher backscattered electron contribution to carbon signal**
- **For simplicity, EDX standardless analysis obtained k-ratios are used. The k-ratios need adjustment to account for factory-to-field configuration variation for a particular SEM\EDX tool (see next slide for details)**

Calibration curve method – Standardless method

EDX spectrum of an ~200Å sputter-deposited (PVD) carbon film on a silicon wafer with 100nm SiO_2 is used to determine the sensitivity and K-ratio adjustment factor.

K-ratio correction factor (CF) based on data of PVD carbon (t=207 Å, ρ = 2.15 g/cm^3)*	
SEM\EDX system measured K-ratio	ϕ–ρ–Z algorithm calculated K-ratio
0.772	0.526
CF = 0.526/0.772 =	**0.681**

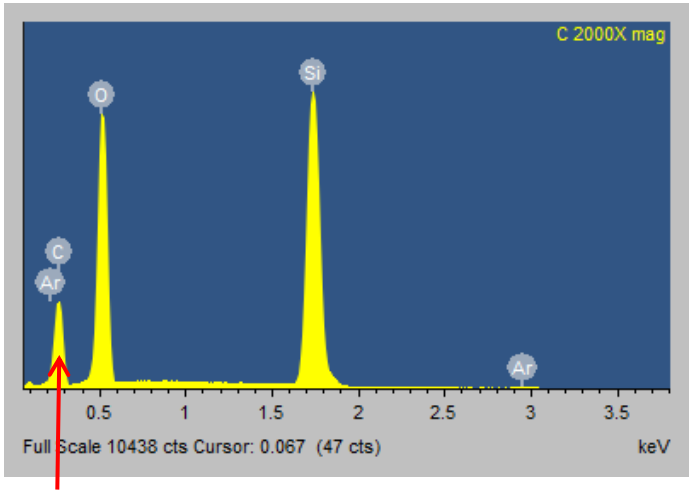
PVD carbon film reference film's density and thickness were determined by X-ray reflectivity

The intensities of SLG and MLG based on 207 Å PVD carbon X-ray intensity

# graphene layer	thicckness (nm)	K-ratio	X-ray intensity (cps)
1	0.345	0.00089	64
2	0.690	0.00179	129
3	1.035	0.00269	193
4	1.380	0.00359	258
5	1.725	0.00450	323
6	2.070	0.00541	389

Assume density of SLG and MLG is 2.15 g/cm^3 and thickness is 0.345nm x number of layers

SEM\EDX spectrum of 200Å PVD C on 100nm thermal SiO_2, e-beam conditions: 5kV, 10nA



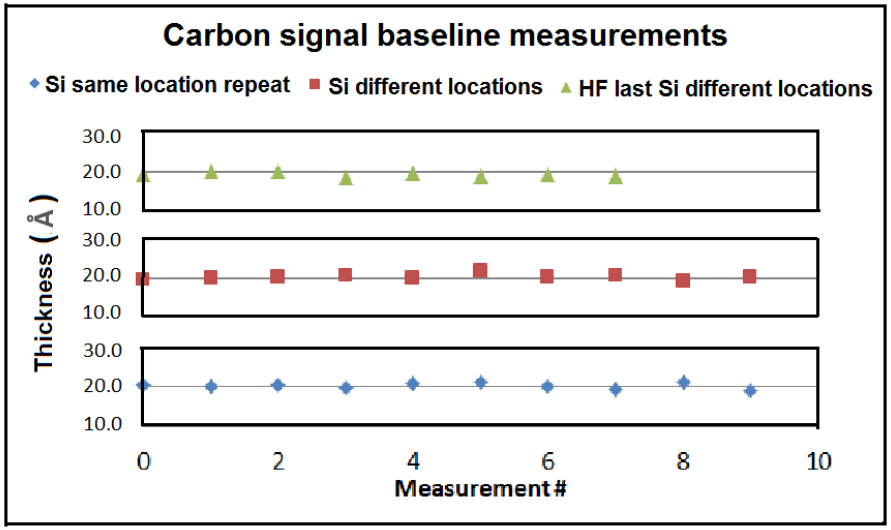
Carbon intensity is 4318 cps

- **Standardless SEM\EDX determined k-ratio is based on factory calibration, which can be affected by discrepancies between the configuration in the factory and the configuration the in actual implementation in the field.**
- **Strong SEM/EDX intensities were predicted by PVD carbon measurement.**

Technique development – Background counts determination

- **Sources of carbon background counts, which limit precision and accuracy for ultra-thin carbon measurements:**
  - **Intrinsic background including signals from bremsstrahlung**
  - **EDX detector-window material, such as carbon polymer, which was used in this study**
  - **Carbon deposition from unclean SEM vacuum, to eliminate such a problem**
    - **Magnetic levitated turbo pump and dry scroll pump are used**
    - **All-metal-parts sample holder**
  - **Sample contamination, reduction methods:**
    - **Minimize sample ambient exposure time**
    - **Clean sample handling practices**
- **The background source was studied by measuring ambient exposed bare Si and H-terminated Si (HF etched) with no oxide or carbon contamination**
  - **Measurement results are summarized in the figure and table on the right**

Conclusions: 1) no evidence of additional carbon signal after e-beam scan, 2) ambient exposed Si had 1Å more signal than cleaned Si, which can be from ambient contamination, 3) the remaining 19.3Å, should be from detector-window material.



SEM e-beam conditions: voltage - 5 kV, current - ~ 10 nA, counting time - 100 seconds, measurement area - 100 um X 100 um

	Si same location repeat	Si different locations	HF last Si different locations
Average	20.4	20.2	19.3
1σ (%)	0.7	0.8	0.6

Technique development - Analysis of measurement precision

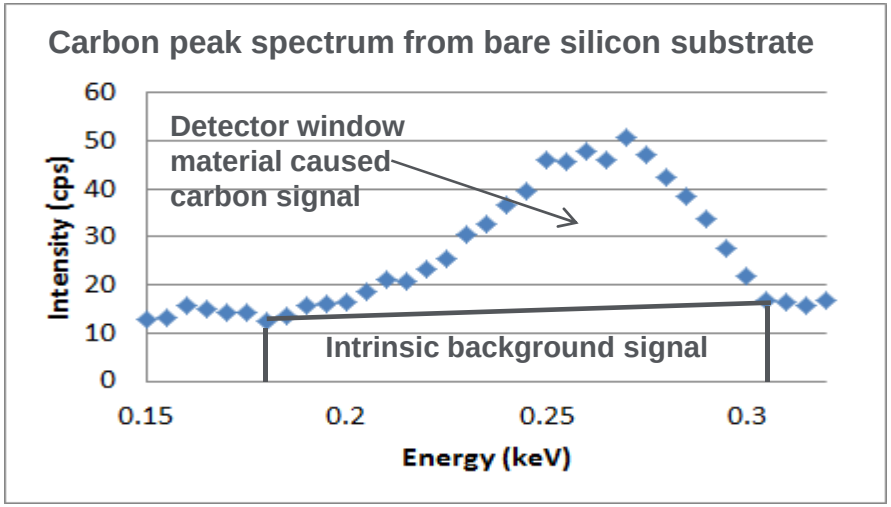
Theoretical standard deviation is based on Poisson statistics:

STDEV = $(N + B)^{1/2}$, where N & B are total photon counts from element and background

= $(n + b)*T)^{1/2}$, where n & b are count rates and T is counting time.

Relative STDEV = $(N + B)^{1/2}/N = (n + b)^{1/2}*n^{-1}*T^{-1/2}$

Here b intrinsic = 400 cps, while b detector = 390 cps
Therefore, for detector with carbon polymer window,
b total = b intrinsic + b detector = 790 cps



Case 1 - b intrinsic only

Precision of graphene thickness measurements (1σ (counts per second) vs. counting time)

Number of graphene layers	Carbon peak intensity (counts/sec)	Counting time (second)				
		1	5	10	20	50
1	64	21.5	9.6	6.8	4.8	3.0
2	129	23.0	10.3	7.3	5.1	3.3
3	193	24.4	10.9	7.7	5.4	3.4
4	258	25.7	11.5	8.1	5.7	3.6
5	323	26.9	12.0	8.5	6.0	3.8
6	389	28.1	12.6	8.9	6.3	4.0

Case 2 - b intrinsic + b detector

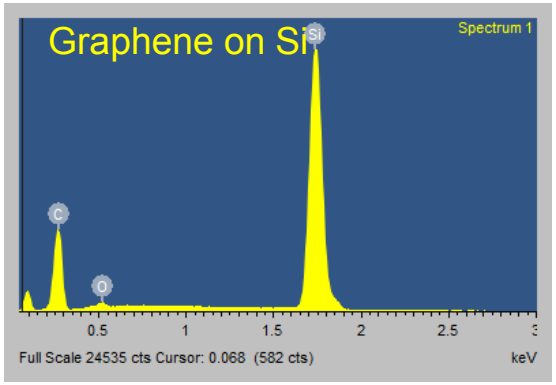
Precision of graphene thickness measurements (1σ (counts per second) vs. counting time)

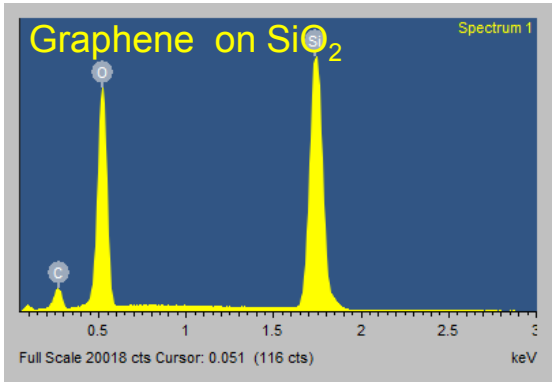
Number of graphene layers	Carbon peak intensity (counts/sec)	Counting time (second)				
		1	5	10	20	50
1	64	29.2	13.1	9.2	6.5	4.1
2	129	30.3	13.6	9.6	6.8	4.3
3	193	31.4	14.0	9.9	7.0	4.4
4	258	32.4	14.5	10.2	7.2	4.6
5	323	33.4	14.9	10.6	7.5	4.7
6	389	34.3	15.4	10.9	7.7	4.9

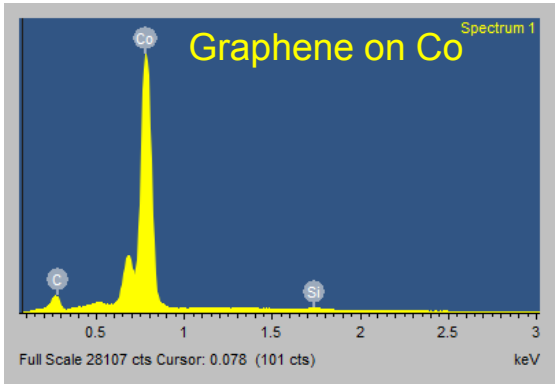
Due to the fact that graphene thickness is quantized with 1 layer thickness to be 0.345nm. In order to distinguish SLG or MLG with 1 layer thickness difference, 10 seconds counting time should be enough for case 1, while 20 seconds counting time should be good for case 2. Here deadtime (~30%) correction is not included.

Technique development – Validation by TEM cross-section

Different thickness of graphitic carbon on different substrate





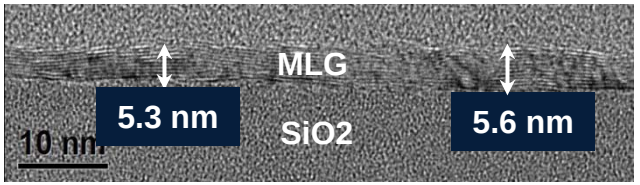


SEM/EDX results compared with TEM cross-section results

Substrate	1st point		2nd point		TEM ~ # of layers	SEM average - TEM (# of layers)
	thickness (nm)	# of graphite Layers *	thickness (nm)	# of graphite Layers*		
Si	25.12	73	26.63	77	70	5
SiO2	6.58	19	6.74	20	15	5
Co	4.67	14	4.39	13	7	7

# of graphite layers was obtained by dividing thickness by 0.345 nm, which is the single layer graphene thickness

TEM section image of MLG on oxide



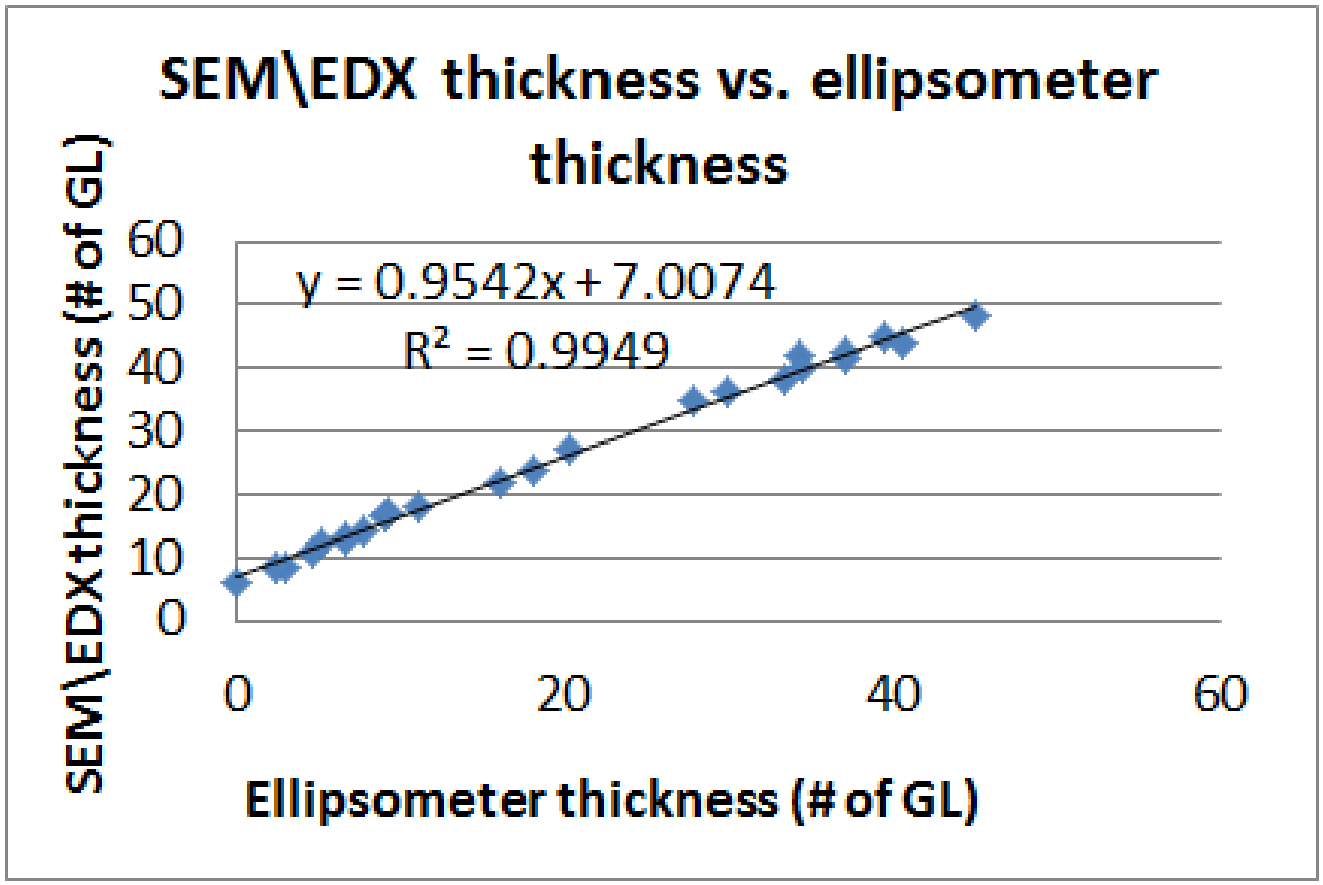
Only count crystalline material thickness

Except for a constant offset, SEM\EDX results are proportional to TEM results.

- **The offset is mainly caused by the carbon signal generated by radiations hitting the polymer window used for protecting the EDX detector**
- **Small portion of the discrepancy can be caused by the different sampling area between the two techniques; in the case of TEM ~100nm, while in the case of SEM\EDX, about several µm.**

Technique development – Validation by ellipsometry

Correlation of SEM\EDX data with ellipsometer data from MLG on 3 kÅ SiO2

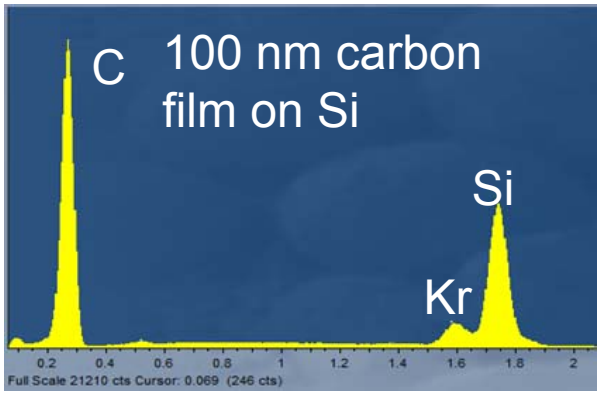


Thickness in # of GLs	
Ellipsometer	SEM\EDX
0	6
2	8
3	9
5	11
5	12
7	13
7	13
8	14
9	17
9	17
11	18
16	22
18	24
20	27
28	35
30	36
33	38
34	42
34	40
37	42
37	42
39	45
41	44
45	48

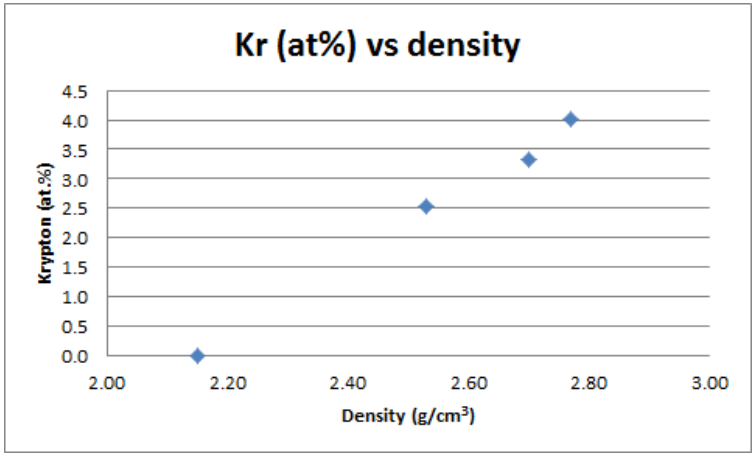
Other than the offset of 7 layer, which is mainly caused by background signal generated by the EDX detector, the correlation between SEM\EDX results and ellipsometer result is very good. The sub-unity slope (0.95) may be attributable to contributions from the surface and\or interface layer to the ellipsometer data.

EDX composition analysis - Sputter gas entrapment study

Effect of inert gas (krypton) entrapment on sputter deposited carbon film



Kr detected in EDX spectra of carbon deposited using Kr gas



Density increase with Kr concentration in carbon film

Calculate true carbon contribution to density

Kr (at%)	Kr (wt.%)	Carbon density measured	Kr contribution to density	Carbon contribution to density
0.0	0	2.15	0	2.15
2.5	16.2	2.53	0.41	2.12
3.3	19.7	2.70	0.53	2.17
4.0	23.3	2.77	0.65	2.12

- **SEM\EDX can provide quick composition analysis**
- **Krypton entrapment can increase the density reading of carbon film but not truly increase the carbon density. The benefit of high-density carbon cannot be realized.**

Conclusions

- SEM\EDX thickness metrology has been demonstrated for graphene and carbon thin film thickness determination. Simplicity in data reduction and thickness calculation are realized.
- Good throughput was demonstrated
- This technique can be applied to any substrates or underlying thin film layers with no EDX peaks that overlap with the carbon peak.
- The method was validated by comparison of its results with TEM results for different substrates and with ellipsometer results for silicon substrate covered with 3kÅ silicon oxide.
- The carbon polymer EDX detector window causes a constant offset of 6 equivalent layers of SLG that needs to be subtracted from the measured thickness. A window material with no carbon element will not have such a problem.
- The method is accurate to within approximately one graphene monolayer. There is some uncertainty from sample contamination by ambient carbonaceous materials. Sample cleanliness and avoidance of SEM chamber carbon background are very important to yield accurate data.
- Versatility of SEM\EDX for composition measurements was also demonstrated by krypton entrapment study of sputter-deposited carbon.

make possible