Carbon-Based Thin Films
for Fuel Cells and Batteries

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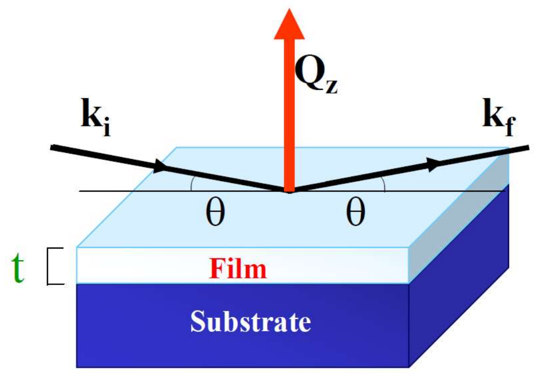
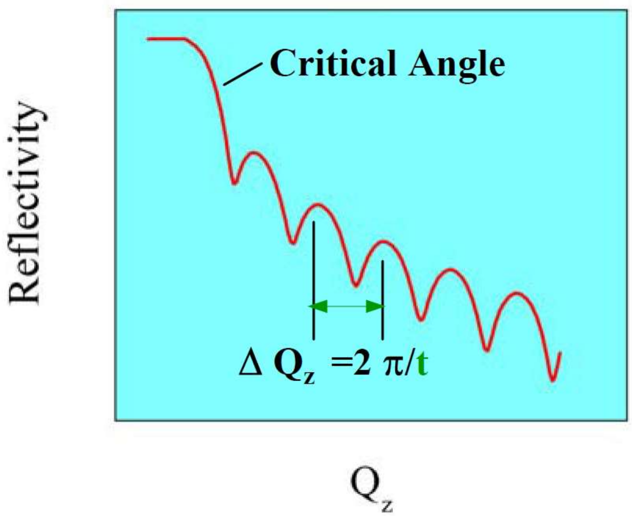
Carbon Film Background

- Nafion has shown lamellar structures when grown on SiO_2, but not when grown on Au or Pt
- In Hydrogen Fuel Cell PEMs, Nafion grows on Carbon-black, which is too rough for reflectometry
- This is a preliminary study to see if we can recreate thin carbon layers smooth enough to grow Nafion with the observable lamellar structures

Specular X-Ray Reflectometry (XRR)





- Specular XRR measures Reflected Intensity vs. grazing angle θ or Q_z with $\theta_i=\theta_f$

$$Q_z=4\pi \sin \Theta / \lambda$$

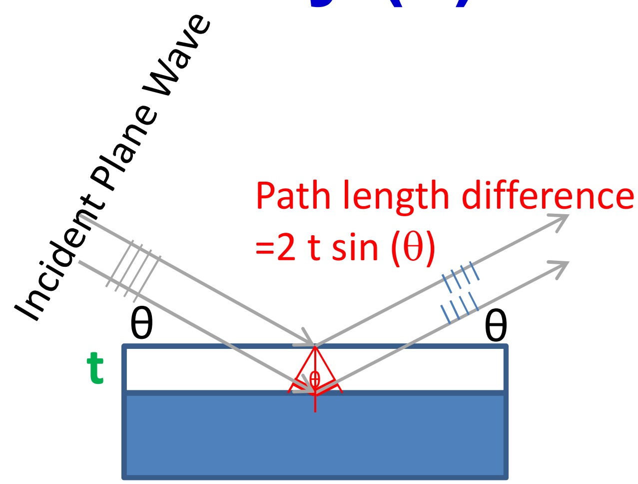
- XRR Provides Depth Profile of the SLD
- SLD is related to Composition, and is proportional to the scattering lengths of the elements Z (i)

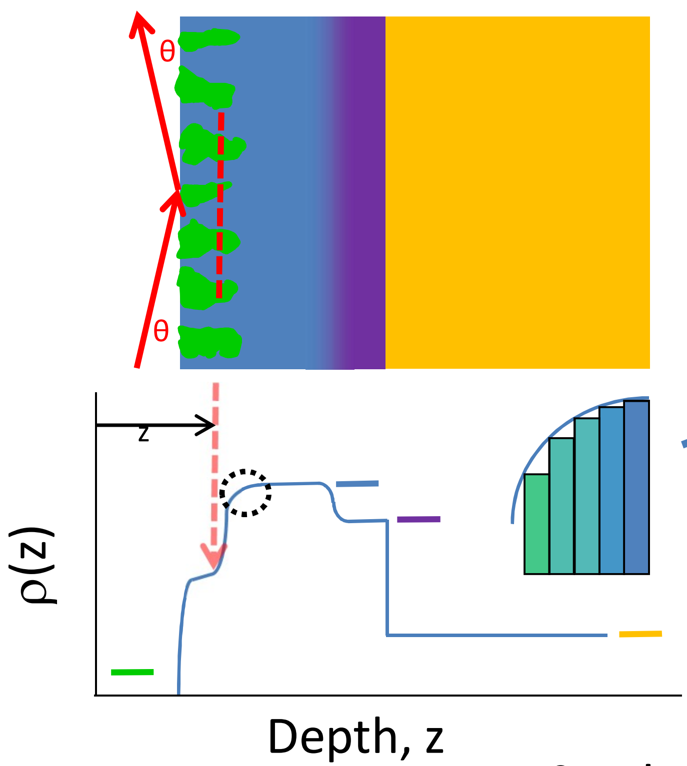
$$SLD(x) = \Sigma_i Z(i)\, n_i(x)$$

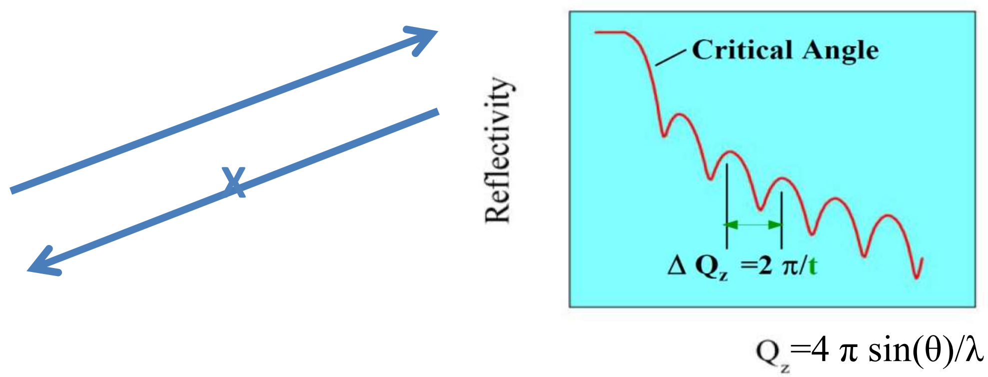
- Averages SLD in the plane perpendicular to x
- Critical Edge due to total external reflection
- Oscillations with period 2π / layer thickness
- Additional layers cause additional beating patterns

Specular X-Ray Reflectometry (2)

- One can calculate the reflectivity from the SLD, but not invert the reflectivity since phase information is not measured
- Therefore we must fit the data to models

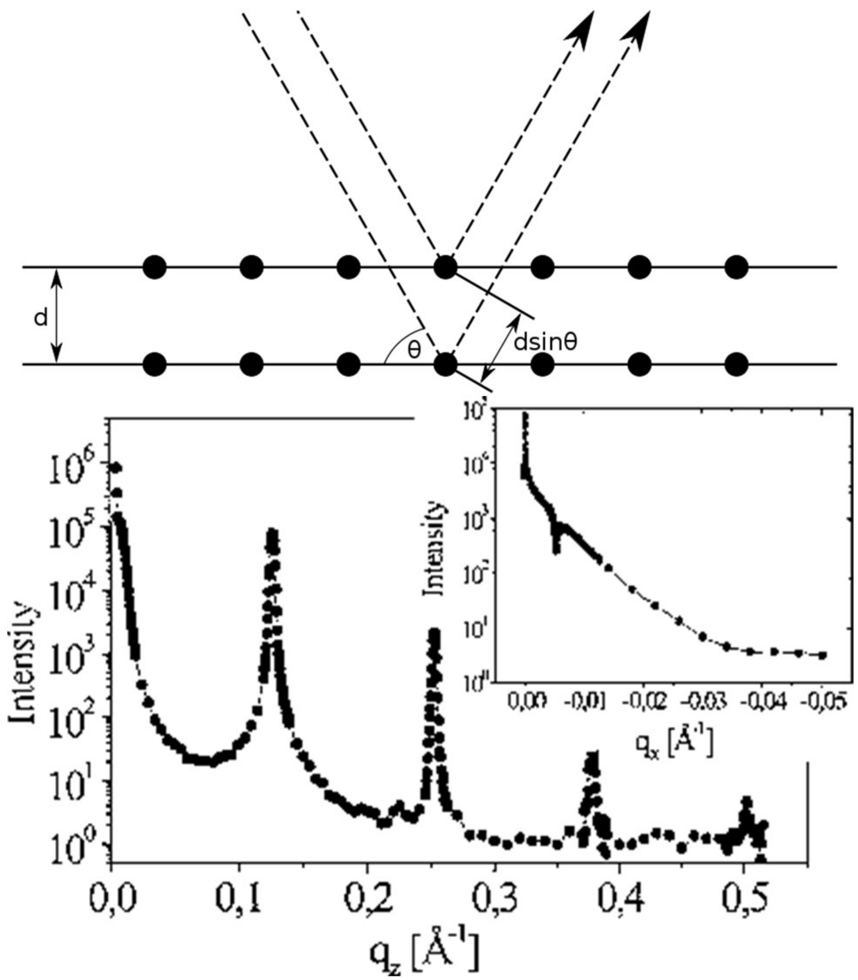






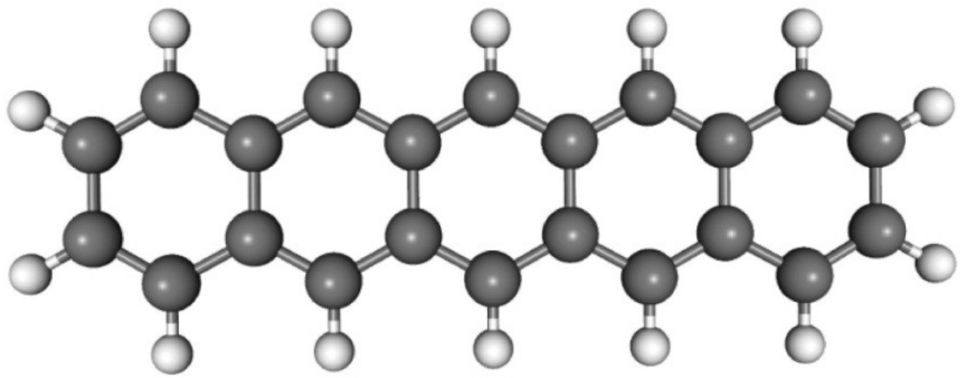
- Specular X-Ray Averages the SLD of materials in the plane
- Gradients can be approximated by a set of uniform slabs
- Can determine the ratio of two known components

Bragg Diffraction

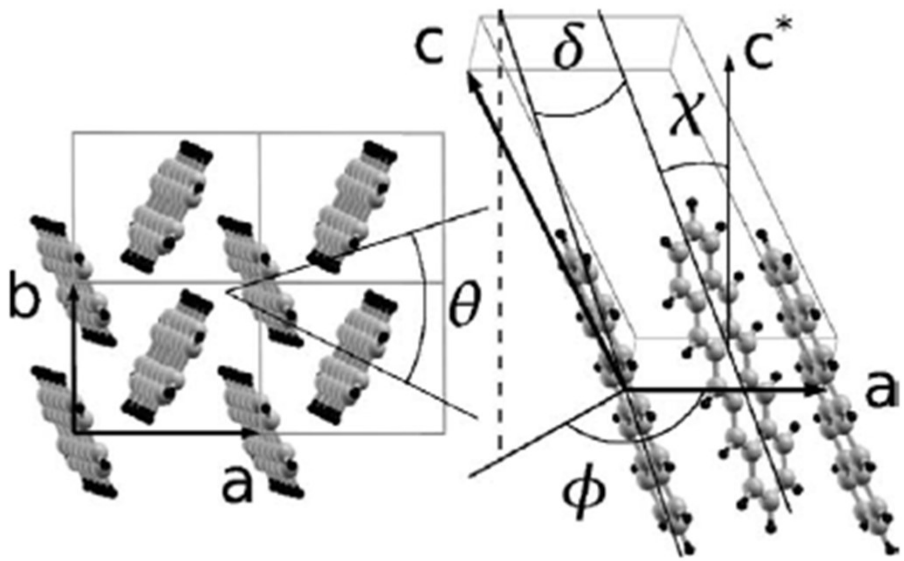


- Materials with crystalline structure will show diffraction patterns when reflecting X-rays
- Because crystal spacings are smaller than thin film thicknesses, the peaks that result are sharper and more spread than those encountered with thin film layer reflectivity

Pentacene Structure



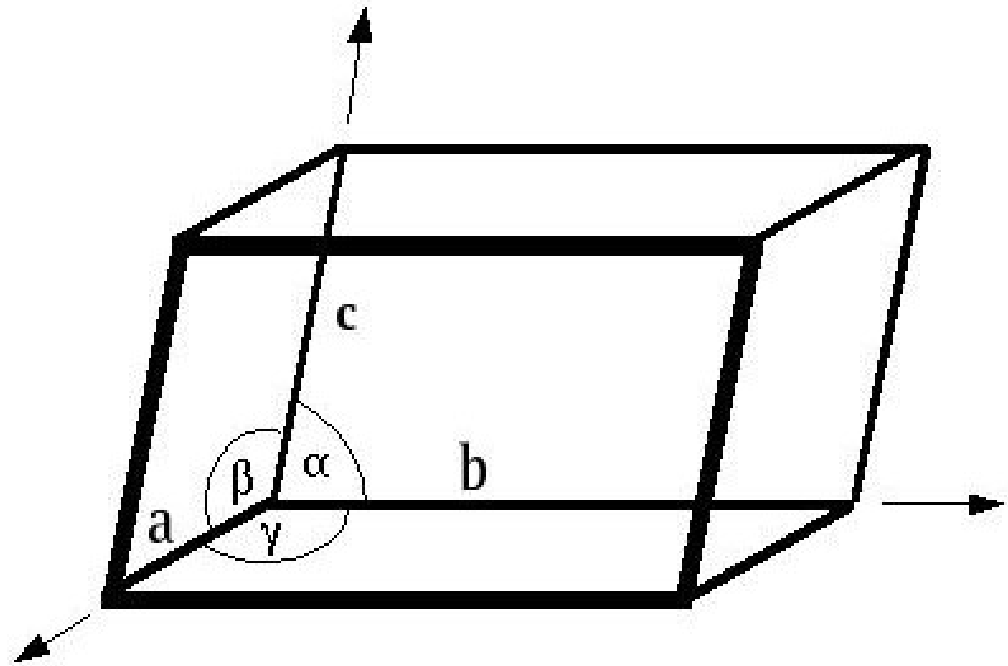
- $C_{22}H_{14}$
- Triclinic Structure
- Characteristic herringbone layout



Pentacene Film Preparation

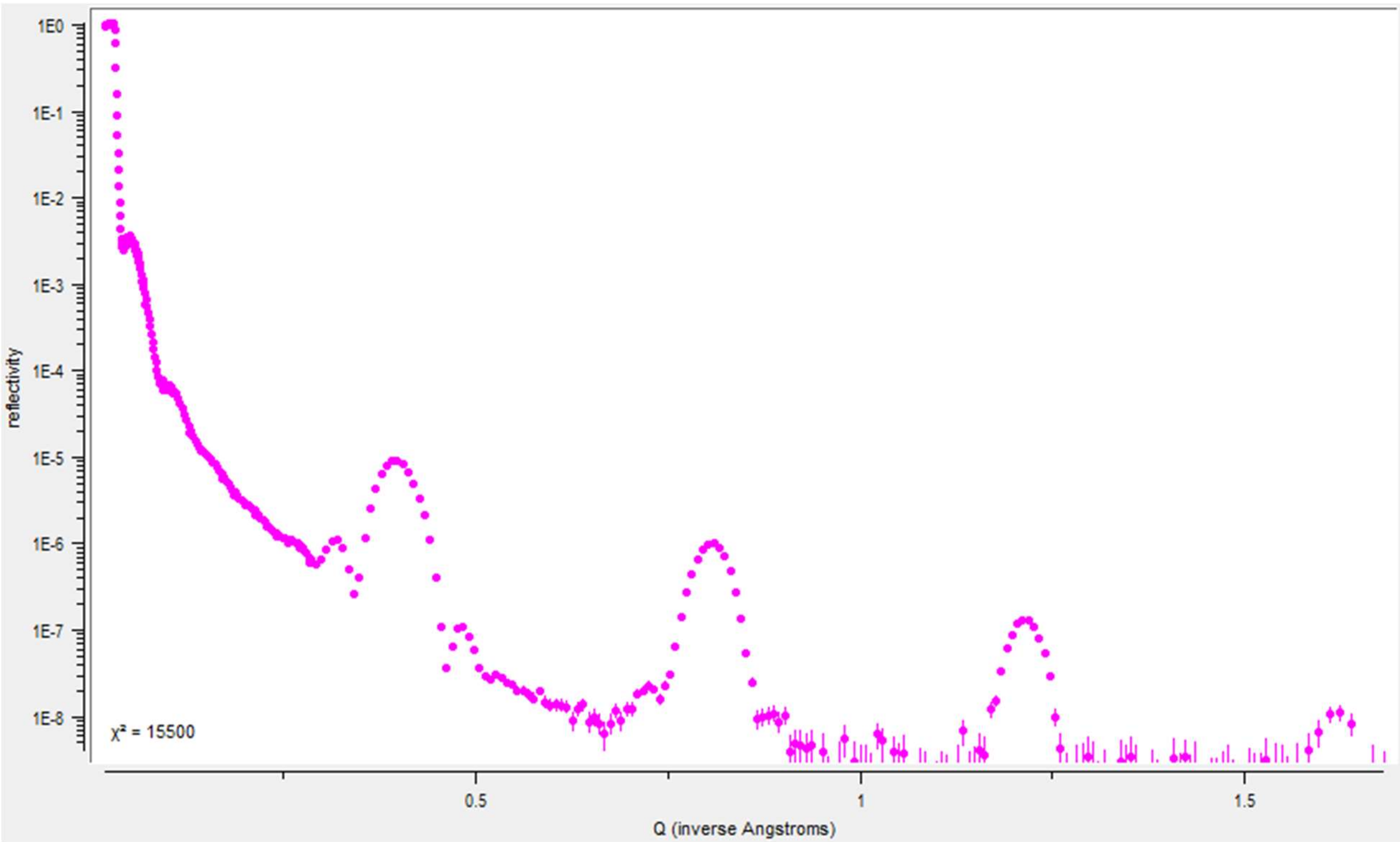
- Thermal evaporation in a vacuum of 2e-7 torr
- Deposition rate was 0.1 Å/sec
- Substrate was kept at room temperature
- Expected thickness was ≈100Å
- Thanks to Kurt Pernstich and David Gundlach at PML for sample preparation

Thin Film and Bulk Crystal Dimensions

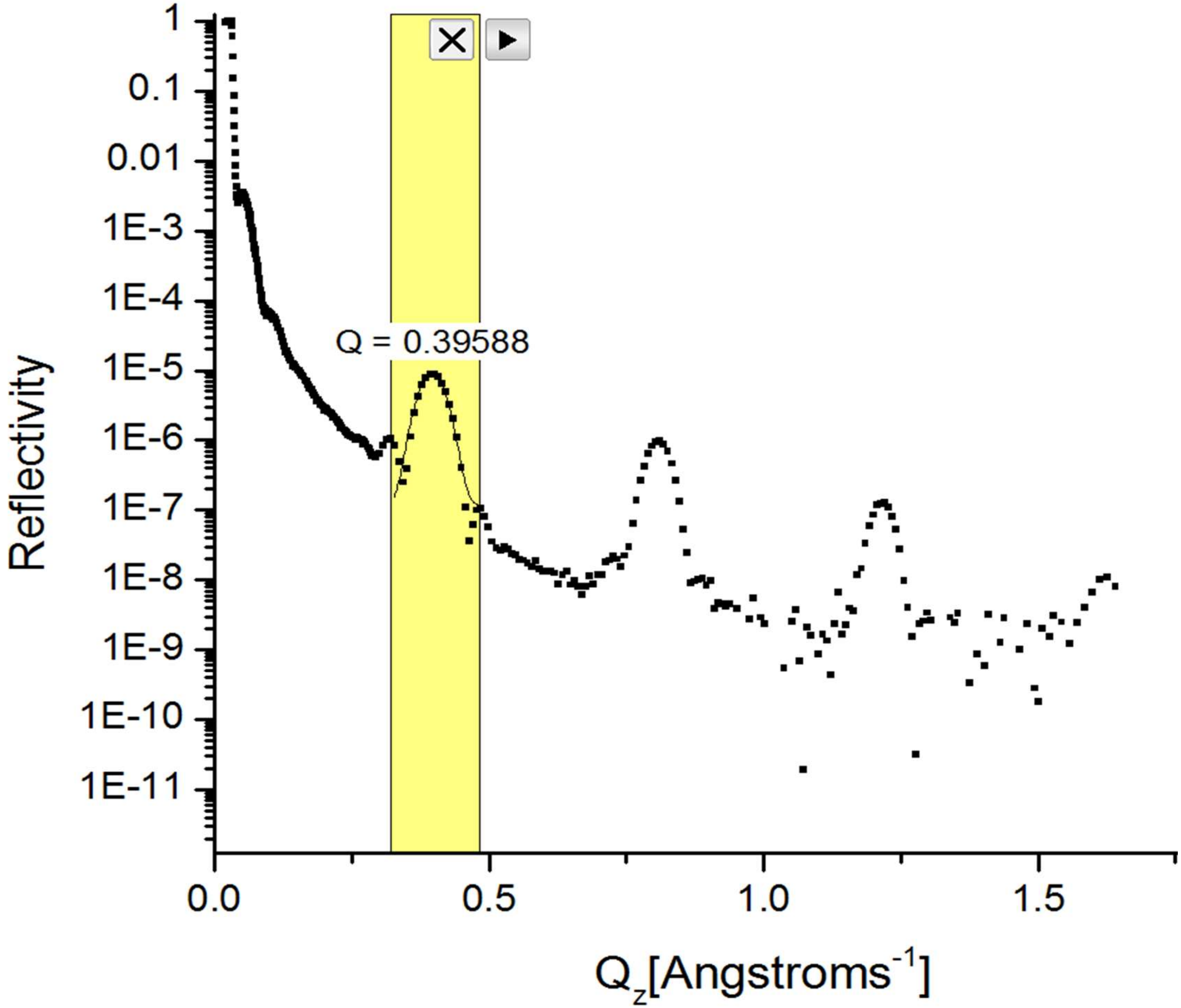


Thin Film Studies	a (nm)	b (nm)	c (nm)	α (deg)	β (deg)	γ (deg)	V (nm^3)	Film Thickness (nm)	d_{001} spacing (nm)
Nabok et al.	0.592	0.754	1.563	81.5	87.2	89.9	0.689	180	1.544
Yoshida et al.	0.593	0.756	1.565	98.6	93.3	89.8	0.693	120	
Schiefer et al.	0.5958	0.7596	1.561	81.25	86.56	89.80	0.697	Not reported	
Bulk (Campbell, 1961)	0.606	0.790	1.601	81.6	77.2	85.8	0.692		1.450

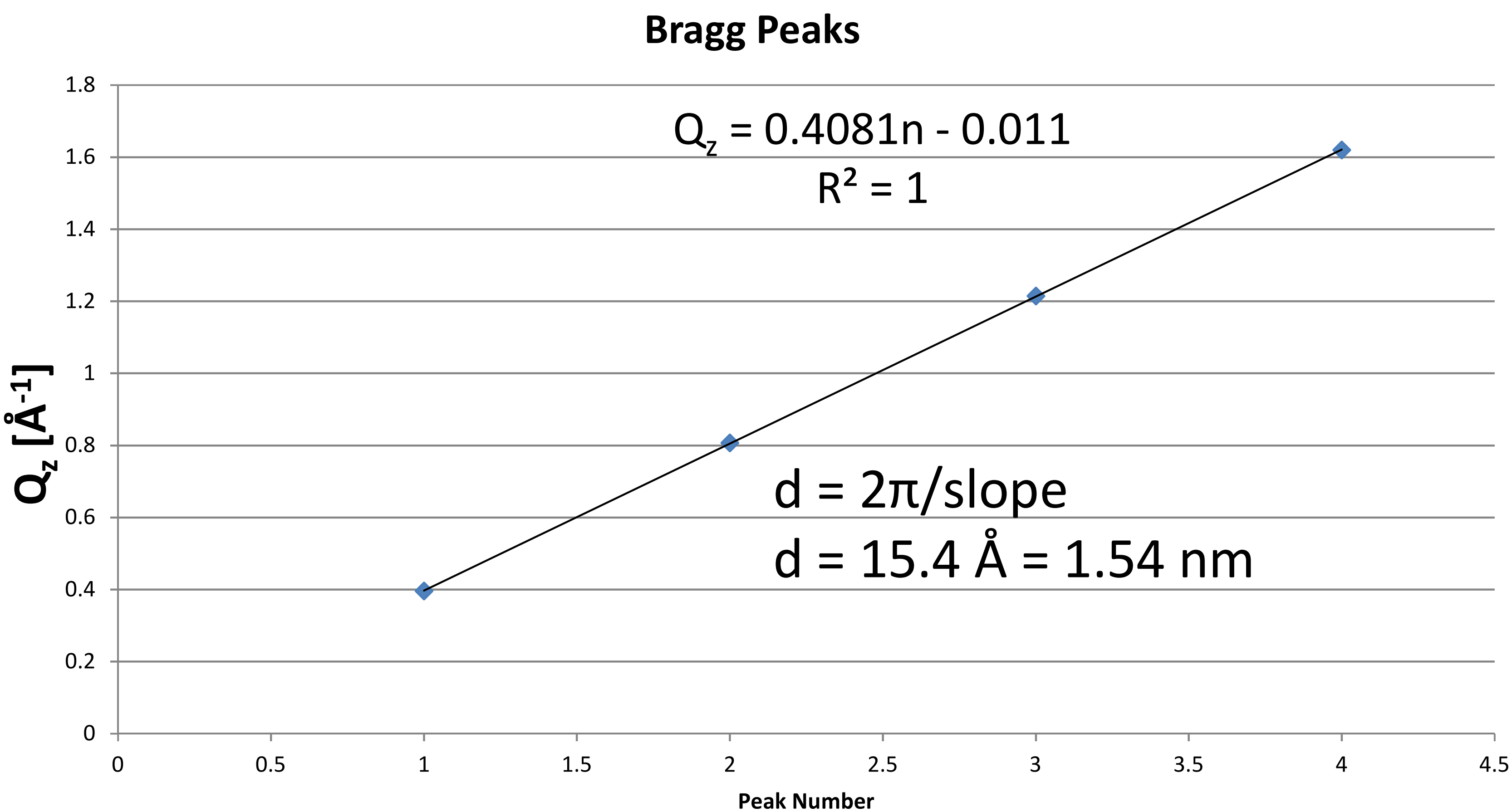
Pentacene Reflectivity



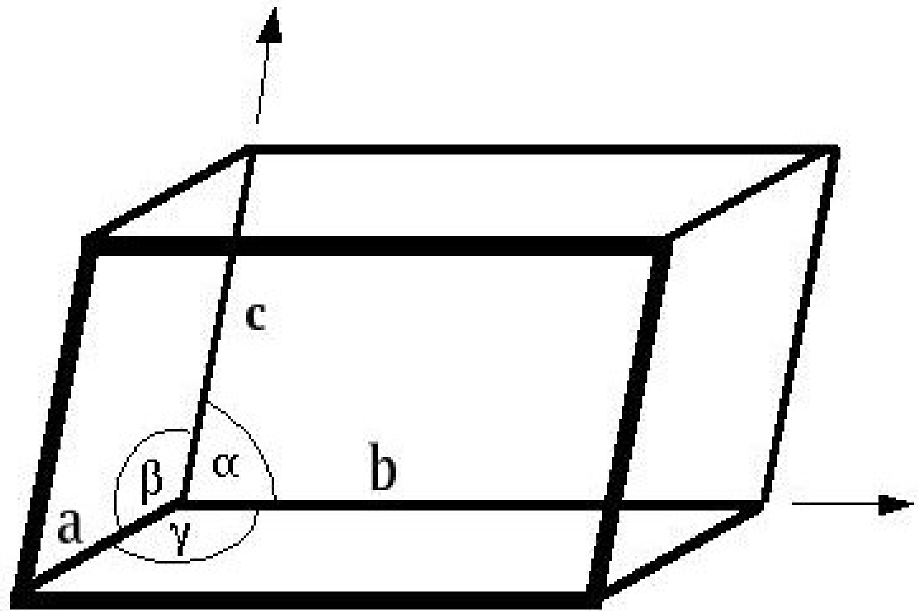
Diffraction Peaks



d_{001} Planar Spacing

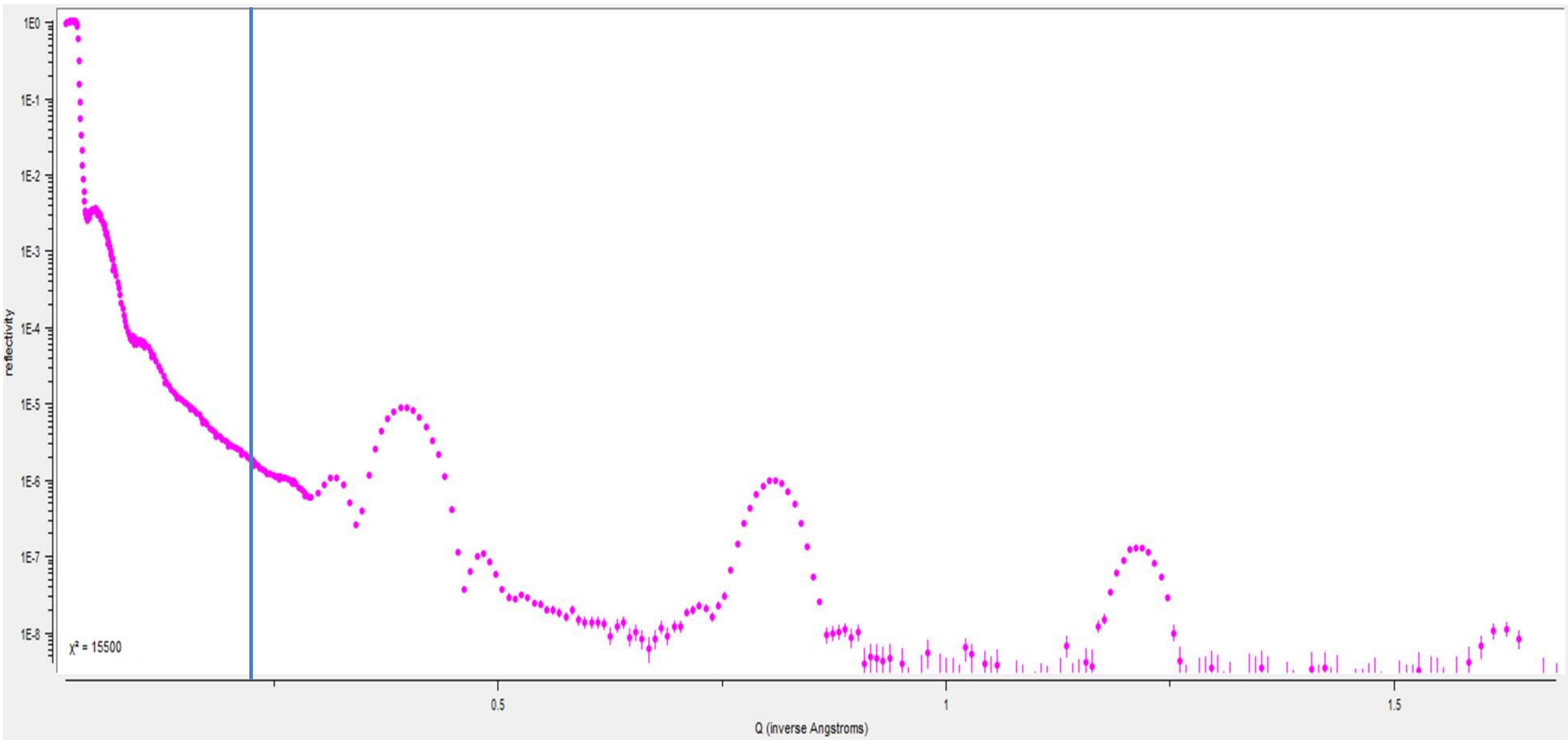


Thin Film and Bulk Crystal Dimensions

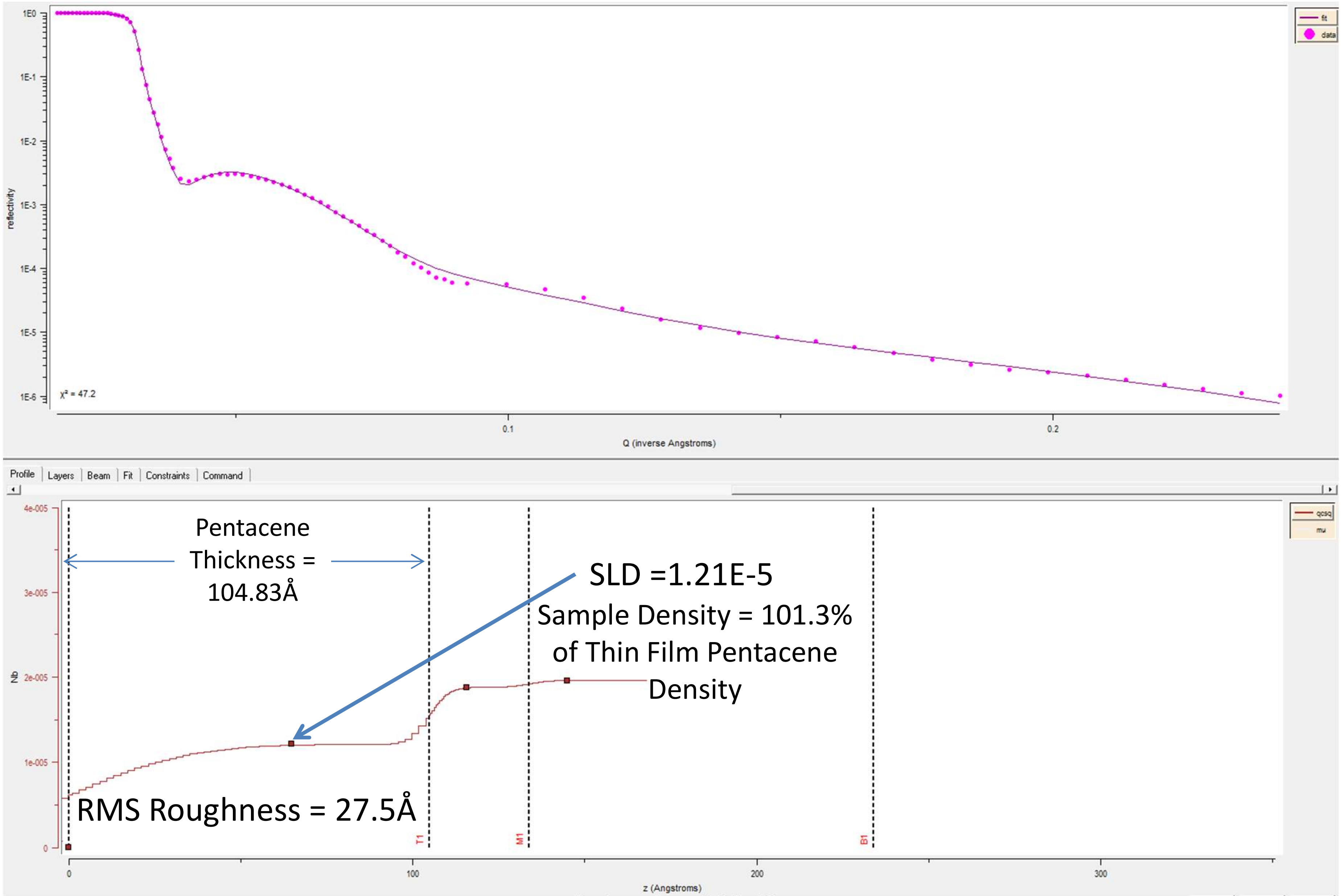


Thin Film Phase	a (nm)	b (nm)	c (nm)	α (deg)	β (deg)	γ (deg)	V (nm^3)	Film Thickness (nm)	d_{001} spacing (nm)	Our d_{001} Spacing (nm)
Nabok et al.	0.592	0.754	1.563	81.5	87.2	89.9	0.689	180	1.544	1.54
Yoshida et al.	0.593	0.756	1.565	98.6	93.3	89.8	0.693	120		
Schiefer et al.	0.5958	0.7596	1.561	81.25	86.56	89.80	0.697	Not reported		
Bulk	0.606	0.790	1.601	81.6	77.2	85.8	0.692		1.450	

Pentacene: Low Angle Reflectometry



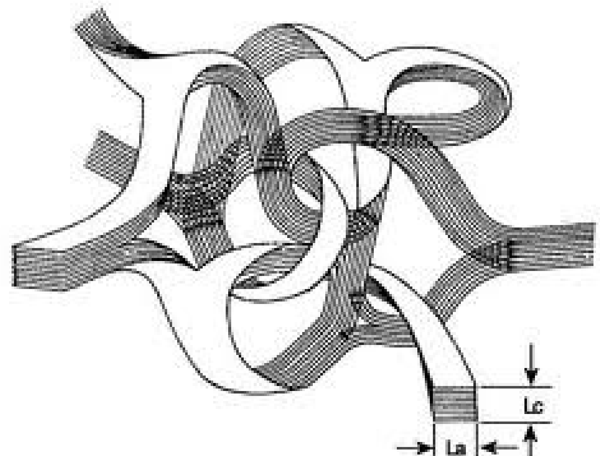
Pentacene Properties Determined by Reflectometry

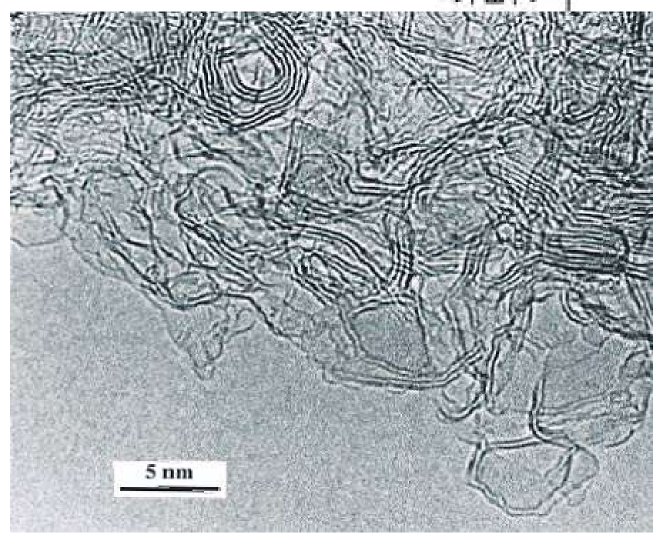


Pentacene Conclusions: Preparing Samples

- Our study indicates that this sample does not have adequate smoothness
- Perhaps another sample preparation technique or the manipulation of preparation parameters would improve smoothness

Glassy Carbon (GC)



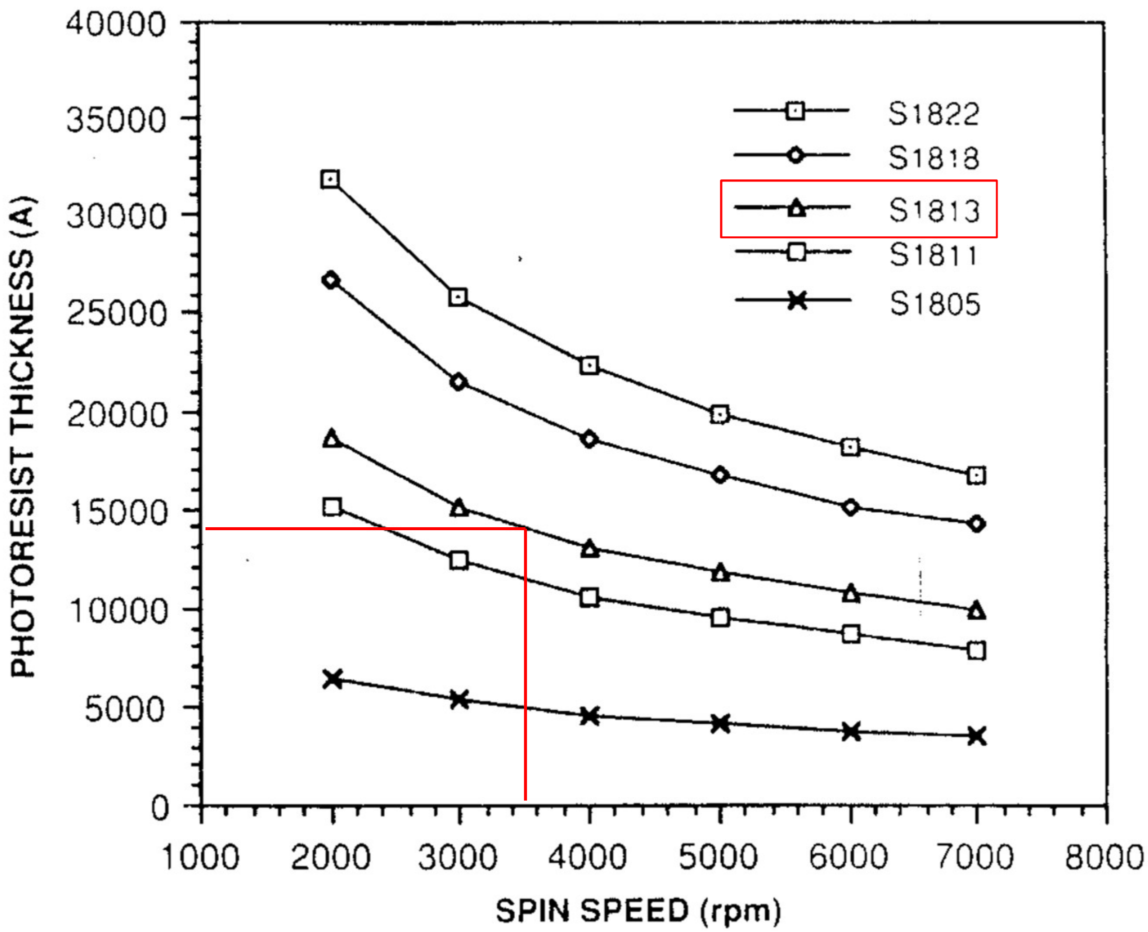


- Comprised of graphite sheets wrapped and twisted (specific structure is highly dependent on precursor)
- Density is 60% of monocrystalline graphite, suggesting high porosity
- However, GC is highly inert, making it ideal for chemical utensils, emission electronics elements, and prosthetic devices

Glassy Carbon Film Preparation

- Mix 7 different concentrations of S1813 Photoresist diluted in PGMEA
- Spin Coat all plates at 3500 rpm for 45sec
- Use Ellipsometry to measure film thicknesses pre-pyrolyzation
- Pyrolyze all samples in forming gas (800^{o}C)
  (thank you to Jerry Bowser and Marc Cangemi at CNST)
- Analyze all samples using X-ray Reflectometry

Preparing GC Samples: Spin Coating

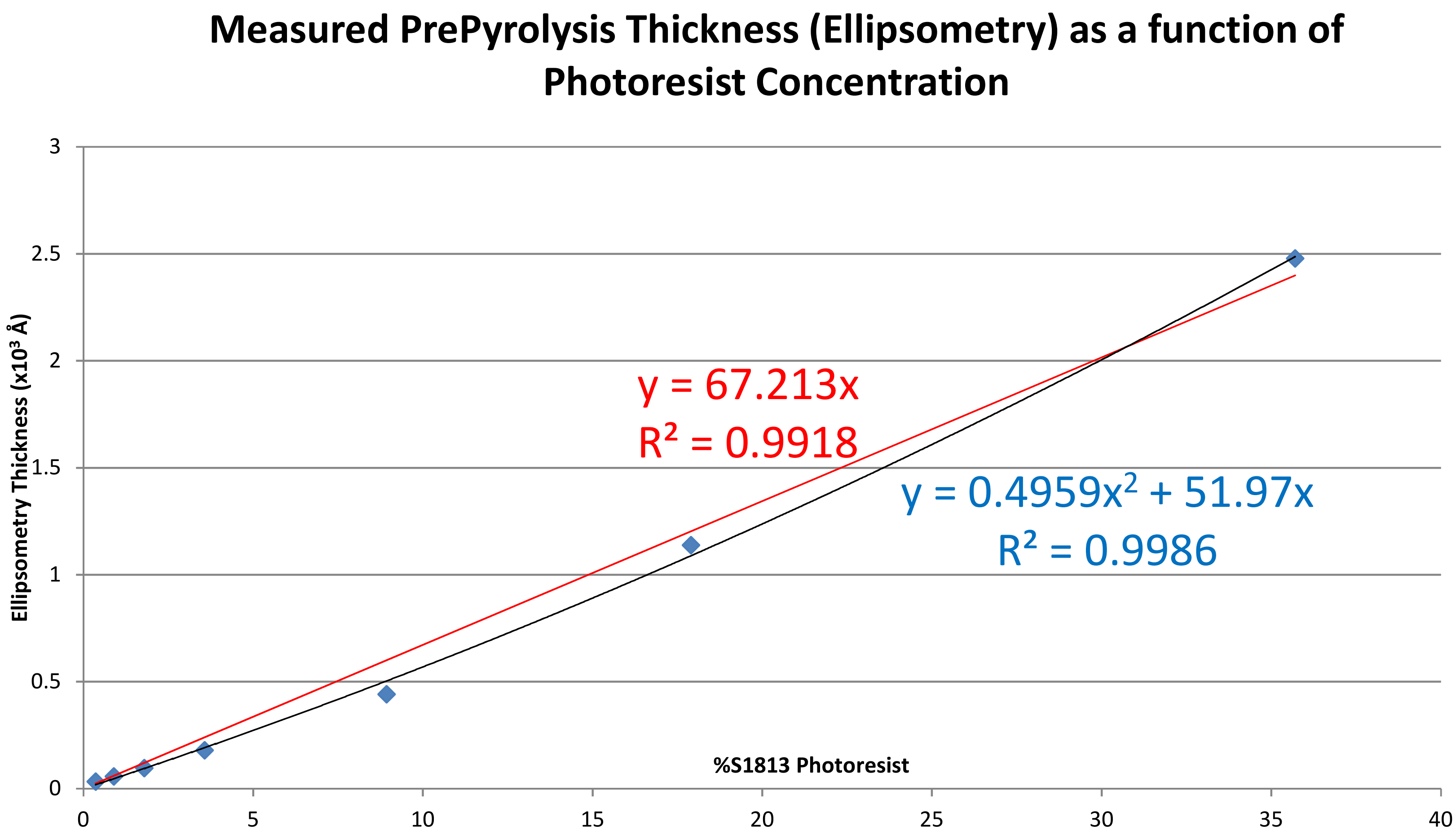


http://www.nanophys.kth.se/nanophys/facilities/nfl/resists/S1813/s1800seriesDataSheet.pdf

Photoresist Dilutions

10 mL of 35.71% S1813 = 3.57 mL S1813 + 6.43 mL PGMEA					
Sample #	Desired Final Thickness	Desired Prepyrolysis Thickness (Å)	%S1813	Vol 36% S1813 (mL)	Vol PGMEA (mL)
1	1000	5000	35.7	3	0
2	500	2500	17.9	1.5	1.5
3	250	1250	8.93	2	6
Sample #	Desired Final Thickness	Desired Prepyrolysis Thickness (Å)	%S1813	Vol 8.9% S1813 (mL)	Vol PGMEA (mL)
4	100	500	3.57	1	1.5
5	50	250	1.79	0.5	2
6	25	125	0.893	0.3	2.7
7	10	50	0.357	0.1	2.4

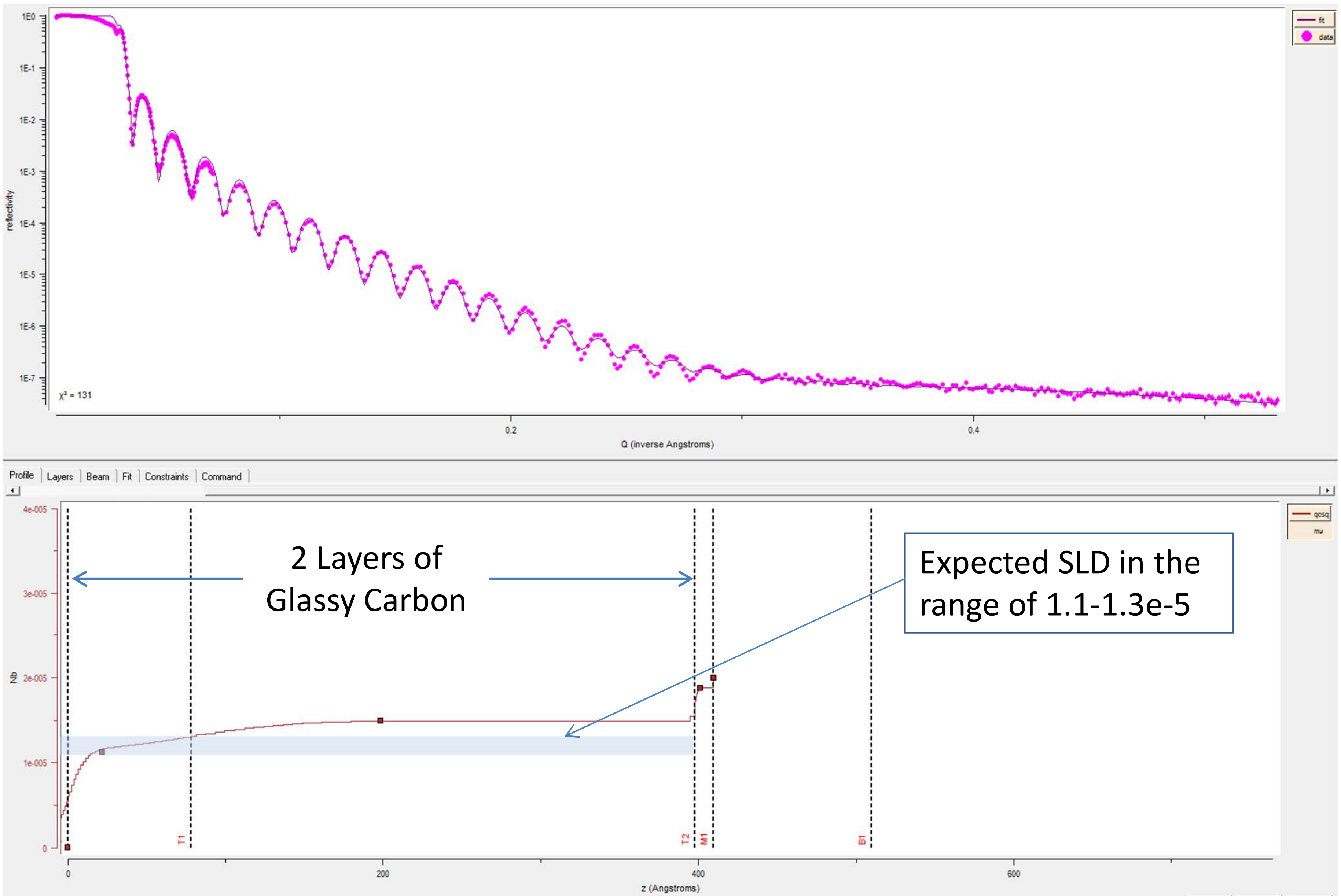
Pre-Pyrolyzation Ellipsometry Thickness



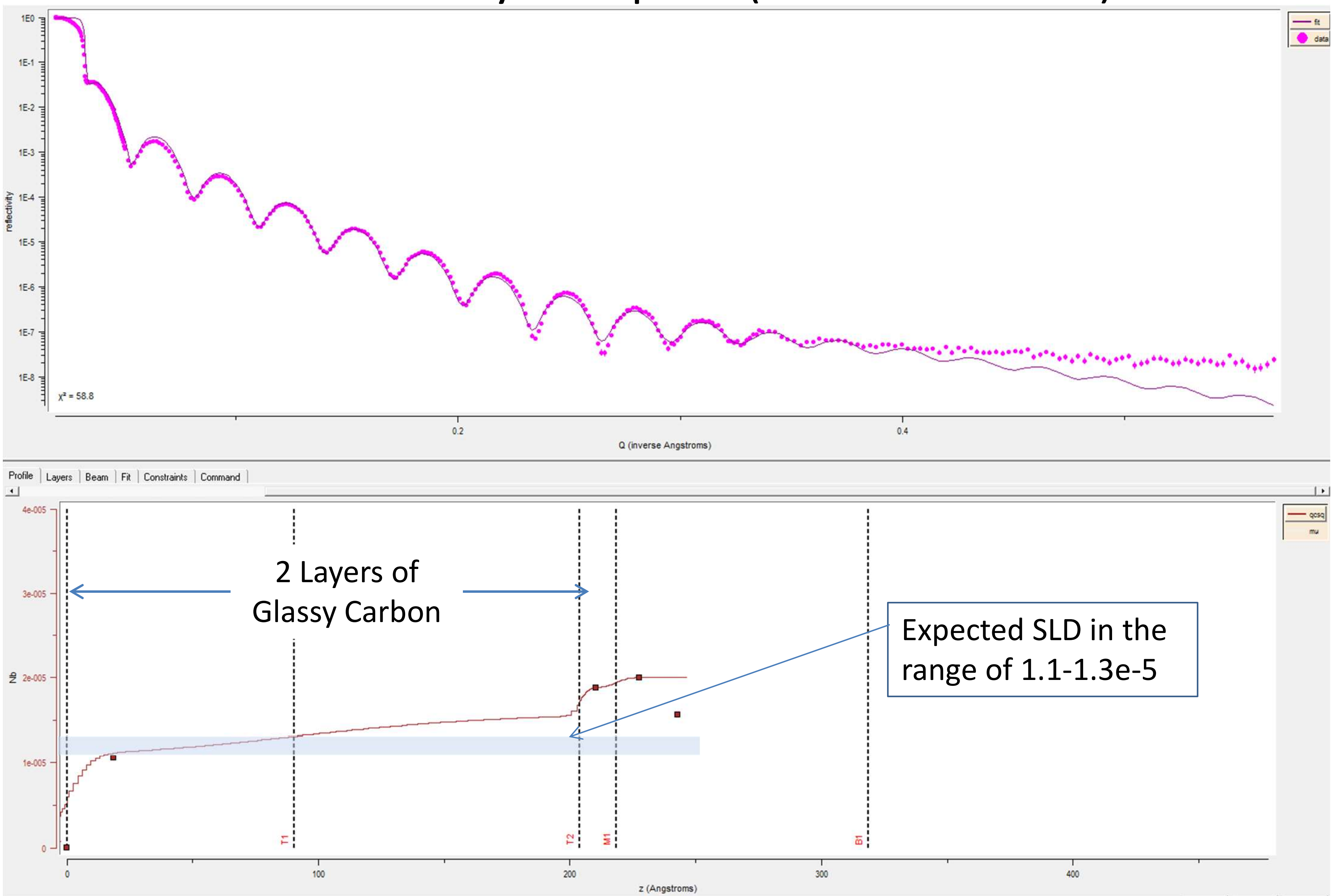
Ellipsometry Check on Spin Coating

Sample #	**%S1813**	**Desired Prepyrolysis Thickness (Å)**	**Measured PrePyrolysis Thickness (Ellipsometry)**
1	35.7	5000	2479
2	17.9	2500	1138
3	8.93	1250	442
4	3.57	500	179
5	1.79	250	96.9
6	0.893	125	56.9
7	0.357	50	33.5

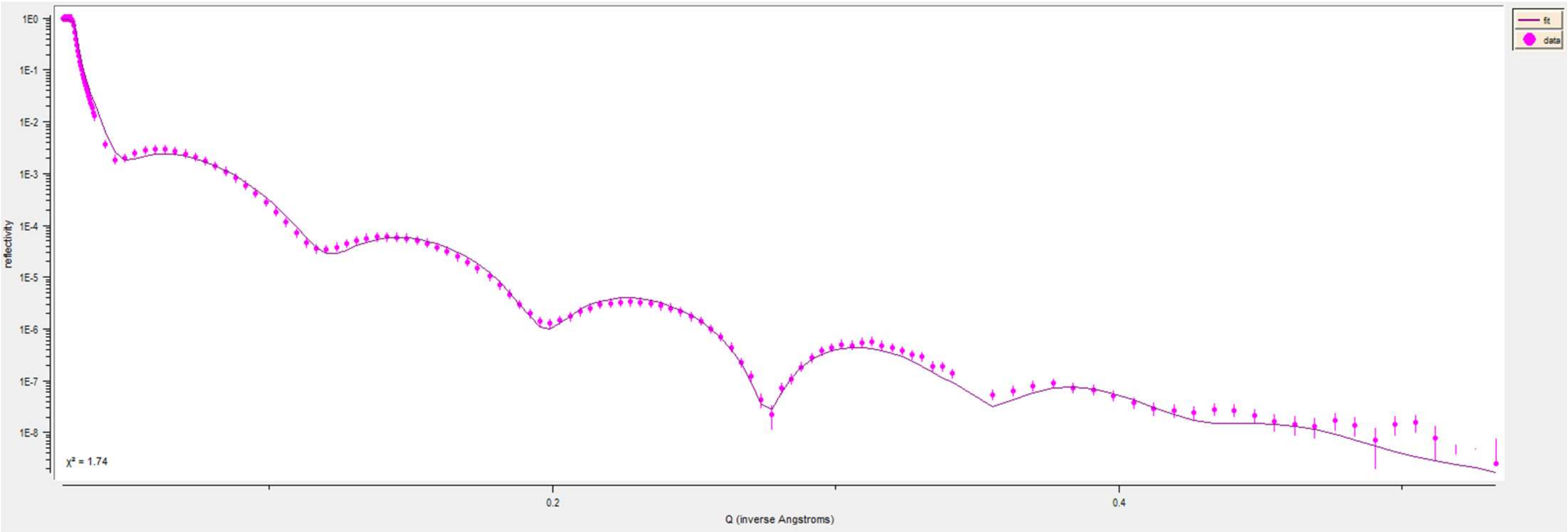
Reflectometry: Sample 1 (36% Photoresist)

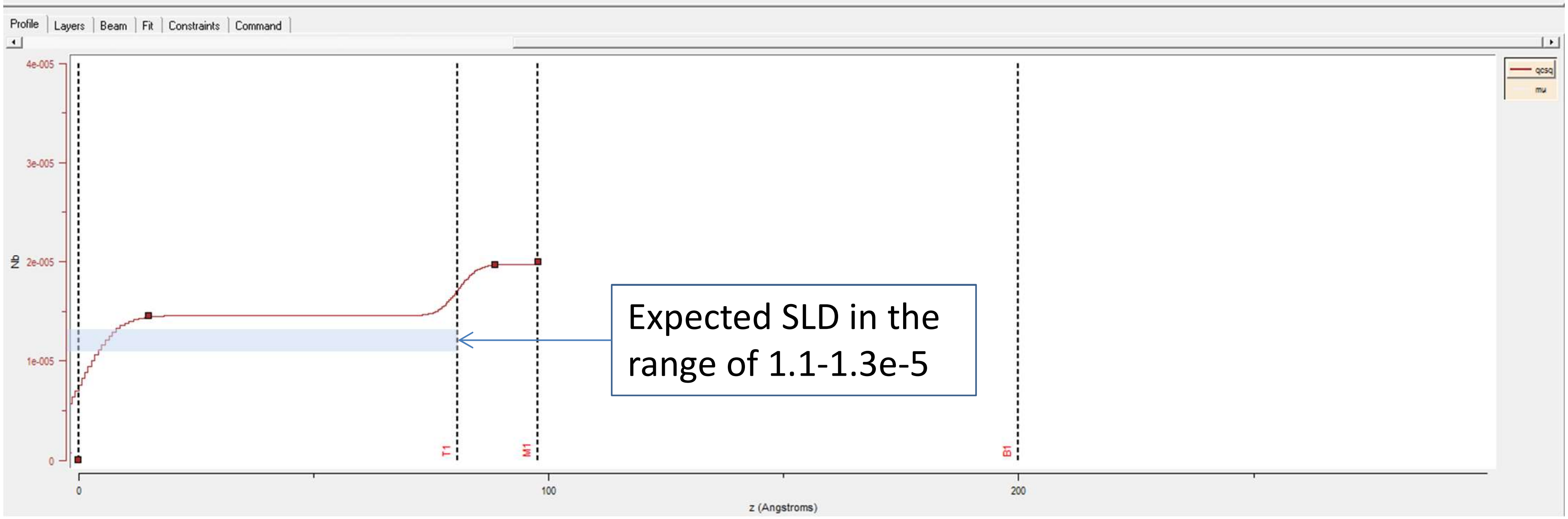


Reflectometry: Sample 2 (18% Photoresist)

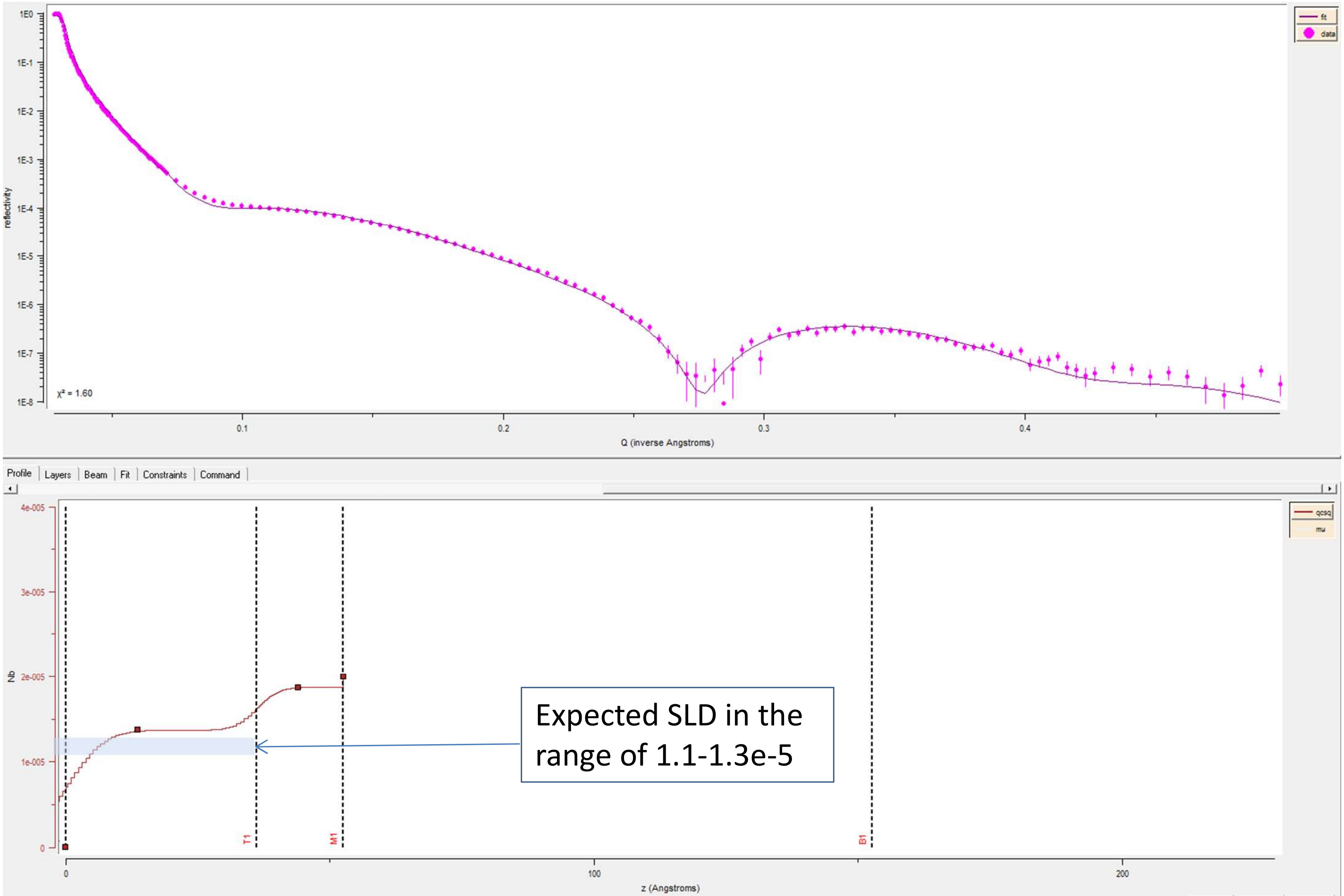


Reflectometry: Sample 3 (8.9% Photoresist)

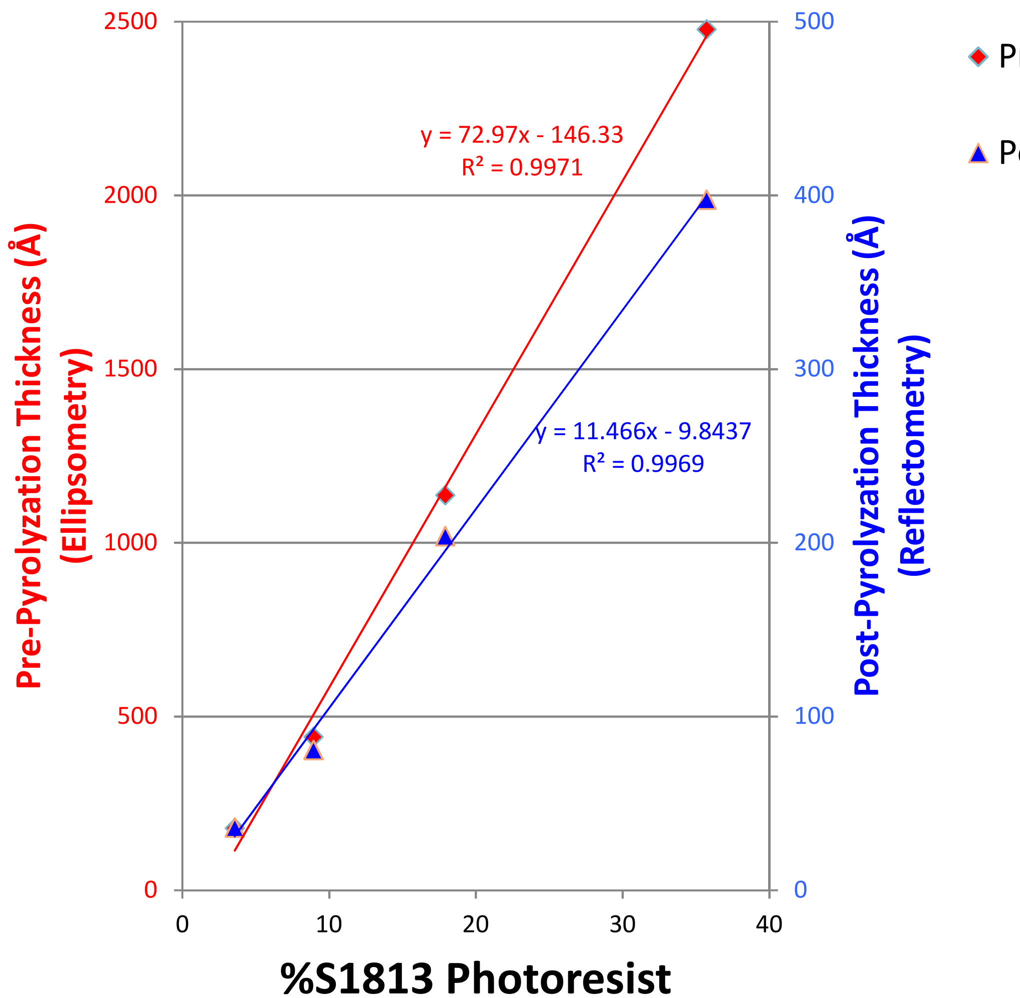


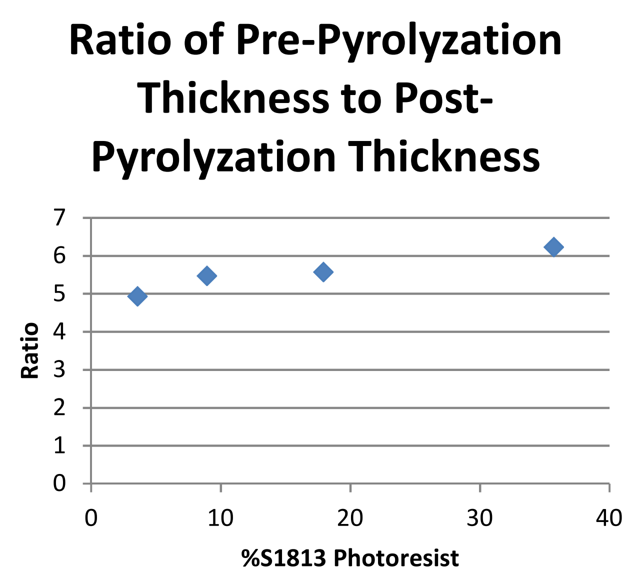


Reflectometry: Sample 4 (3.6% Photoresist)



Post Pyrolyzation Thickness vs. Concentration



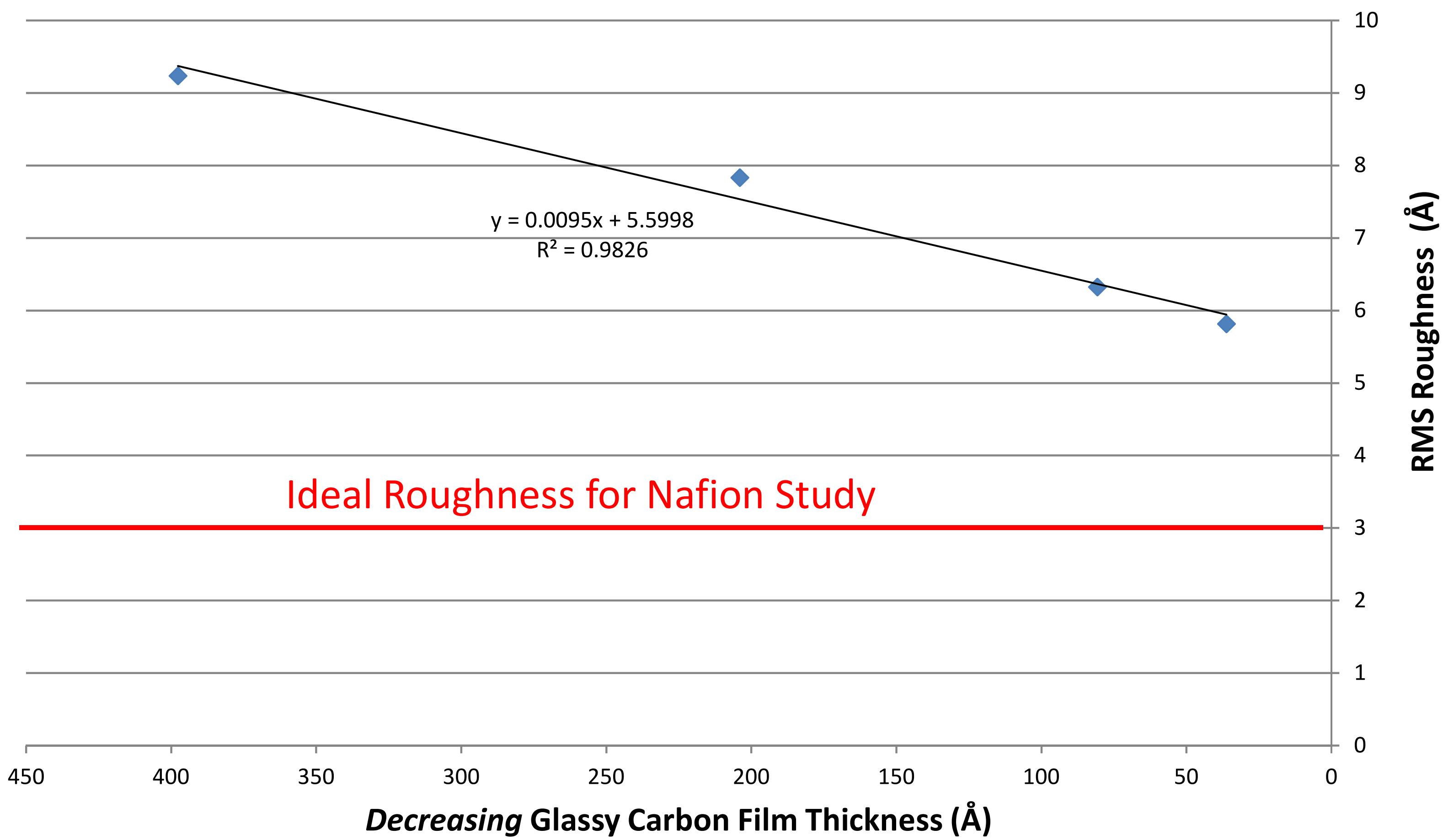


Comparison of Post-Pyrolyzation Thicknesses

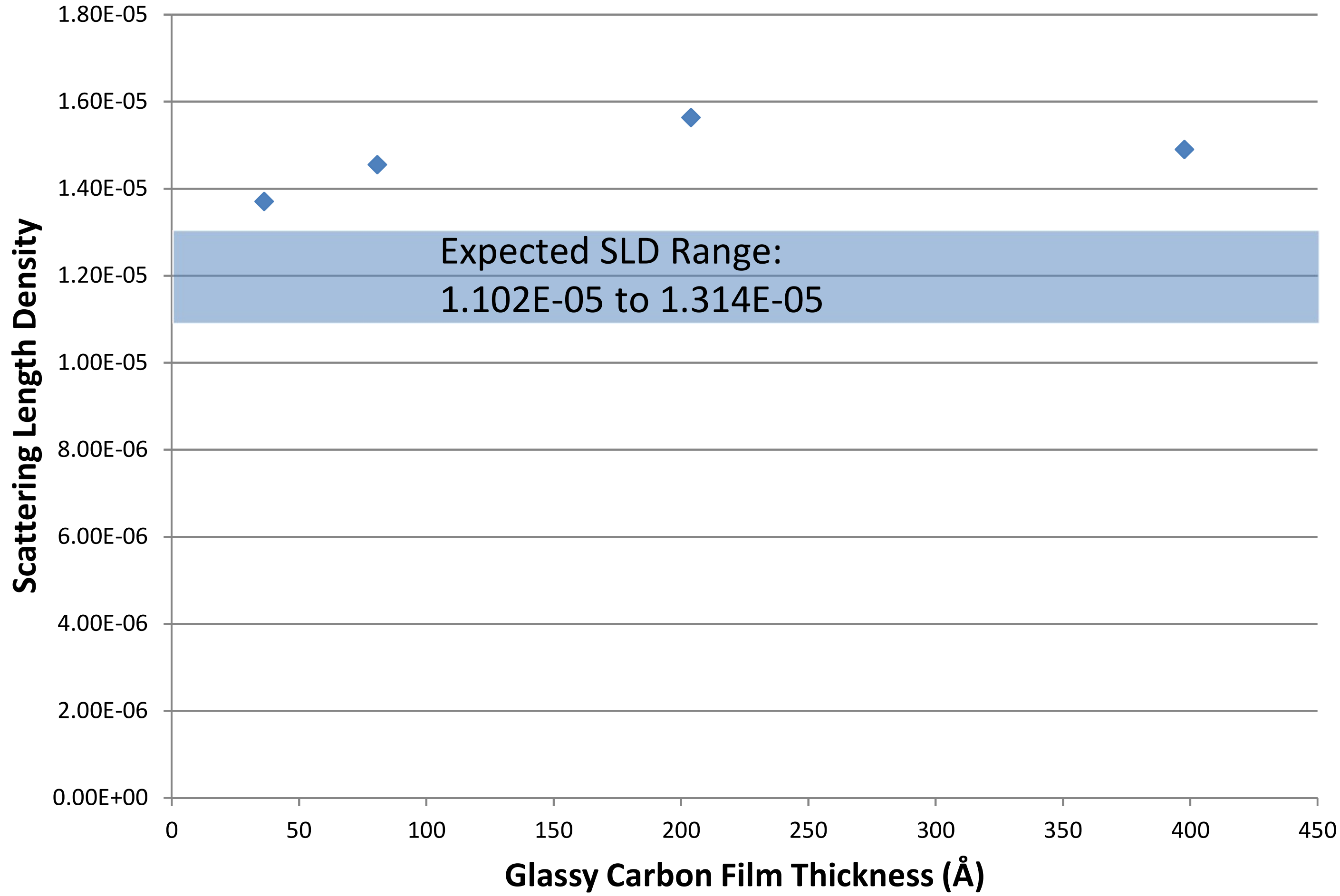
Sample #	%S1813	Desired Prepyrolysis Thickness (Å)	Measured PrePyrolysis Thickness (Ellipsometry)	Desired Final Thickness	Measured Final Thickness (X-Ray Reflectometry)
1	35.7	5000	2479	1000	398
2	17.9	2500	1138	500	204
3	8.93	1250	442	250	80.7
4	3.57	500	179	100	36.2

RMS Roughness vs. Film Thickness

Roughness decreases with decreasing thickness



Scattering Length Density vs. Thickness



Conclusions

- Neither type of carbon sample produced adequate smoothness for Nafion study, although Glassy Carbon is approaching ideal smoothness
- Possible next steps
  - Grow Pentacene at higher temperature and recheck smoothness
  - Use a different Glassy Carbon preparation technique
    - pre-baking
    - manipulating forming gas pressure
    - pyrolyzation in vacuum

Acknowledgements

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