# Continued Investigations in Carbon-Based Thin Films
## for Fuel Cells and Batteries

Michael Thompson
Thomas S. Wootton High School
Rockville, MD
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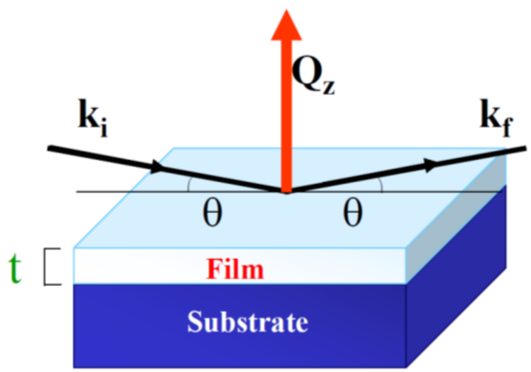
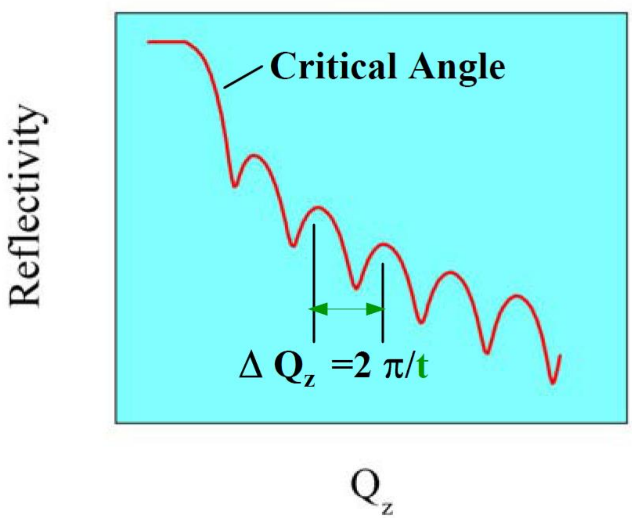
NIST Center for Neutron Research

# Carbon Film Background

- Nafion has shown lamellar interface 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 an attempt to grown thin, smooth carbon layers and characterize the Nafion interfaces that might exist in PEMs.

# Specular Reflectometry




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

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

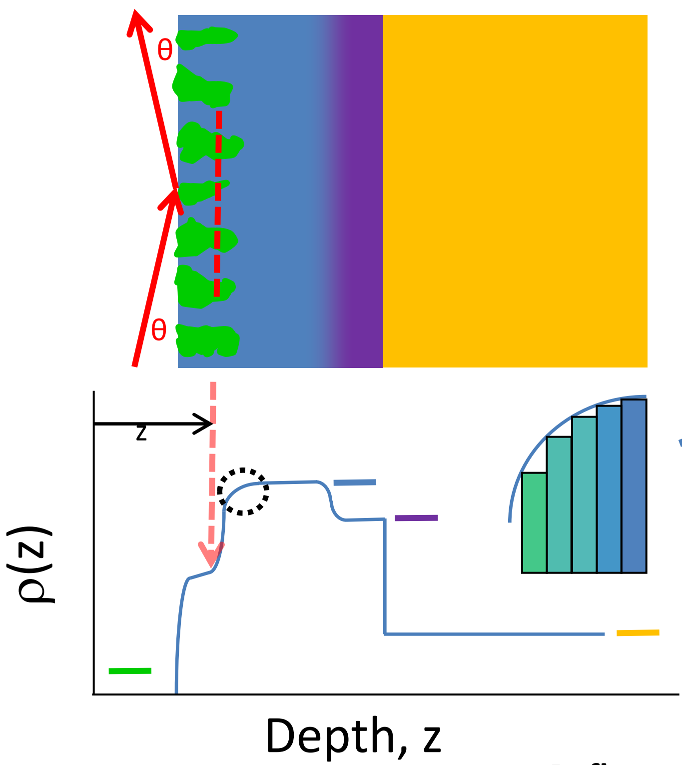
- XRR and NR Provide Depth Profile of the SLD
- SLD is related to Composition, and is proportional to the scattering lengths of the elements Z (i)

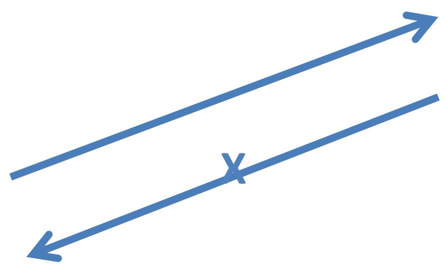
  $$SLD(x) = \Sigma_i Z(i)\, n_i(x)$$

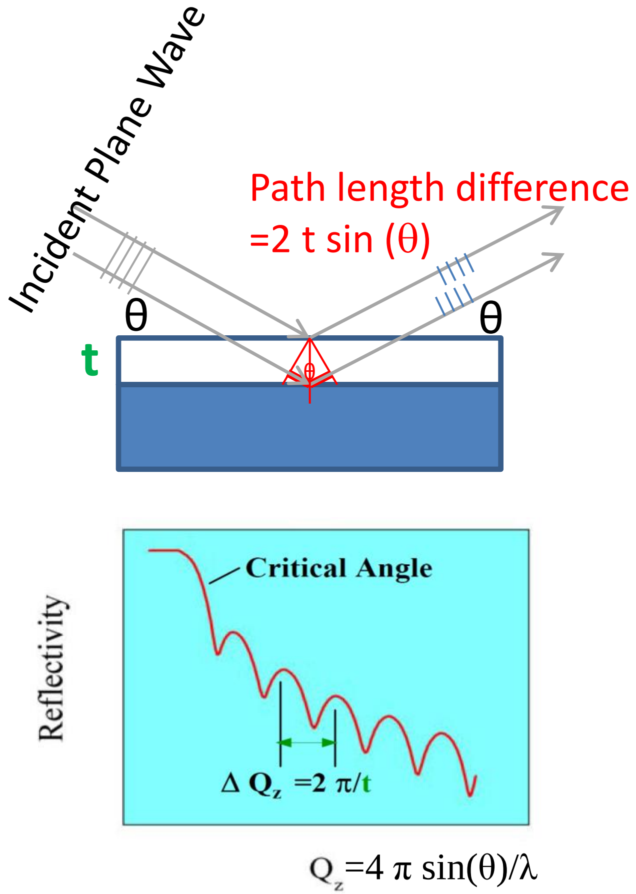
- Averages SLD in the plane perpendicular to x
- Critical Edge due to total external reflection
- Oscillations with period $2\pi$ / layer thickness
- Additional layers cause additional beating patterns

# Specular 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

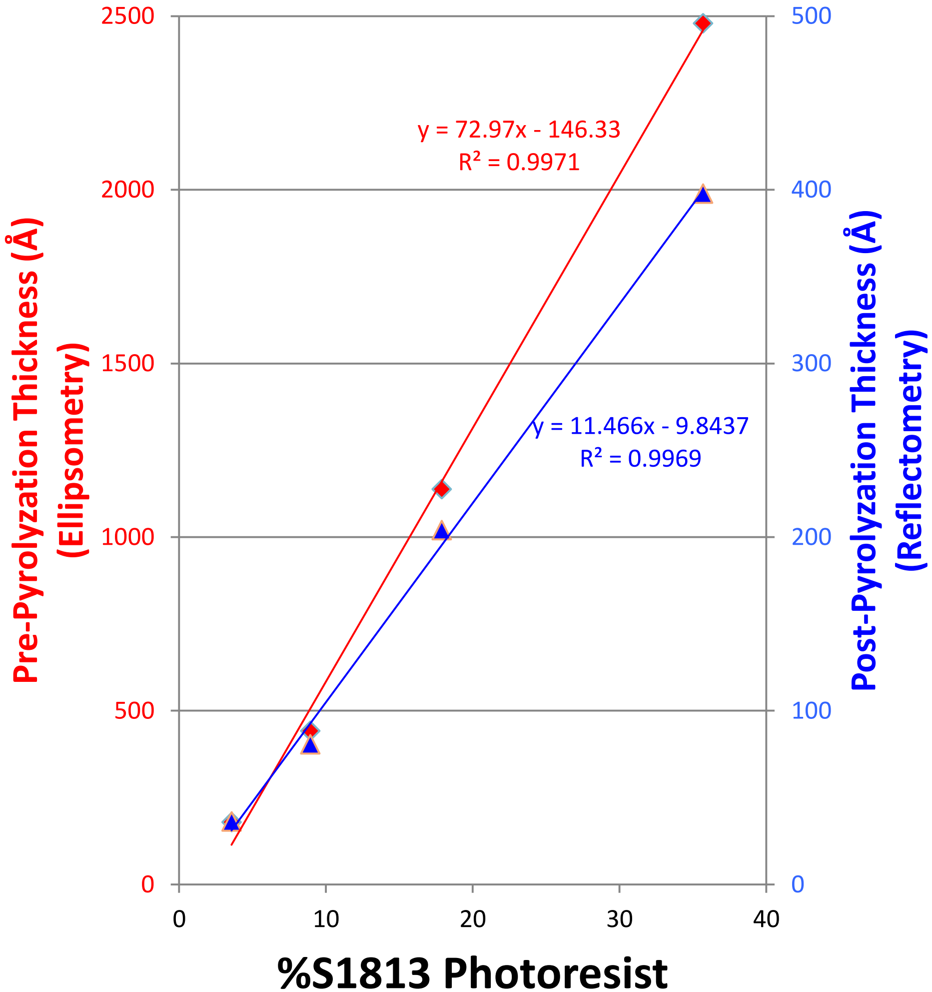


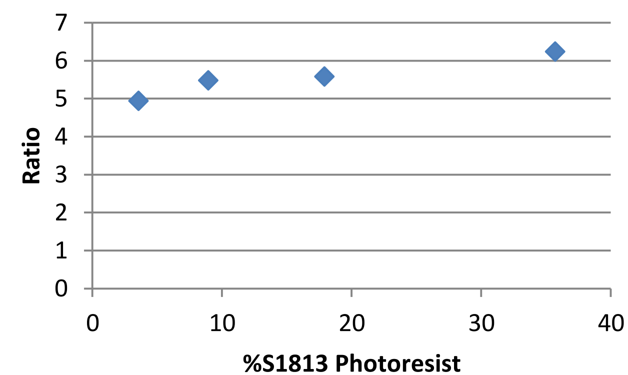




- Reflectometry averages the SLD of materials in the plane
- Gradients can be approximated by a set of uniform slabs
- Can determine the ratio of two known components

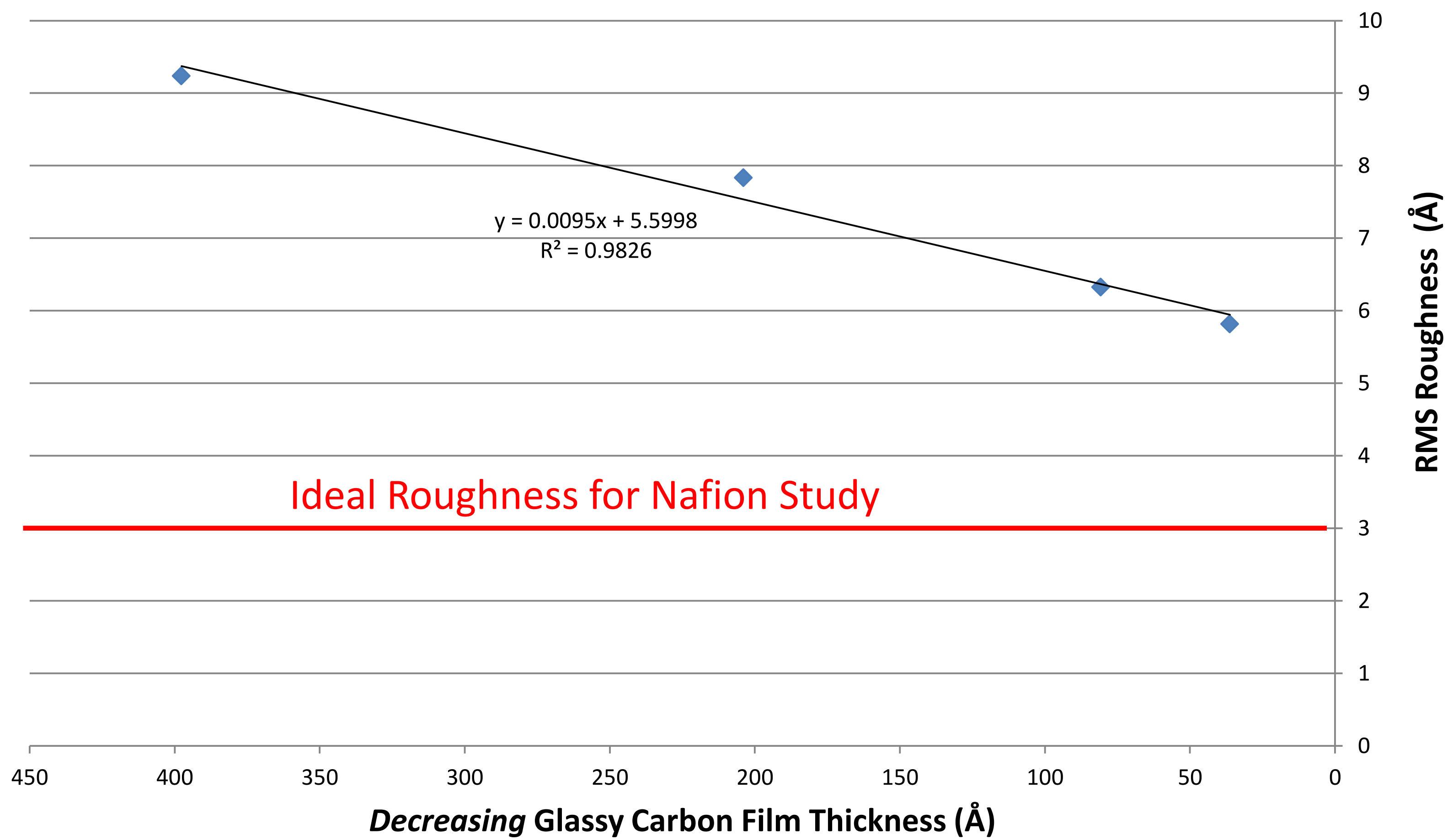
# Post Pyrolyzation Thickness vs. Concentration



# RMS Roughness vs. Film Thickness

## Roughness decreases with decreasing thickness



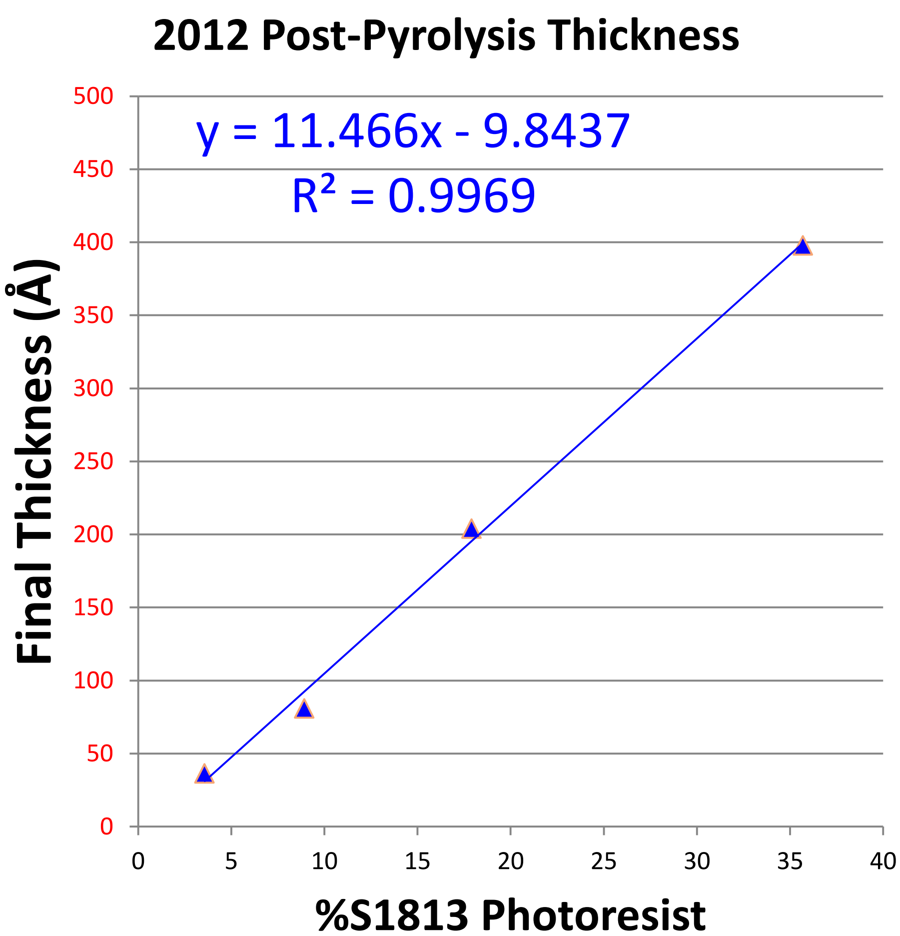
# Previous Pyrolyzed Photoresist Thicknesses based on Concentration

| 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 |

# 2013 Glassy Carbon Film Preparation

- Use 2012 data to determine photoresist concentrations needed to achieve 2 target film thicknesses: 30 Å and 50 Å
- Mix 2 different concentrations of S1813 Photoresist diluted in PGMEA
- Spin Coat each concentration on 2 thick and 2 thin wafers at 3500 rpm for 45sec
- Soft bake half of the samples overnight
- Pyrolyze all samples in forming gas ($1000^{o}$C)
- Analyze all samples using XRR and pick most suitable for Nafion investigation
- Spin coat Nafion layer on thin carbon film
- Use XRR and NR in multiple environments to characterize the Nafion/Carbon film interface

# Determining 2013 Photoresist Concentrations




By entering the target thicknesses of 30 Å and 50 Å into the best fit equation, we determine S1813 concentrations of 3.47% and 5.22%.

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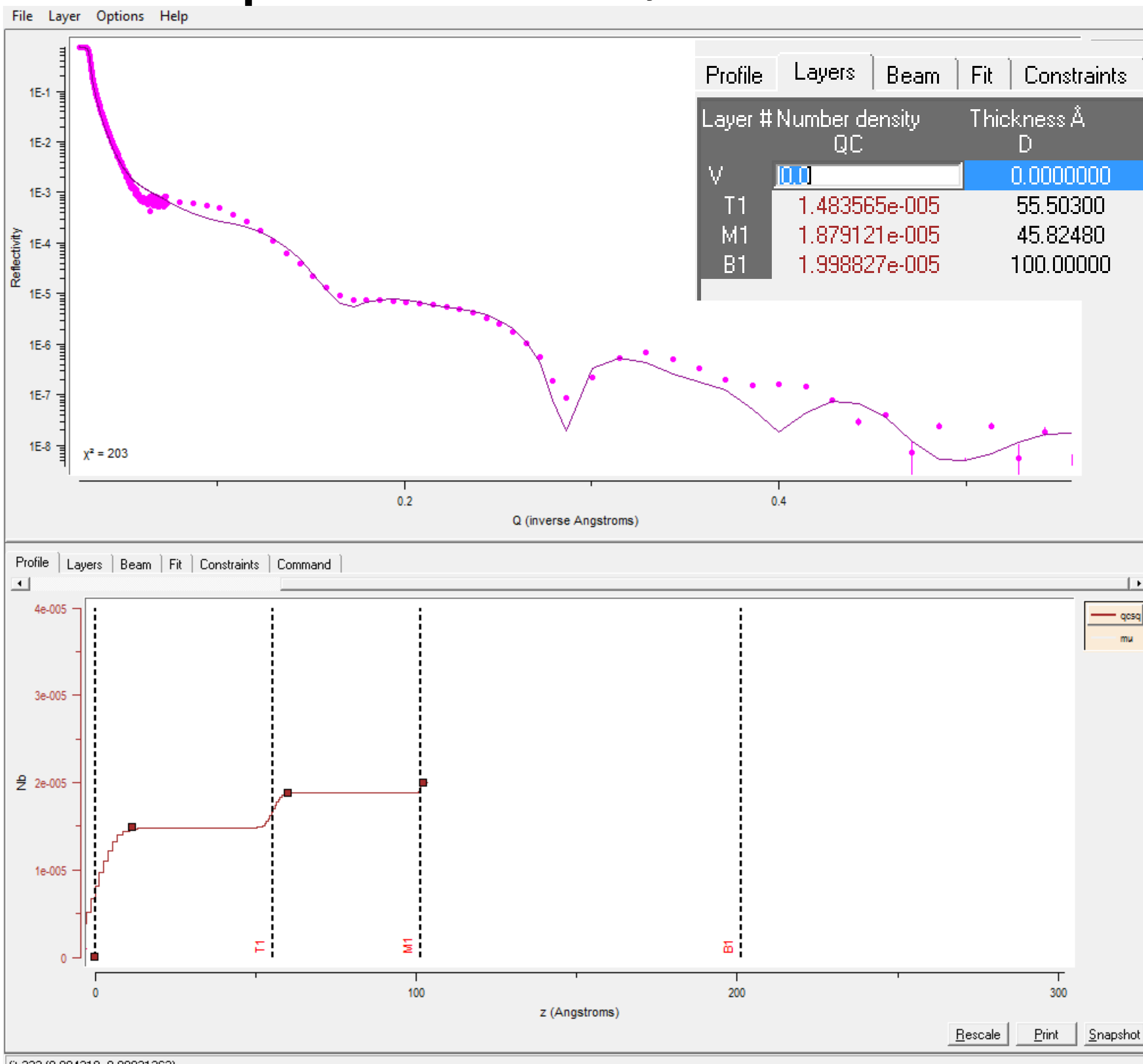
# Slide Preparation

- First, dilute S1813 to 10% in PGMEA (1 mL S1813 + 9 mL PGMEA = 10 mL solution)
- Adjust to final concentrations
  - 3.47% = 3.47 mL of 10% + 6.53 mL of PGMEA
  - 5.22% = 5.22 mL of 10% + 4.78 mL of PGMEA
- Spin-coat all labeled slides at 3500 rpm for 45 seconds
- Soft-bake half of all samples (1b, 2, 3, & 5) at 200$^{o}$ C overnight
- Have all samples pyrolyzed in forming gas at CNST.
- Because of time constraints, perform quick XRR to see which sample has ideal thickness for Nafion study. (These were only done for thick wafers; thin wafers are available for follow-up/further study)

# Preliminary Results

- Sample #3: 3.47% S1813 with Soft-Bake

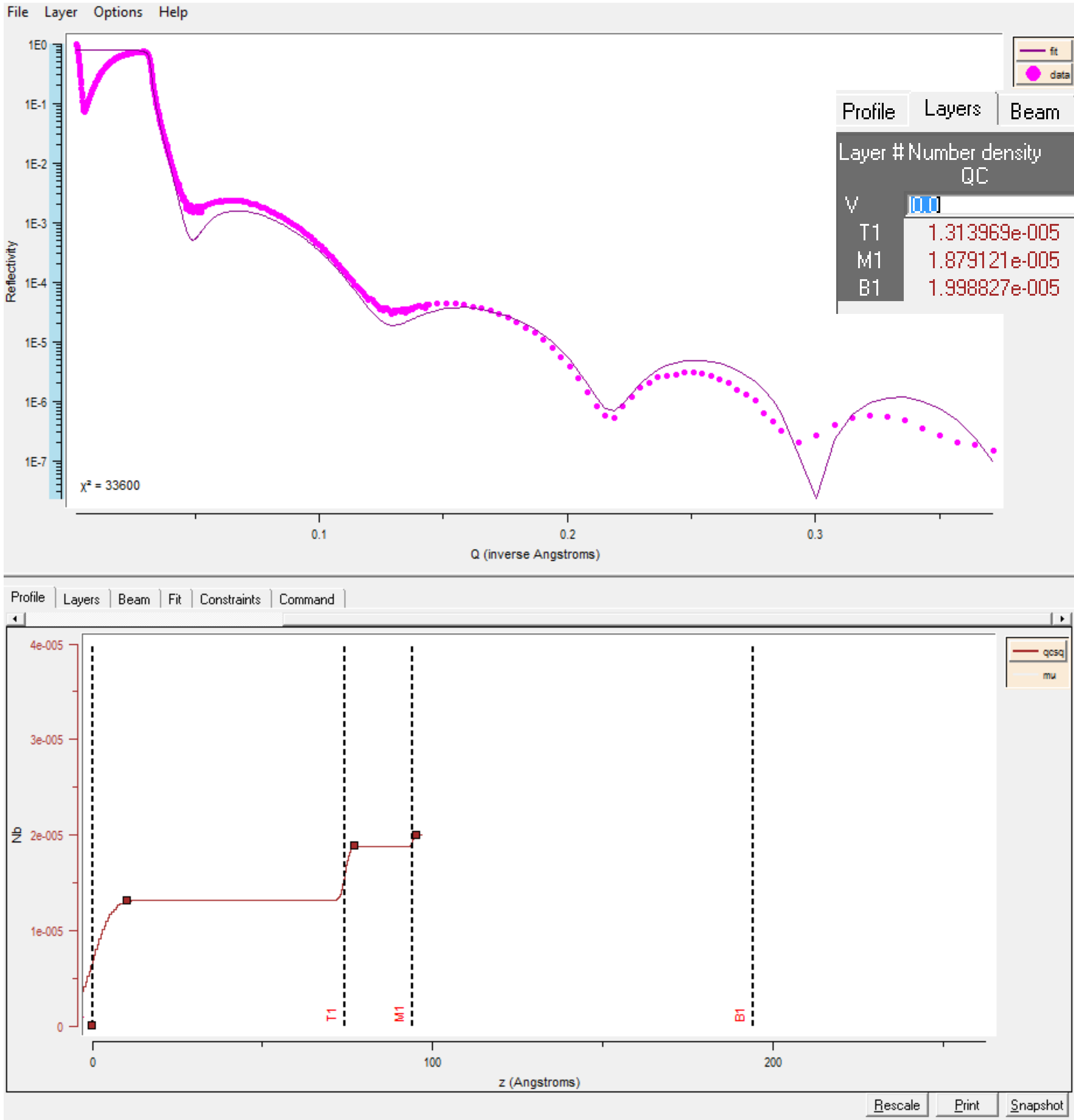



Profile | Layers | Beam | Fit | Constraints | Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption Å⁻¹ MU |
|---|---|---|---|---|
| V | 0.0 | 0.0000000 | 1.000000e-010 | 0.0000000 |
| T1 | 1.483565e-005 | 55.50300 | 11.75290 | 1.000000e-007 |
| M1 | 1.879121e-005 | 45.82480 | 4.538210 | 7.995350e-007 |
| B1 | 1.998827e-005 | 100.00000 | 1.0000000 | 1.521960e-006 |

A quick analysis indicated that this sample missed its target by too great a margin: We achieved 55 Å while aiming for 30 Å. The difference could possibly be due to impurities or unwanted absorption in the bake oven. For this reason, we avoided baked samples.

# Sample #5: 5.22% S1813; Soft-Bake




Profile | Layers | Beam | Fit | Constraints | Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption $Å^{-1}$ MU |
|---|---|---|---|---|
| V | 0.0 | 0.0000000 | 1.000000e-010 | 0.0000000 |
| T1 | 1.313969e-005 | 74.30000 | 10.40000 | 6.539450e-008 |
| M1 | 1.879121e-005 | 19.80000 | 2.670000 | 7.995350e-007 |
| B1 | 1.998827e-005 | 100.00000 | 1.0000000 | 1.521960e-006 |

Here again we see an overshoot of desired thickness (74 Å instead of 50 Å). This is outside the range of desired thickness and also probably contains unwanted impurities. We pursued analyses of the two unbaked samples: #4 and #25.

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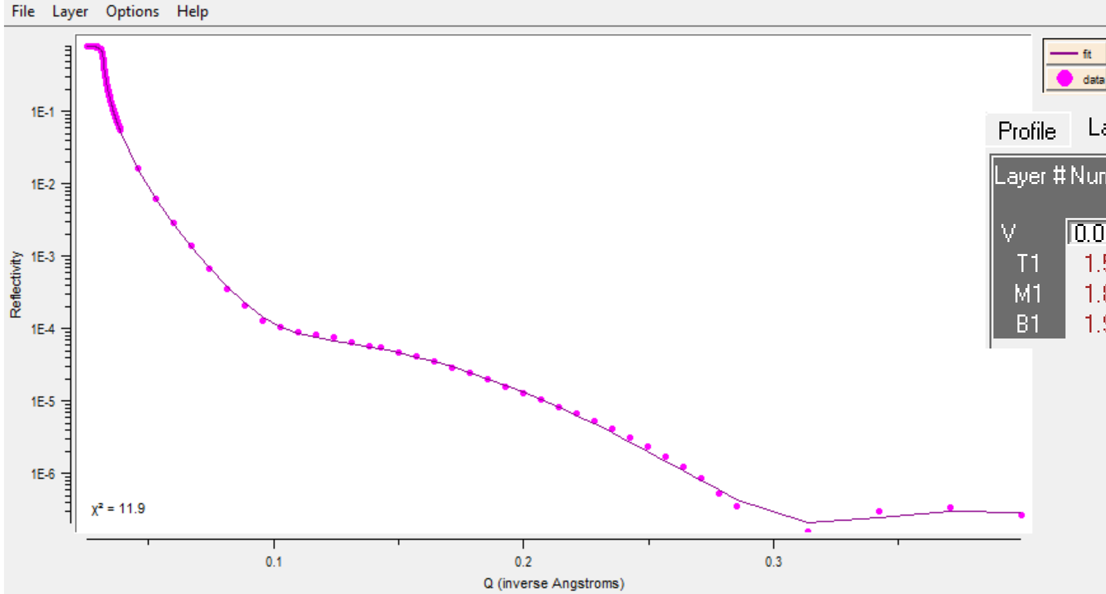
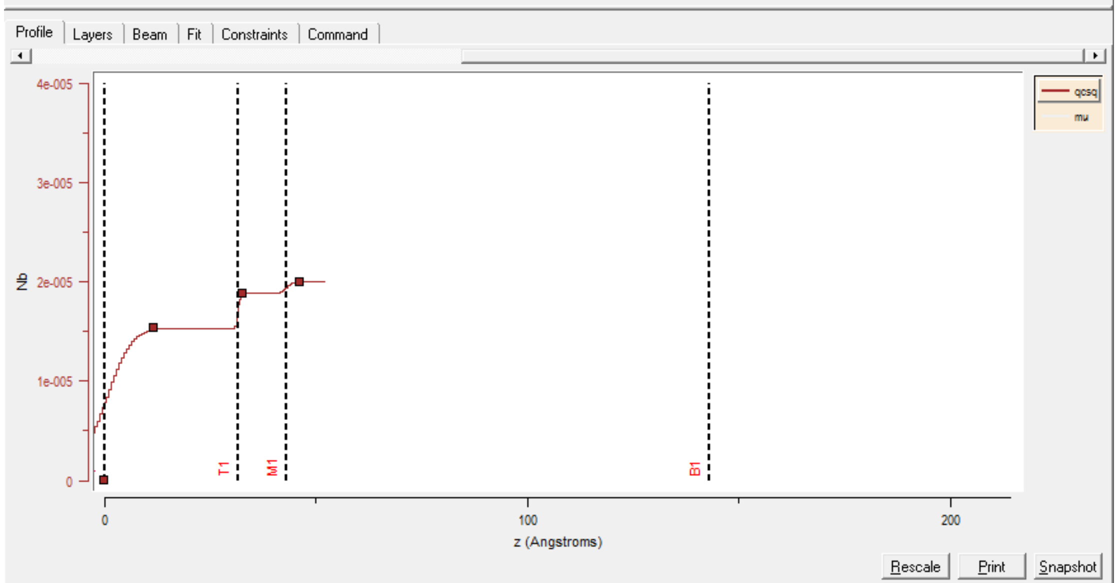
# Sample #4: 3.47% S1813; No Bake




Profile | Layers | Beam | Fit | Constraints | Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption $Å^{-1}$ MU |
|---|---|---|---|---|
| V | 0.0 | 0.0000000 | 1.000000e-010 | 0.0000000 |
| T1 | 1.530000e-005 | 31.60000 | 11.60000 | 7.664000e-008 |
| M1 | 1.879121e-005 | 11.50000 | 1.0000000 | 7.995350e-007 |
| B1 | 1.998827e-005 | 100.00000 | 3.000000 | 1.521960e-006 |




This XRR fit shows the non-baked sample fits pretty closely to the target thickness (31.6 Å, aiming for 30 Å). We proceeded with NR but were only able to take one set of scans in a $D_2O$ wet bath environment.

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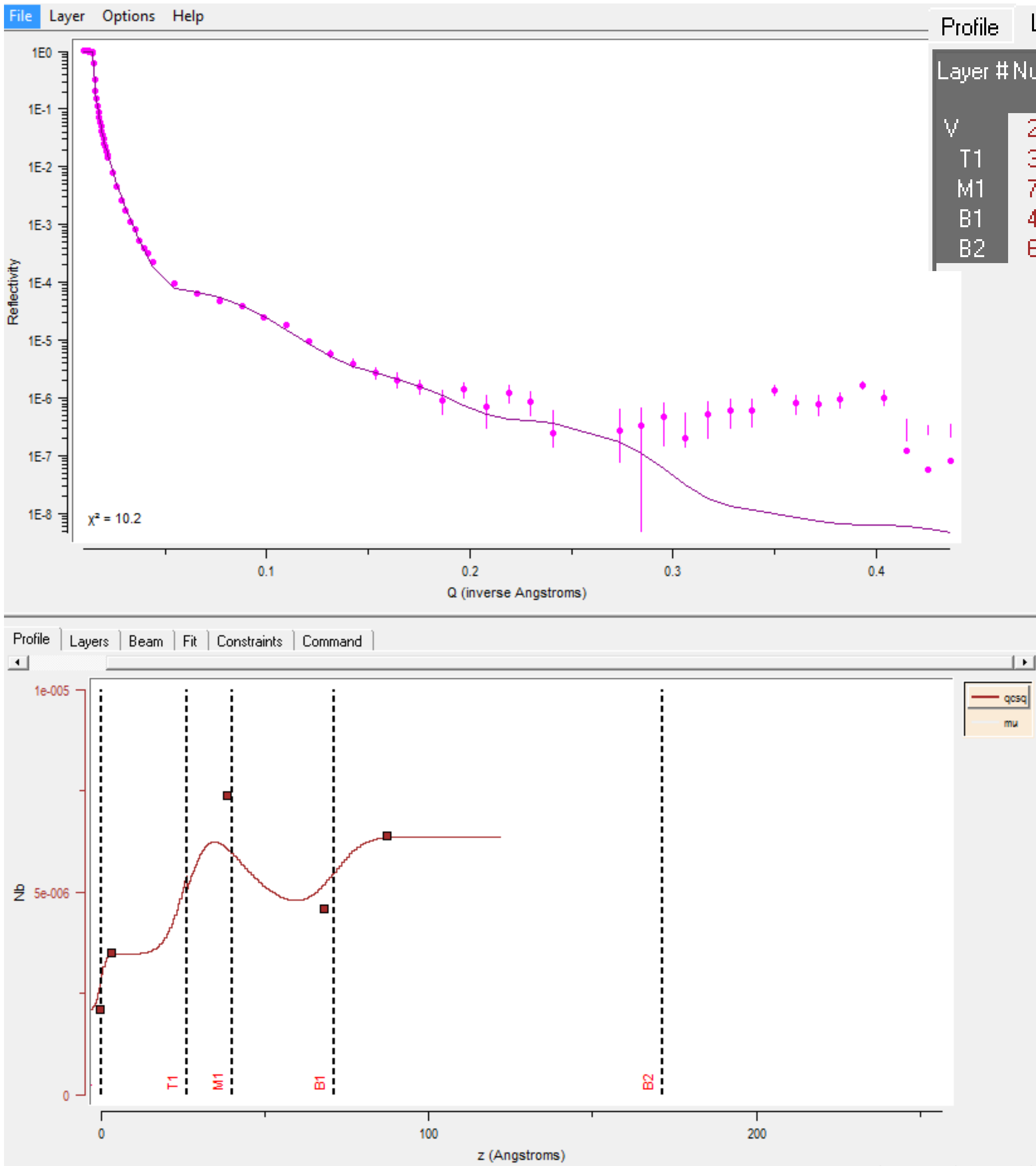
# Sample #4; NR in $D_2O$ Liquid




Profile | Layers | Beam | Fit | Constraints | Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption $Å^{-1}$ MU |
|---|---|---|---|---|
| V | 2.072516e-006 | 0.0000000 | 1.000000e-010 | 2.254040e-010 |
| T1 | 3.467310e-006 | 26.40000 | 3.320000 | 9.952960e-011 |
| M1 | 7.360001e-006 | 13.80000 | 12.40000 | 7.556940e-012 |
| B1 | 4.550001e-006 | 30.90000 | 28.20000 | 7.556940e-012 |
| B2 | 6.360269e-006 | 100.0 | 16.40000 | 1.627870e-012 |

The NR data show a PPR layer with a thickness around 30 Å as well, but there is also a transition layer between the $SiO_2$ and the PPR. The roughness revealed in the PPR layer is much too high.

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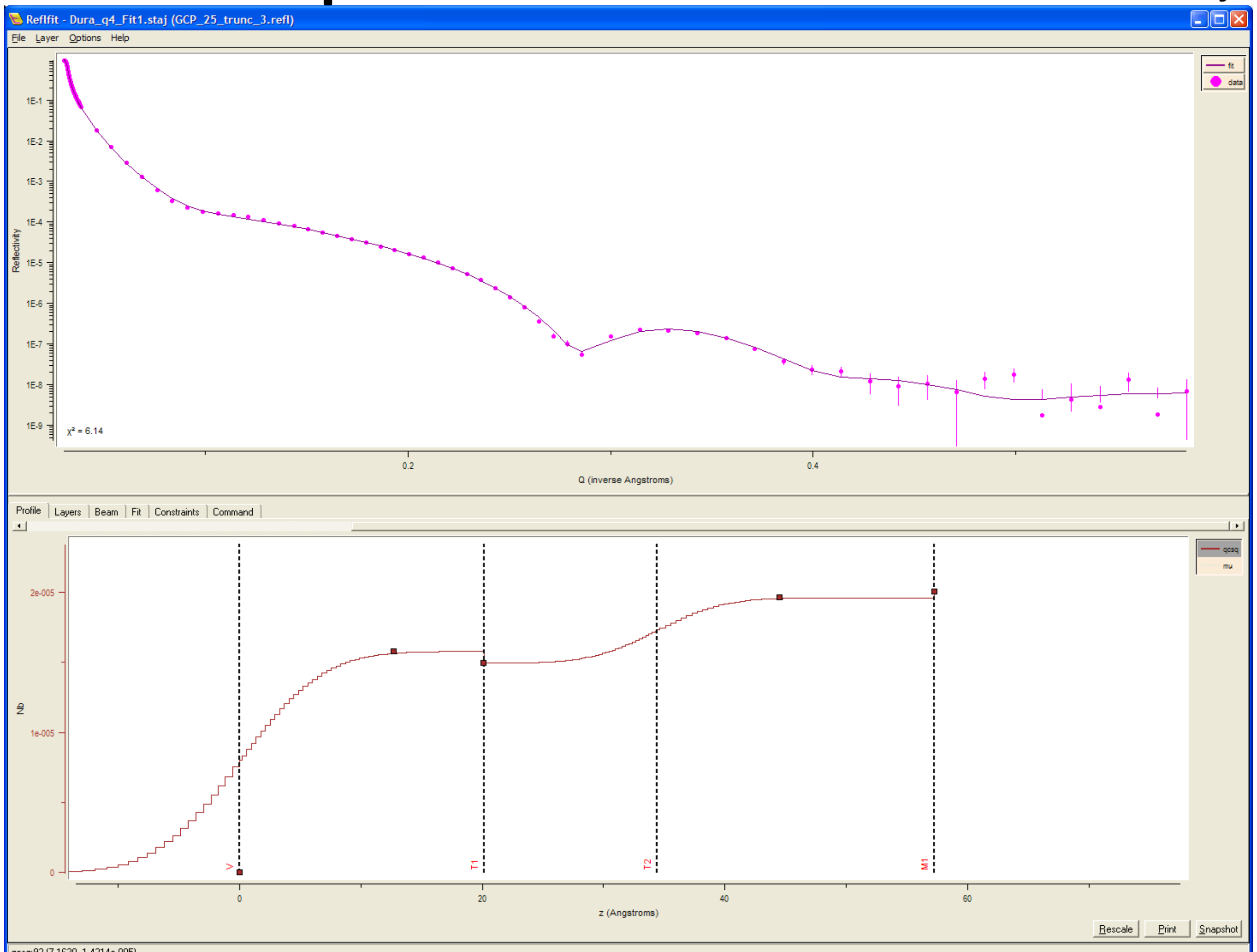
# Sample #25: 5.22% S1813; No Bake




Reflfit - Dura_q4_Fit1.staj (GCP_25_trunc_3.refl)

File Layer Options Help

Profile Layers Beam Fit Constraints Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption $Å^{-1}$ MU |
|---|---|---|---|---|
| V | 0.0 | 0.0000000 | 1.000000e-010 | 0.0000000 |
| T1 | 1.575920e-005 | 20.13390 | 12.69600 | 2.460000e-007 |
| T2 | 1.492159e-005 | 14.28720 | 1.000000e-010 | 1.230000e-007 |
| M1 | 1.956333e-005 | 22.86480 | 10.08080 | 7.995350e-007 |
| B1 | 1.998827e-005 | 100.00000 | 1.000000e-010 | 1.521960e-006 |

The target thickness for the 5.22% solution was 50 Å, but this XR fit indicates a total thickness for the PPR of ~34 Å. We extended the analysis for this sample, using NR in a dry environment and in a 90% RH ($D_2O$) environment. This was the sample that we put Nafion on for additional NR measurements. (Thanks to Joe Dura for completing this data fit.)

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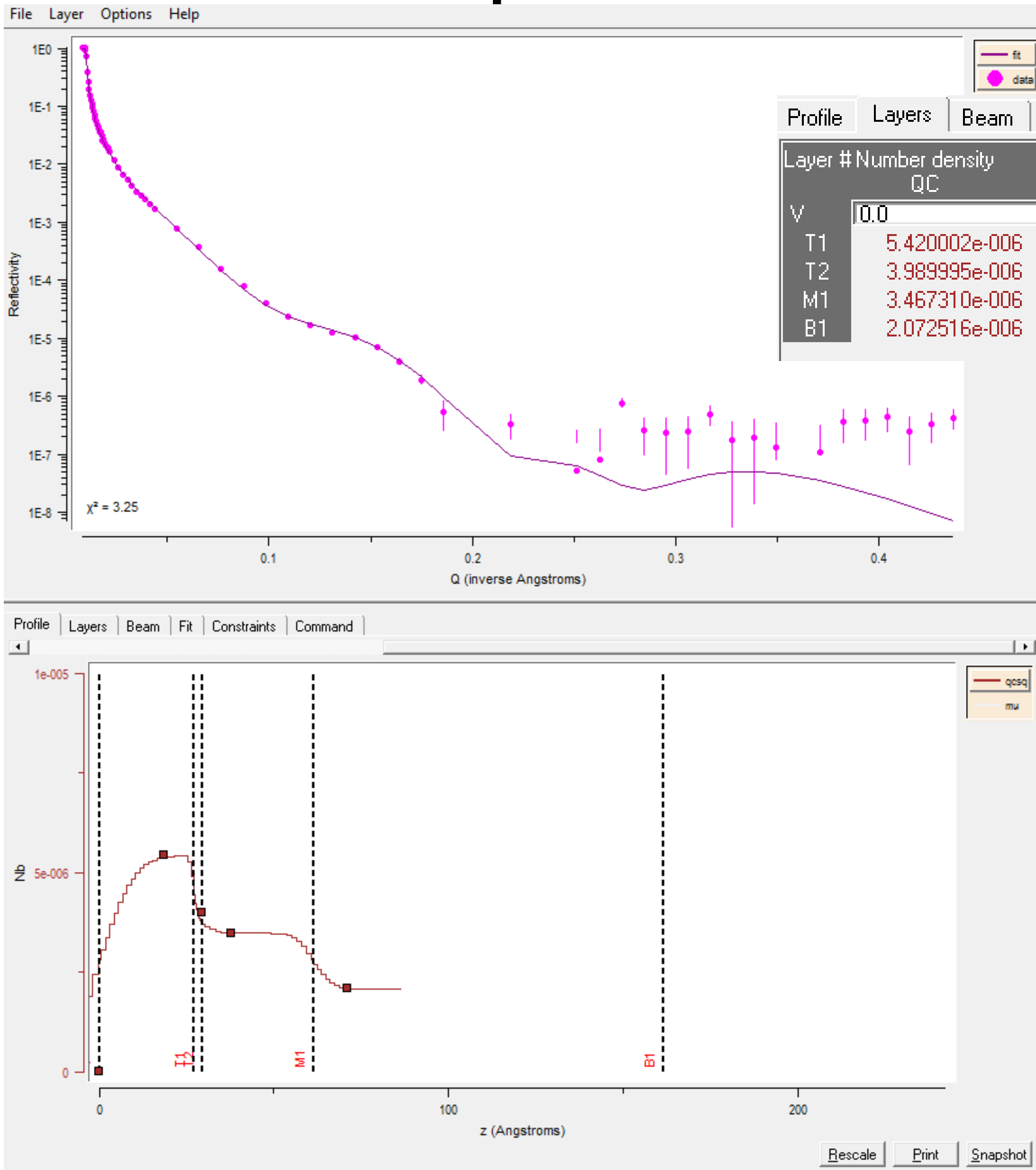
# Sample #25: NR in Dry Cell

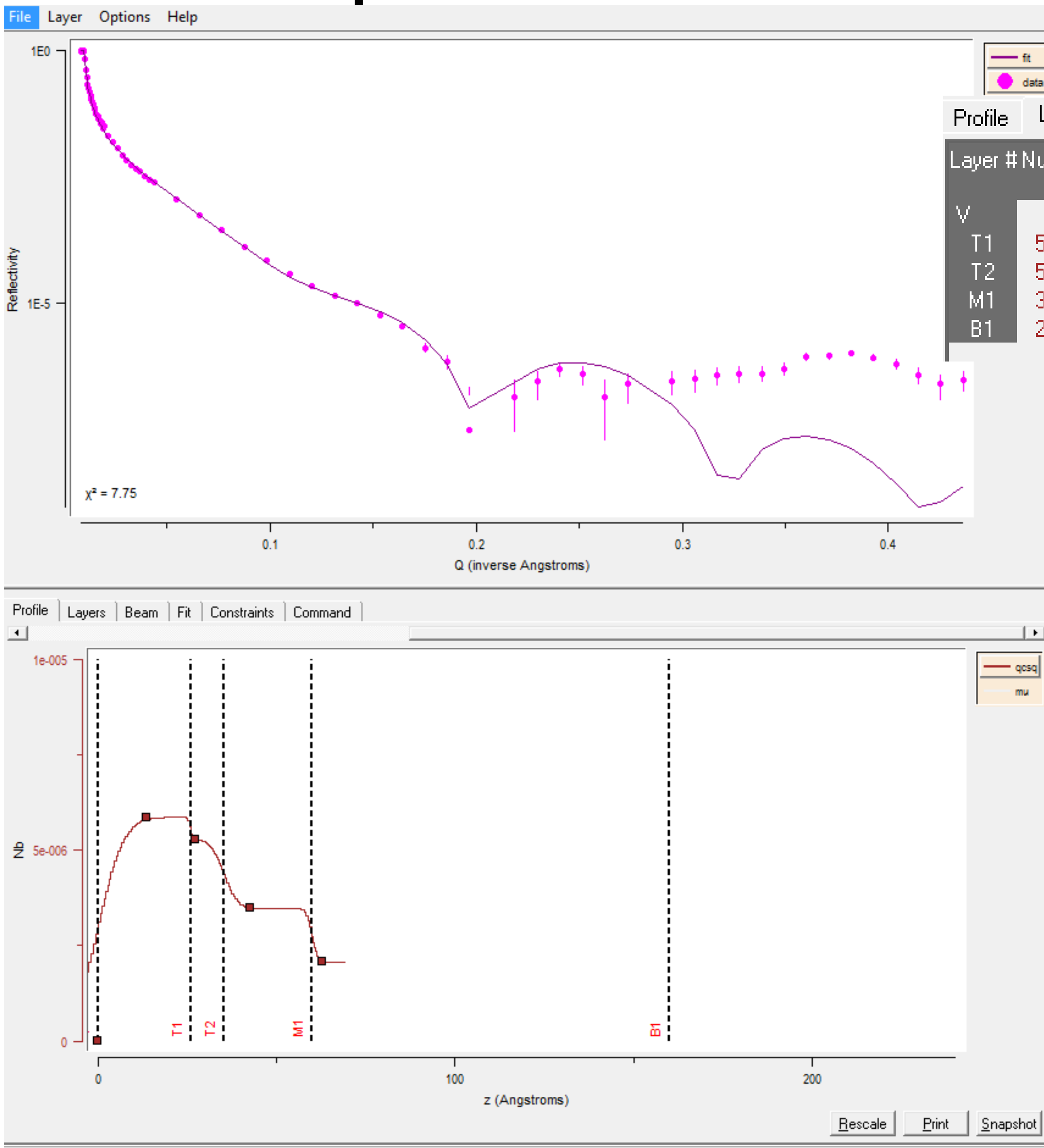



Profile | Layers | Beam | Fit | Constraints | Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption Å⁻¹ MU |
|---|---|---|---|---|
| V | 0.0 | 0.0000000 | 1.000000e-010 | 0.0000000 |
| T1 | 5.420002e-006 | 27.10000 | 18.60000 | 7.556940e-012 |
| T2 | 3.989995e-006 | 2.561330 | 2.270000 | 7.556940e-012 |
| M1 | 3.467310e-006 | 31.90000 | 8.170000 | 9.952960e-011 |
| B1 | 2.072516e-006 | 100.00000 | 9.630000 | 2.254040e-010 |

NR data for the same sample fit to a thinner total thickness (~29.7 Å) and greater total roughness.

# Sample #25: NR in 90% RH ($D_2O$)




Profile | Layers | Beam | Fit | Constraints | Command

| Layer # | Number density QC | Thickness Å D | Roughness Å RO | Absorption $Å^{-1}$ MU |
|---|---|---|---|---|
| V | 0.0000000 | 0.0000000 | 1.000000e-010 | 0.0000000 |
| T1 | 5.849999e-006 | 26.00000 | 13.70000 | 1.627870e-012 |
| T2 | 5.280005e-006 | 9.370000 | 1.180000 | 7.556940e-012 |
| M1 | 3.467310e-006 | 24.60000 | 7.190000 | 9.952960e-011 |
| B1 | 2.072516e-006 | 100.00000 | 3.0 | 2.254040e-010 |

NR data in $D_2O$ vapor reveal a bit higher total layer thickness (~35 Å). The majority of the SLD measures higher, indicating pores filled with the vapor.

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# Adding Nafion to Sample #25

- Spin-coat 1:16 solution of Nafion in Ethanol onto sample
- Bake for one hour at 60$^{o}$C
- Collect NR data in various environments
  - Dry (Argon gas)
  - 90% RH $D_2O$
  - 90% RH $H_2O$
- Thanks to Ben Jones for data fits that follow

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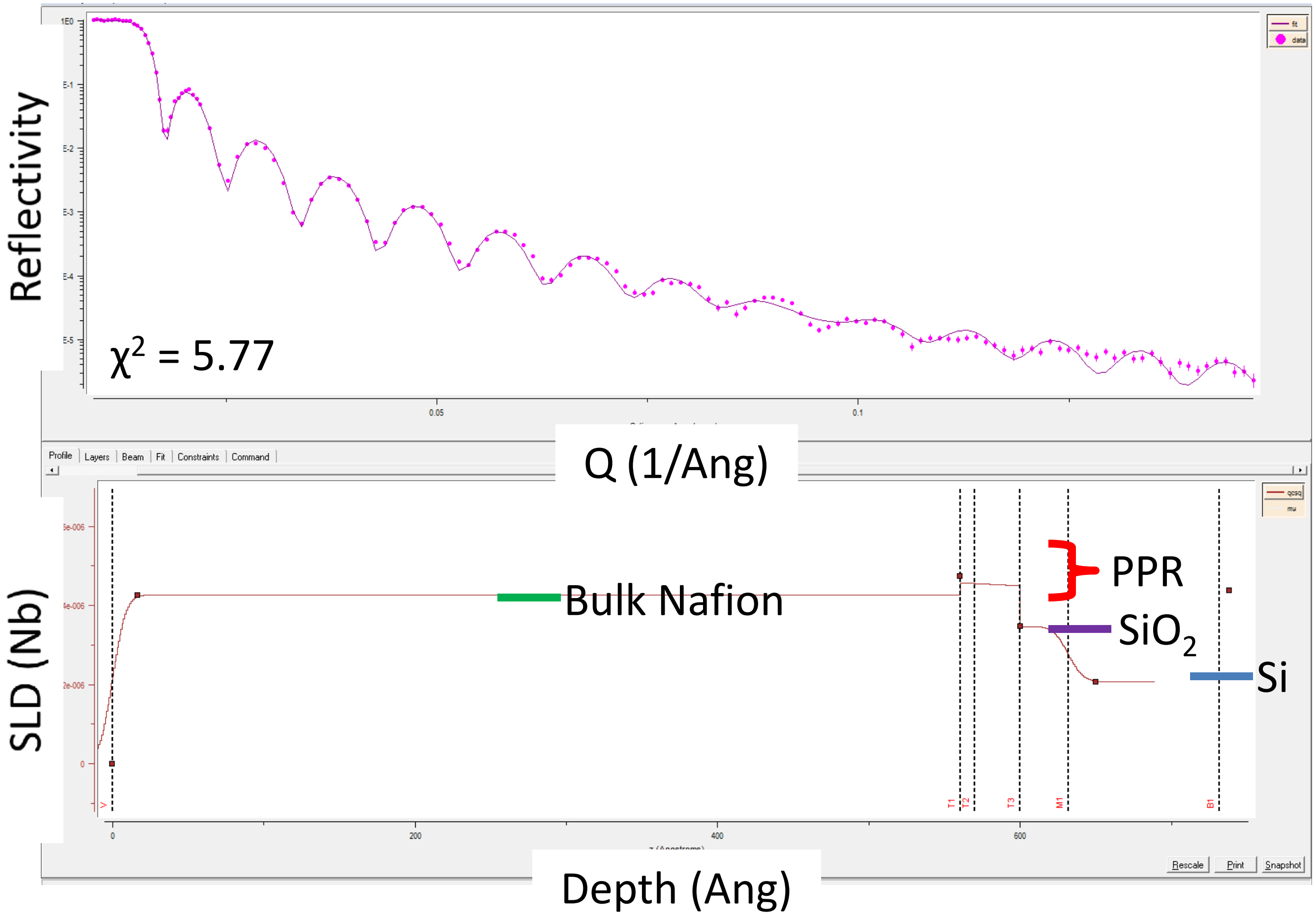
# Fit Neutron Data

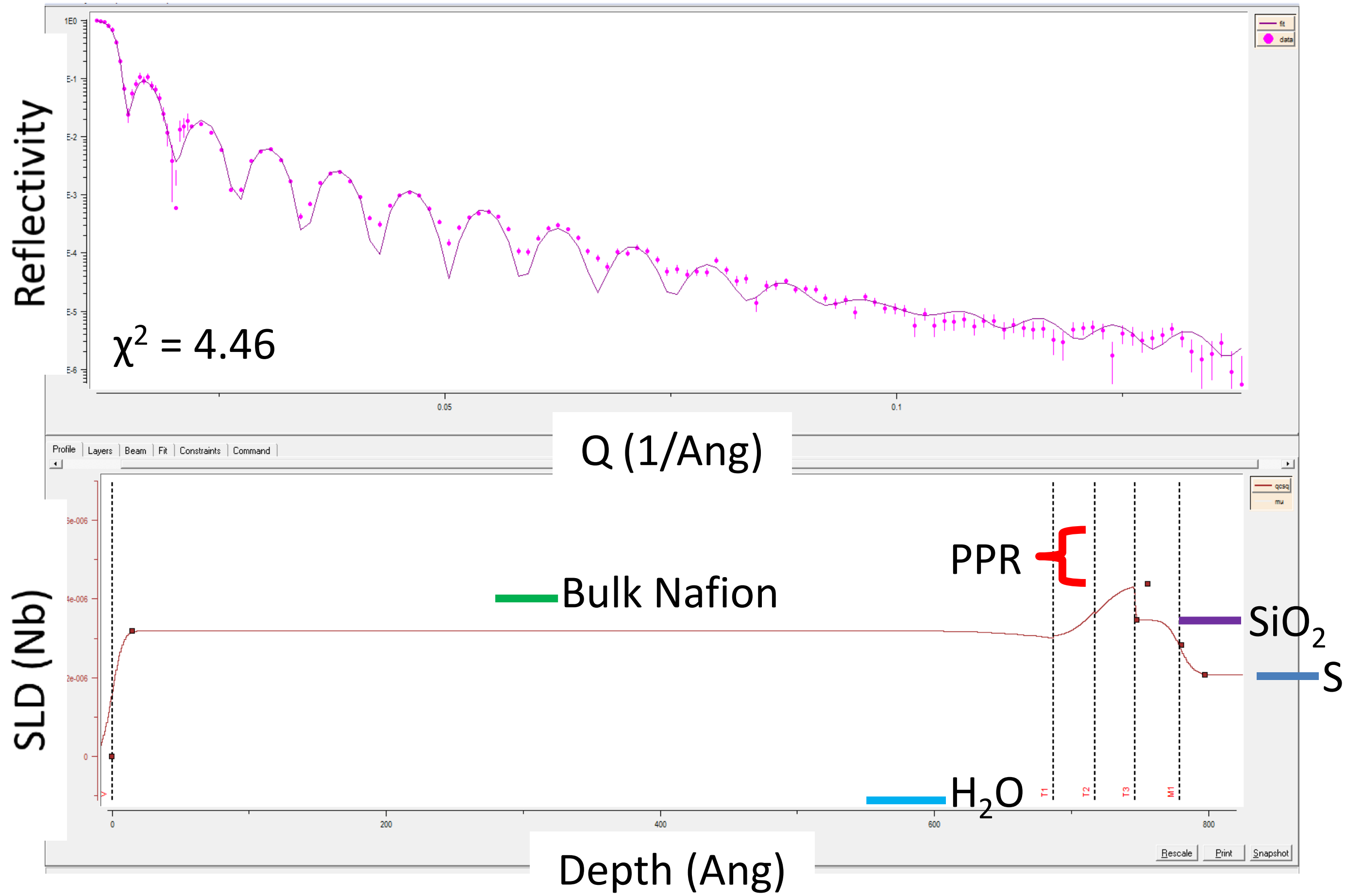
Dry Nafion/PPR




Dry Nafion on PPR reveals a thin layer of high sld under the bulk Nafion with a sharp interface

# Fit Neutron Data

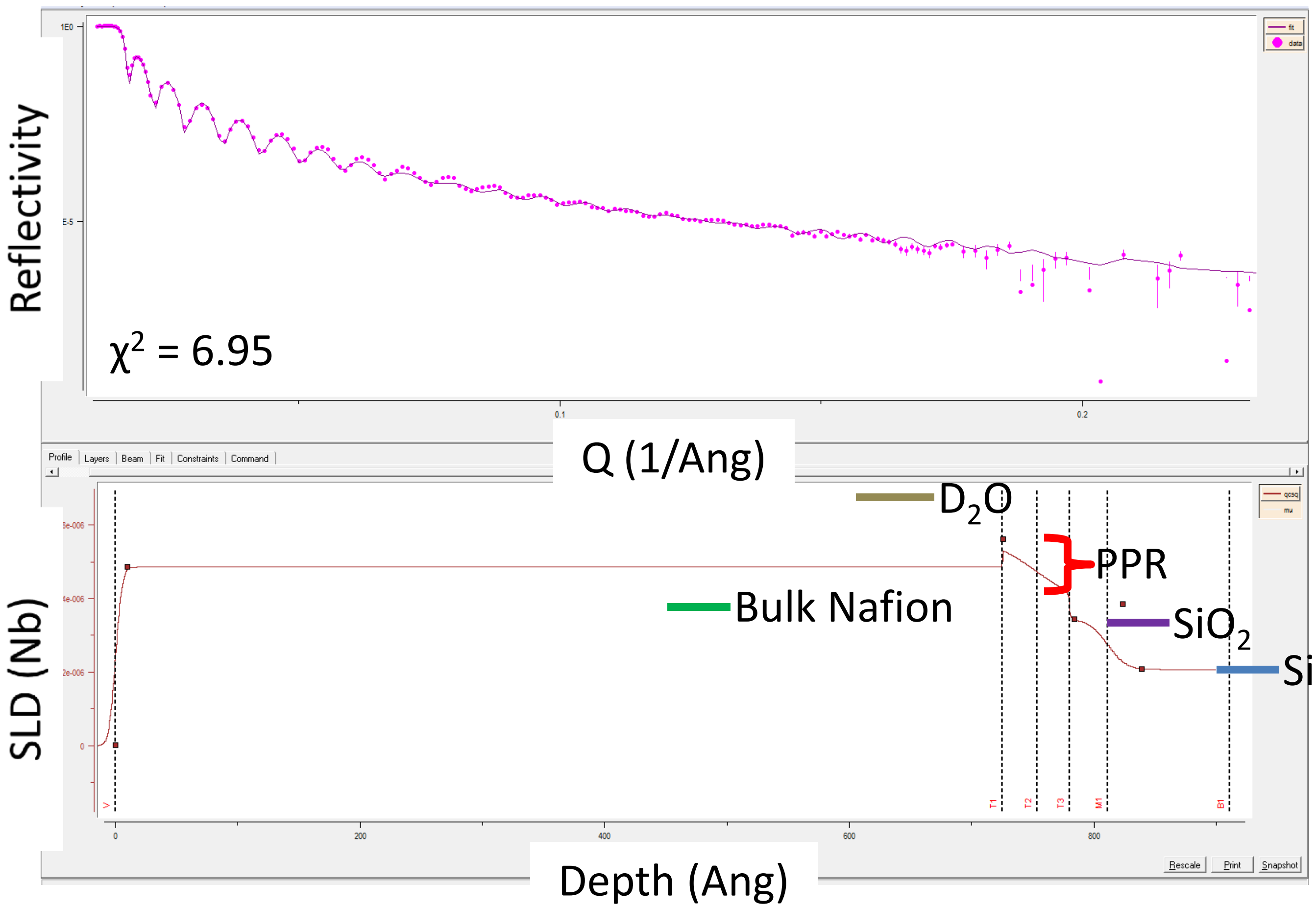
Nafion/PPR in $H_2O$ vapor, RH = 90%




$H_2O$ vapor reveals a strong dip in sld between Nafion and the PPR layer, corresponding to a single water-rich layer at the interface

# Fit Neutron Data

Nafion/PPR in $D_2O$ vapor, RH = 90%




$D_2O$ reveals a strong peak in sld between the Nafion and PPR layers, also corresponding to a single water-rich layer at the interface

# Conclusions

- We did not hit target roughness values with carbon films
- Variations in Nafion SLD in $H_2O$ and $D_2O$ vapor indicate either porosity within the layer or a water-rich layer at the interface with the PPR
- We do not see the lamellae seen on $SiO_2$
- Simultaneous fitting of two data sets would provide better indicators of layer structures

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# Next Steps

- Investigate different photoresists or possibly combinations of photoresists to minimize roughness
- Change the pyrolyzation environment to vacuum
- Investigate Nafion on graphene

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# Simple Scientific Method-Finding Meaning in the World

**Observe**

- Seek new environments to observe
- Observe your actions/influence on the environment you are observing

**Describe**

- Observations are limited by language
- Language/knowledge enhance observation

**Relate**

- It is not science until it is shared with others
- Participating means serving as author and audience

# Scientific Method