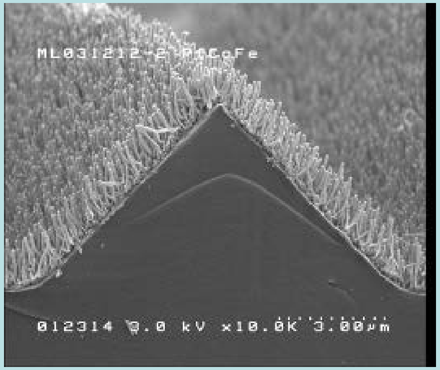
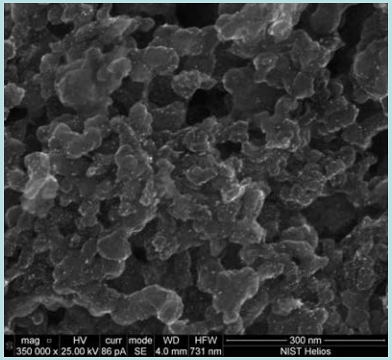
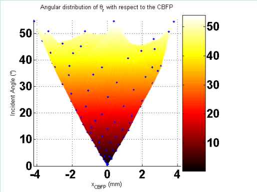
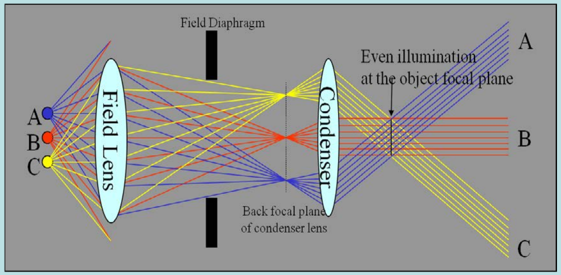




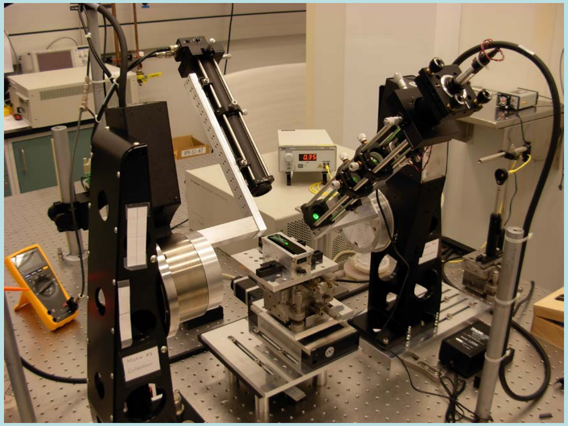
Metrology for Fuel Cell Manufacturing



2013 DOE Hydrogen and Fuel Cells Program Review Project ID# MN006
May 15, 2013



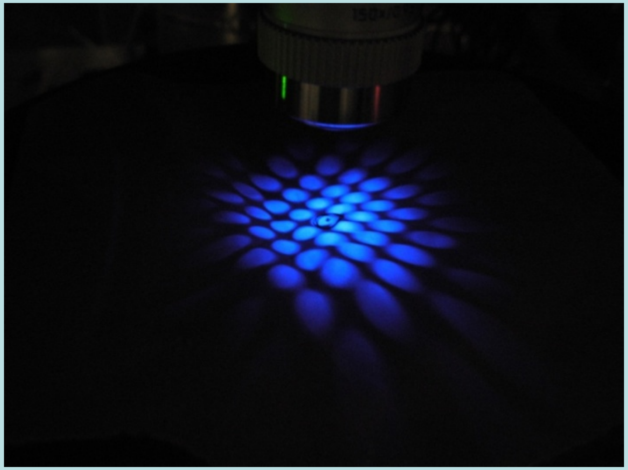
Mike Stocker (NIST)



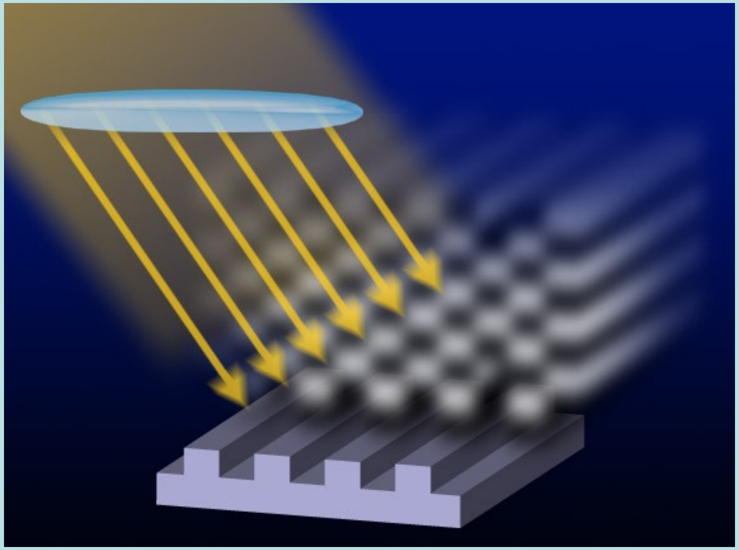
National Institue of Standards and Technology (NIST)

Surface and Nanostructure Metrology Group

- **Optics Project Team**
  - **Dr. Richard Silver - Group leader / Physicist**
  - **Mike Stocker – Metrologist**
  - **Dr. Bryan Barnes – Physicist**
  - **Dr. Hui Zhou – Chemical Physicist**
  - **Dr. Yeung-Joon Sohn – Optical Physicist**
  - **Dr. Egon Marx – Theoretical Physicist**
  - **Francois Goasmat – Computer Scientist**
  - **Dr. Jing Qin – Optical Physicist**



Expertise: optical based semiconductor metrology, microscope characterization, E & M simulation, scatterfield microscopy, tool design, target design, defect inspection, measurement uncertainty, etc.



Overview

Timeline

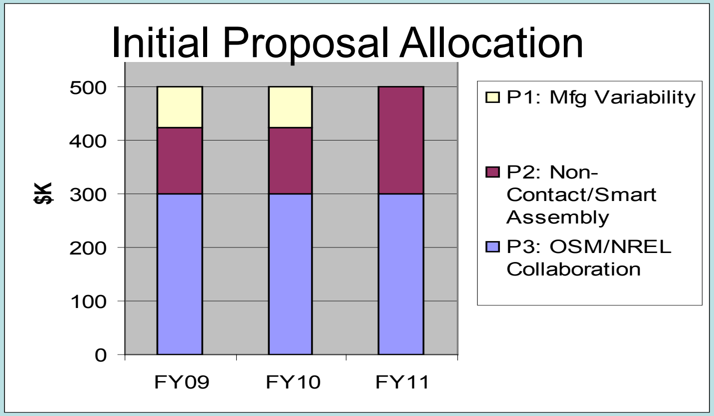
October 1, 2009
September 30, 2013

Barriers

F. Low Levels of Quality Control and Inflexible Processes

Partners

Interactions & Collaborations with several leading fuel cell membrane suppliers.



Overall Budget

- FY12 - DOE $175K
- FY13 – DOE $150K – This money was provided through an IAA extension, allowing 2011 shortfall money to fund sub-project #3 (Optical Scatterfield Microscopy)

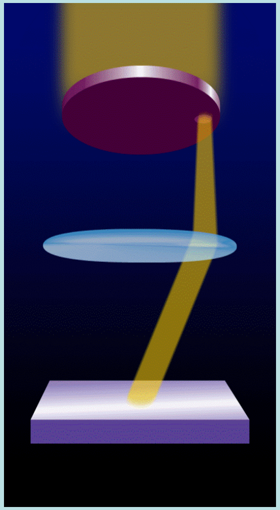
The DoE investment at NIST in developing high-throughput optical process control methods leverages significant investments by NIST to develop an accurate optical metrology infrastructure for semiconductor and nanomanufacturing. The investment by DoE also helps NIST directly focus metrology resources in support of future energy needs.

Subproject Overview

P3 - Optical Scatterfield Metrology for Online Catalyst Coating Inspection of PEM (Fuel Cell) Soft Goods

Objective: Using catalyst coated samples provided by manufacturers with variations in critical parameters (i.e., Pt and Pt alloy catalyst loading) and inclusion of various types of defects characterized using standard methods (XRF, SEM), evaluate the Optical Scatterfield Metrology Tool's sensitivity to these parameters.

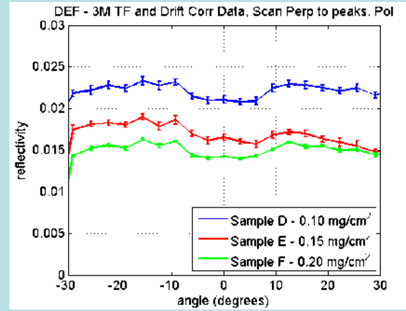
Approach: The Optical Scatterfield Microscopy technique employs both simulation and physical measurement of samples. **Simulation** is a key aspect of the approach as it allows one to develop accuracy when making optical measurements that require nanometer uncertainties. It provides a flexible and efficient platform to evaluate and optimize measurement parameters even before samples are measured. **Experimentally**, the approach involves acquiring angle or wavelength resolved data on one of three in-house custom designed and fabricated scatterfield capable microscopes, a commercial ellipsometer from Sopra, or our new in-house designed Large Aperture Projection Scatterometer,(developed specifically for fuel cell research)



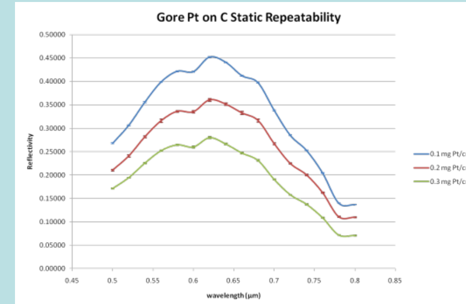
Benefits (Relevance): Provide PEM CCM and GDE manufacturers with an automated high-throughput approach for performing process control inspection of Pt loading with sensitivity equal to or better than that currently provided with XRF (and other parameters of interest simultaneously). Simulations will give insight and enable manufacturers to tune their measurement equipment to the parameters of interest. For dual side simultaneous catalyst coating operations, this method will provide the ability to concurrently perform Pt loading measurements on both sides of a CCM **independently** versus XRF, which is a "total" sample loading measurement.

Significant Past Accomplishments

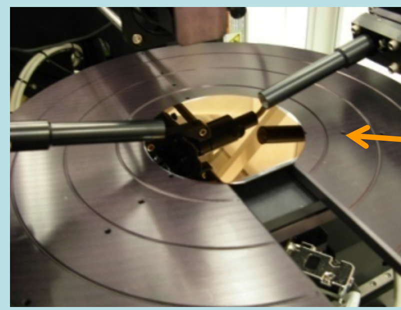
- Angle-resolved measurements of 3M PtCoMn NSTF CCM, demonstrating ~ 0.01 mg/cm^2 level sensitivity
- Angle-resolved measurements of 3M pure Pt NSTF CCM, demonstrating measurable sensitivity (not quite as good as PtCoMn results)
- Angle- and wavelength-resolved measurements of W.L. Gore samples, demonstrating sensitivities on order of 0.03 to 0.05 mg/cm^2
- Worked with 3M to generate various samples that allowed for optical property measurements of perylene
  - Successfully determined n & k of perylene
- Used this optical property data in simulations to demonstrate improved qualitative theory-to-experiment agreement
- Completed optical design of new Large Aperture Projection Scatterometer tool
  - Motivation; improve S/N ratio, engineer large diameter measurement area for higher throughput without compromising sensitivity, non-imaging reduces sensitivity to membrane vertical motion and sample variation



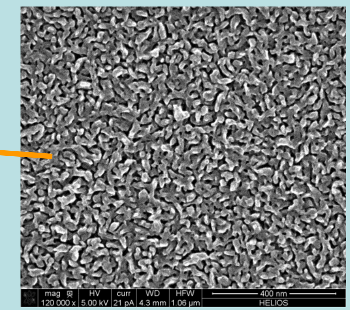
Angle-resolved scan of 3M PtCoMn samples, 150X, 3 location average



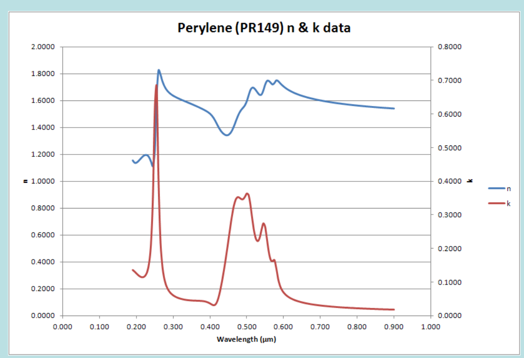
Wavelength-resolved scan of W.L. Gore Pt nanoparticle on Carbon, 150X, static repeatability



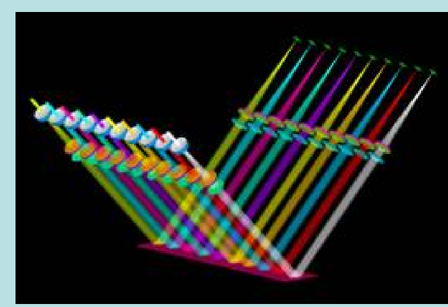
3M perylene sample on ellipsometer to measure n & k



SEM image of 3M perylene sample



n & k for bulk Perylene / PR149

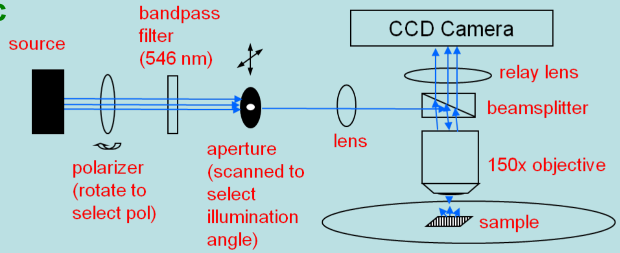


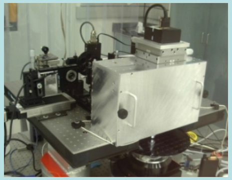
Optical design of Large Aperture Projection Scatterometer

Where we've been, where we're going, what's next?

Scatterfield Microscope

Schematic



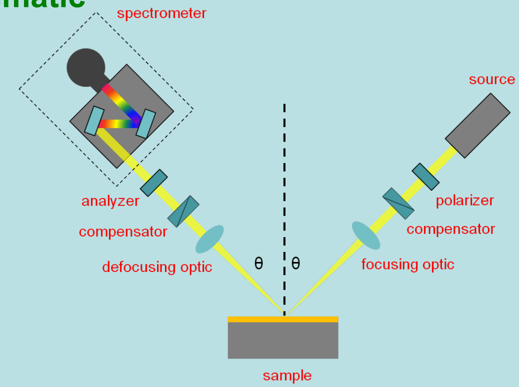


Instrument Photo

- **Started with this tool 4 years ago**
- Imaging / High-magnification / **(Small spot size)**
- Open architecture enables complete engineering of illumination and collection paths
- Can measure reflectivity of CCM samples as function of polarization, wavelength, and illumination/collection angle
- The fuel cell data we generate, for example, are images acquired as a function of illumination angle. (reflectivity calculated for each image is proportional to Pt loading)
- **Issues that needed additional study:**
  - Vertical motion of sample complications
  - S/N ratio improvement
  - Wavelength scan not ideal on OSM tool
  - Pt loading measurement sensitive to local defects and sample position
  - Dynamic loading measurements at webline speeds
  - Need to be able to measure optical properties of CCM materials

Spectroscopic Ellipsometer

Schematic



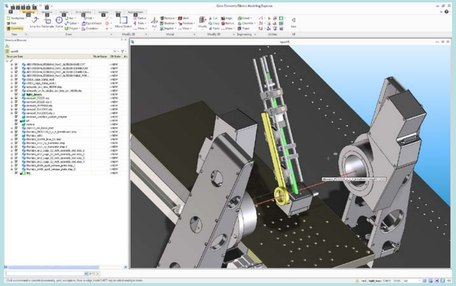
Instrument Photo

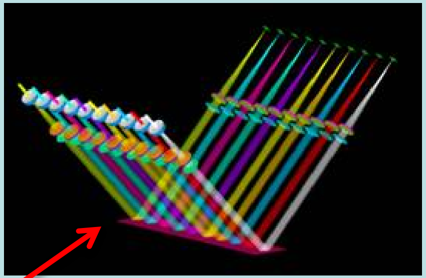
- **Purchased this tool 2 years ago** for optical property determination of fuel cell materials **(beam is focused, so it also has small spot size)**
- **Not an imaging tool**, measures changes in polarization of reflected light from sample
- Operates in two modes
  - Ellipsometer – measure optical properties
  - Scatterometer – measure reflectivity as function of angle and wavelength
- Successfully measured perylene optical properties
- Worked well in measuring Pt loading on Gore samples as function of wavelength
- **Following challenges remain:**
  - Vertical motion of sample potential problem
  - Pt Loading measurement sensitive to local defects and sample position
  - Dynamic loading measurements at webline speeds.

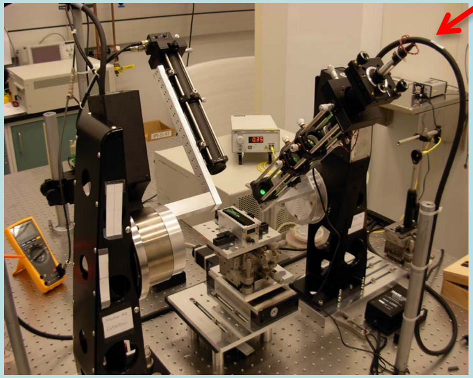
↓ DESIGNED AND BUILT NEW INSTRUMENT!!! ↓

Accomplishments 2012→2013 Construction of Large Aperture Projection Scatterometer (LAPS)

- **Constructed NEW LAPS instrument, specifically for fuel cell metrology research!!!**
  - **Primary motivation for building this tool**
    - Big spot size (adjustable) for large are data averaging
    - Better signal to noise (more powerful source, more sensitive detector)
    - Ability to make measurements at webline speed–high throughput
    - Ability to quantify the coupled vertical motion of membranes

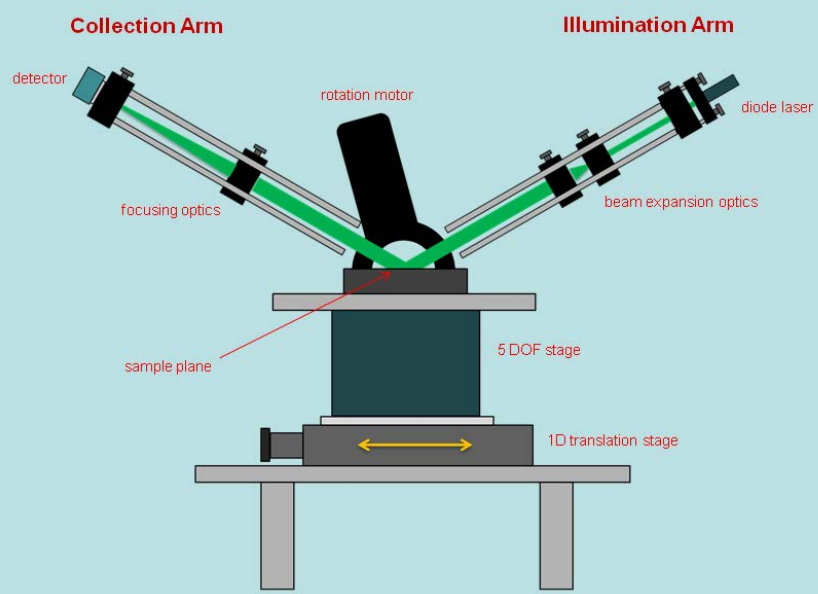




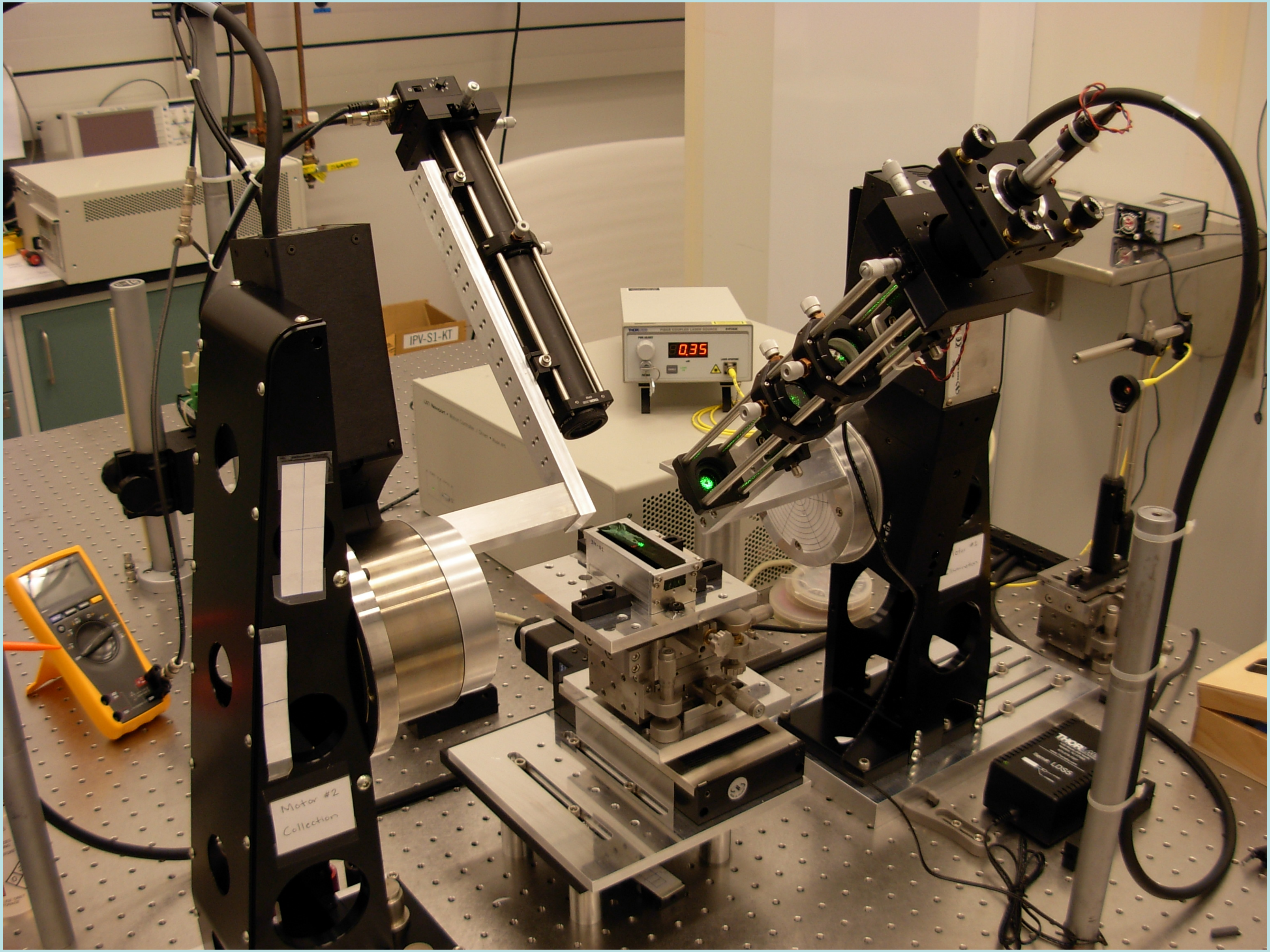


NOTE: This tool is just one segment in the multiple source / multiple detector design

- Completed mechanical design
- Procured instrumentation (~$40K)
- Fabricated required parts
- Developed optical and mechanical alignment procedures
- Aligned and tested tool
- Wrote LabVIEW motion control and data acquisition routines
- Took preliminary data on 3M and Gore CCM samples
- Optical tool is just coming online. A significant amount of characterization and calibration is required.

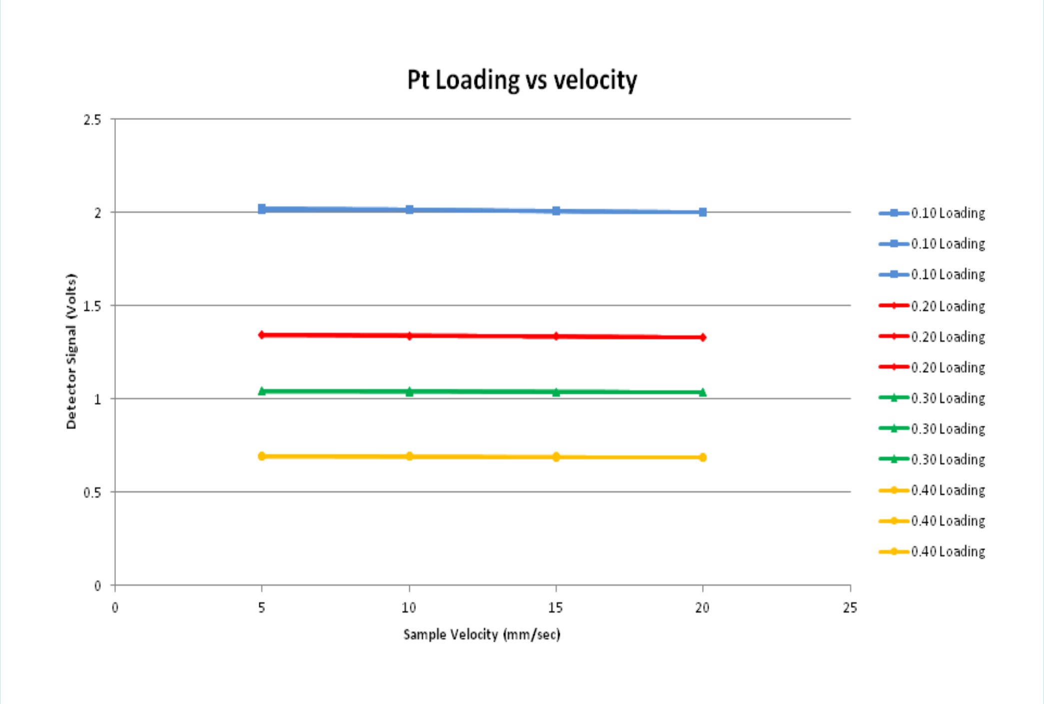


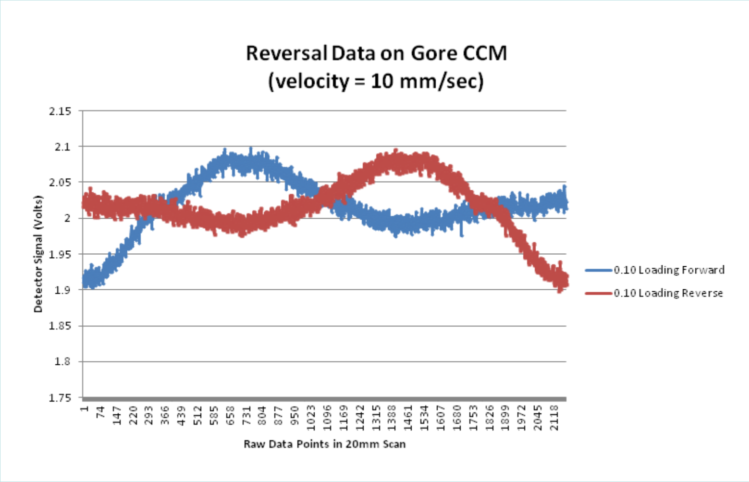
Accomplishments 2012→2013 Construction of Large Aperture Projection Scatterometer (LAPS)

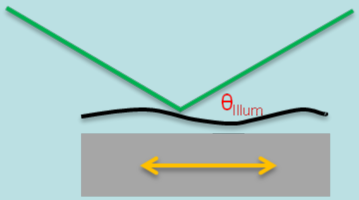


Accomplishments 2012→2013 LAPS Preliminary Dynamic Loading Measurement Data

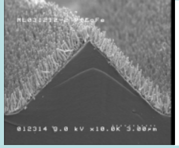
- **Gore CCM Pt Loading Dynamic Preliminary Measurements**
  - Measured W.L. Gore Pt on Carbon CCM samples (A510/M710.18/C510) as a function of velocity, simulating a 1 ft/min to 4 ft/min webline.
  - Sample loadings were 0.10, 0.20, 0.30, and 0.40 mg Pt/cm^2.
  - Good sensitivity and repeatability, no dependence on velocity
  - Measured intensity as a function of step number shows slight variability in forward and reverse scans
    - Likely due to local changes in illumination angle of incidence, caused by sample buckling



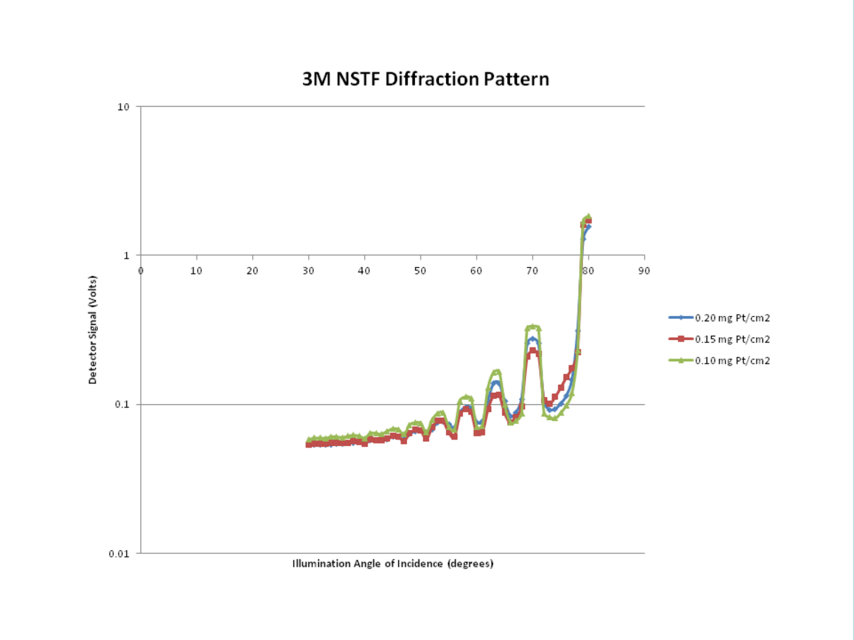




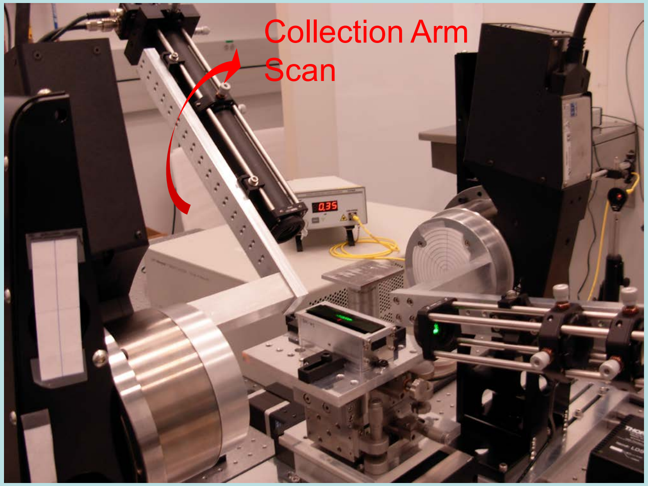
Accomplishments 2012→2013 3M NSTF Diffraction Pattern

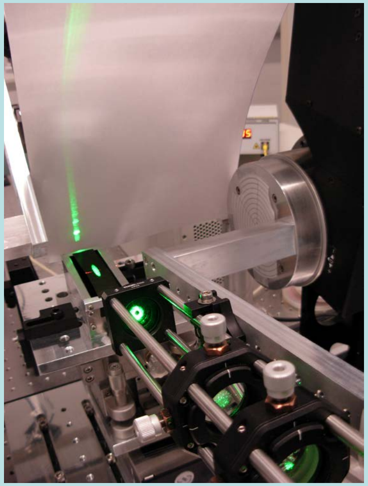


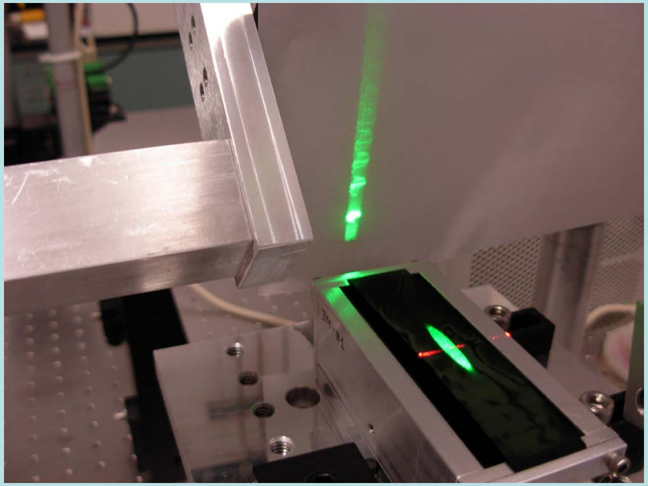
- **Measurement of 3M NSTF Diffraction Pattern**
  - We have successfully measured the diffraction pattern as a function of Pt loading. The samples are PtCoMn NSTF.
  - The diffraction presents a new measurement challenge that requires further study
  - The amplitude of different peaks contains key info about the materials and surface
  - In this particular measurement, the Illumination Arm is held at 80 degrees and the Collection Arm is scanned from 80 to 30 degrees.
  - Studying this effect to determine the best method to measure it effectively is a priority.
  - Notice certain peaks show excellent sensitivity



Note data plotted on log scale!







Collaborations and Interactions

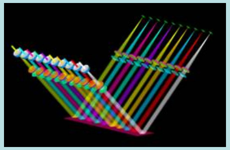
- Continued collaborations with **3M Company** and **W. L. Gore** to further develop and advance OSM and LAPS as a viable manufacturing metrology solutions for performing Pt Loading measurements as well as defect detection measurements.
- Engaging in R&D discussions with **leading semiconductor metrology toolmaker** for future collaborations to develop real OSM or LAPS process control prototype measurement system.

Summary

- In past accomplishment reports, we have successfully demonstrated Pt loading measurement sensitivities at the level of competing technologies
- **There remains significant work to properly measure the optical properties** of the CCM constituent materials to enable accurate simulations for quantitative theory-to-experiment agreement. For this methodology to become a robust effective metrology solution, we need to be able to accurately model the samples to generate quantitative simulation data.
- To further understand the underlying measurement science and develop the necessary rigor, we designed and built a custom optical metrology tool (Large Aperture Projection Scatterometer). The tool is now operational. We still need to comprehensively characterize and calibrate this tool.
- We have acquired preliminary LAPS data on Gore (as function of velocity) and 3M (diffraction pattern) samples.
- This new tool will be used to measure large format samples at typical webline speeds.
- Develop a quantitative understanding of the causes when non-monotonic trends in the data appear when plotting reflectivity versus the scanned parameter. (i.e., reflectivity and loading relationships need to follow predictable trends).

Future Work

- The most pressing challenge to achieving quantitative fuel cell manufacturing is to develop the simulation infrastructure to enable the underlying rigor with acceptable uncertainties and sensitivities. Although we have demonstrated initial theory to experiment data fits, different manufacturers using different methods and materials for their membranes require adaptability of the methodology. This means a flexible model that allows different geometrical parameters and normalization procedures. Once a robust modeling and fitting algorithm has been established, the method is generally broadly applicable to different membrane types.
  - It should be noted that the same modeling and data fitting procedures have been broadly applied to three dimensional nanometer structures for the semiconductor manufacturing industry and achieve sub-nanometer uncertainty and sub-nanometer resolution
- A multiple-beam and dual-side LAPS hardware architecture capable of dramatically increasing throughput will require significant further design work and research.
- Continue working with industrial collaborators to create samples that allow optical property measurements of CCM constituent materials. The next materials to characterize are the actual proton exchange membrane (Nafion® and 3M membrane) and amorphous carbon.
- Finish characterizing and calibrating the LAPS tool
- Measure larger format samples at webline speeds. We already have another stage (Newport XMS160) to integrate that will increase travel to 6 inches and speeds in excess of 30 ft/min.
- Answer outstanding questions regarding the diffraction and scattering of the periodic 3M NSTF samples and optimize for Pt loading determination.
- Demonstrate quantitative theory-to-experiment agreement on traditional carbon/Pt nanoparticle and 3M NSTF CCMs
- Continue to investigate applicability of OSM and LAPS to fuel cell defect detection. Solicit industry input as to the types/sizes/distributions of defects that cause real performance losses
- Publish OSM fuel cell results in refereed journal

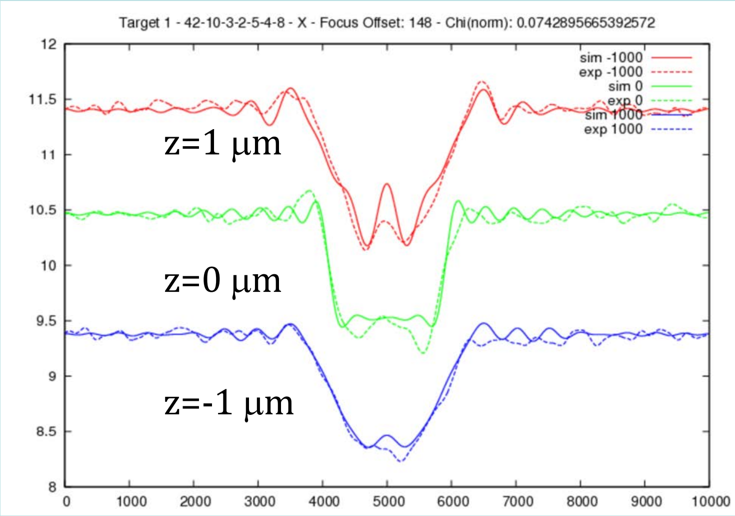


Technical Backup Slides

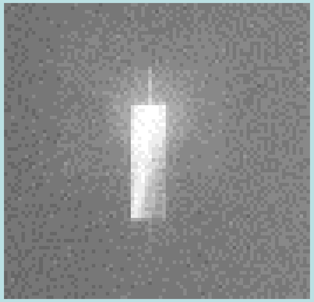
Example of exceptional theory-to-experiment agreement in our semiconductor research efforts

Illumination: X-polarized light

14 nm linewidth theory-to-experiment

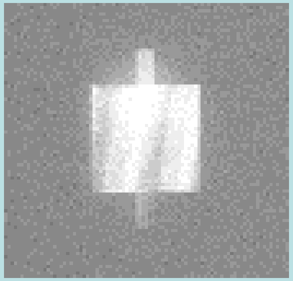


Best Fits: 5 nm SiO_2 cap
45 nm Si height
7 nm at 1.0h
11 nm at 0.8h
14 nm at 0.5h
16 nm at 0.3h
24 nm at base

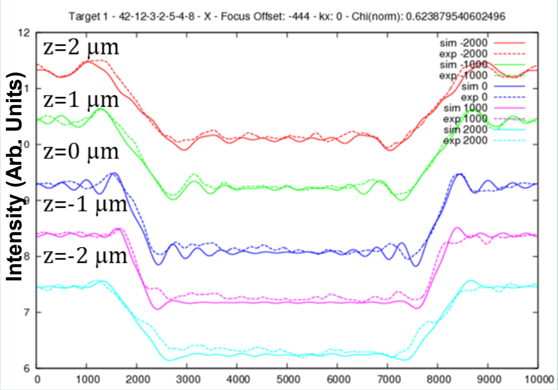


SEM image of sub-wavelength 30 line target

16 nm linewidth theory-to-experiment

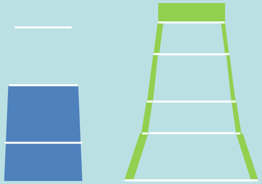


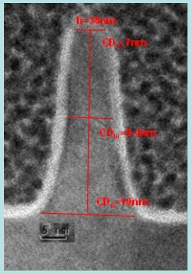
SEM image of sub-wavelength 100 line dense targets



	Target 1
Height (nm)	42 ± 0.024
CD [1.0 h] (nm)	9
[0.8 h](nm)	13
[0.5 h] (nm)	16 ± 0.017
[0.3 h] (nm)	18
[0.0 h] (nm)	26

16 nm CD, 100 line arrays – experimental fits with uncertainties.



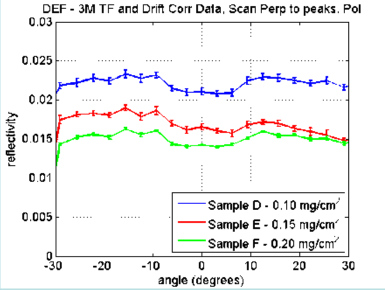


Parametric model

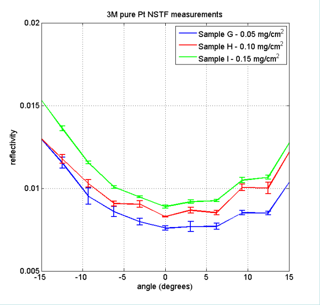
Significant Past Accomplishments

Experimental sensitivity on

- Sample Loadings: 0.10, 0.15, and 0.20 mg/cm^2
- 2010 AMR demonstrated successful application of approach to measurement of catalyst loading (**sensitivity ~ 0.01 mg/cm^2**)
- GO decision for continued work



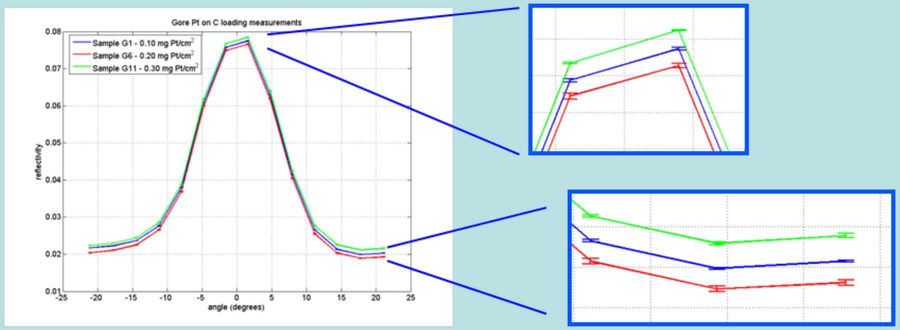
Angle-resolved scan of 3M PtCoMn samples, 150X, 3 location average



Angle-resolved scan of 3M pure Pt samples, 150X, 3 location average

2nd Sample Package: Pure Pt NSTF CCM

- Sample Loadings: 0.05, 0.10, 0.15 and 0.20 mg/cm^2
- 2010 AMR demonstrated sensitivity
- Pt loading determination feasible for pure Pt samples, but not as good as the PtCoMn samples.

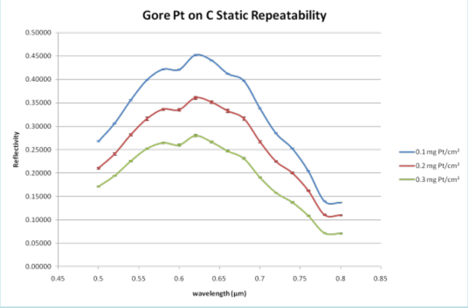


Angle-resolved scan of W. L. Gore Pt nanoparticle on Carbon, 150X, 3 location average

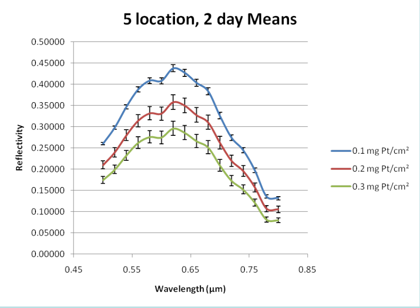
3rd Sample Package: W.L. Gore Pt nanoparticle on Carbon CCM (A510/M710.18/C510)

- Sample Loadings: 0.10, 0.20, 0.30, 0.40 mg/cm^2
- Made angle-resolved measurements on SF tool, demonstrated sensitivity on the order of 0.03 to 0.05 mg/cm^2
- Performed wavelength-resolved measurements on in-house ellipsometer, demonstrated sensitivity on the order of 0.03 to 0.05 mg/cm^2
- Further experimental work and model simulation needed to achieve 0.01 mg/cm^2

a)

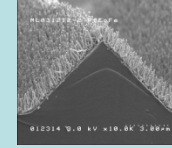


b)



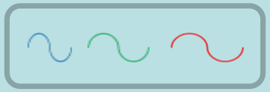
Wavelength-resolved scan of W. L. Gore Pt nanoparticle on Carbon, 150X, a) static repeatability for 3 locations 5 times each, b) reproducibility for 5 locations over 2 day period

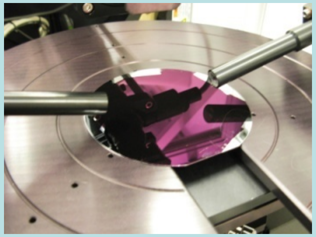
Accomplishments 2011→2012 Perylene Optical Properties

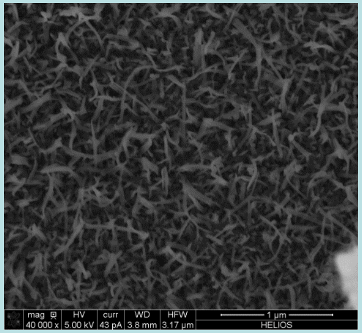


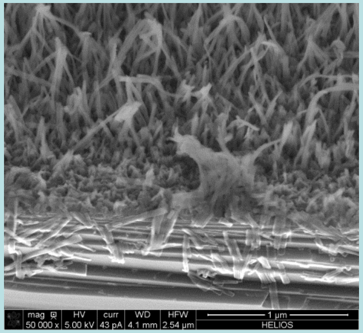
- **Working Towards Accurate CCM E&M Scattering Models**
  - Collaborating with 3M to generate samples that enable measurement of optical properties of CCM constituent materials. We need **accurate inputs** for the models.
- **2011 1st 3M Perylene/PR149 (Annealed) Sample Set**
  - Made spectroscopic ellipsometry (SE) baseline measurements of six 4” Si wafers and provided to 3M for creating Perylene (PR149) samples
  - Sample set: 3 wafers with 1500 Å coating and 3 wafers with 1800 Å coating
  - Acquired SEM data on samples
  - Performed SE measurements on samples to obtain perylene n & k
  - **Measurements difficult** and limited by spatial dimensions of the surface texture
- **2012 2nd New 3M Perylene/PR149 (Unannealed) Sample Set**
  - Provided another round of 4” Si wafers to 3M for new round of samples without annealing. These will give us information about the **bulk properties** of Perylene.
  - Acquired SEM data on samples
  - Performed SE measurements (see subsequent slide)

Scale of surface spatial variations on the same order as the wavelengths



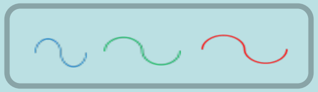


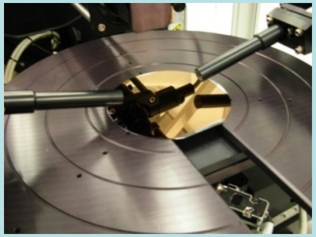


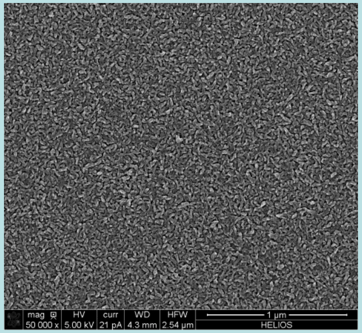


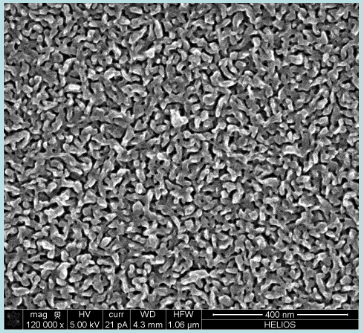
1st 3M Perylene (Annealed) Sample set

Scale of surface spatial variations less than the wavelengths





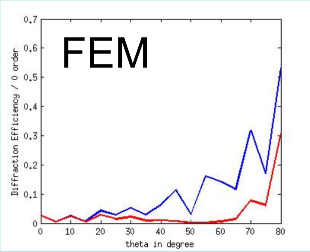


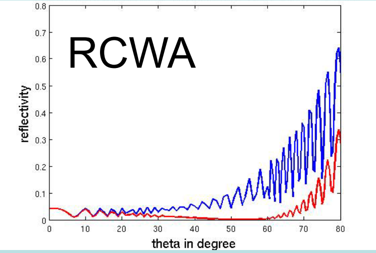


2nd 3M Perylene (Unannealed, No Whiskers) Sample set

Accomplishments 2011→2012 – CCM E&M Scattering Modeling

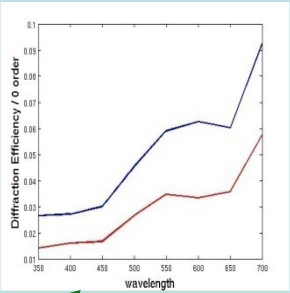
- **Comparing 2D RCWA and 2D FEM model outputs for 3M NSTF CCM**
  - Simulation: 0.250 μm EMA catalyst layer on top a 20 μm finite Ionomer substrate, angle-resolved at 450 nm wavelength
  - Both polarizations (blue – s pol, red – p pol) trend the same direction with similar reflectivity values as a function of angle.
  - The increased number of oscillations in the RCWA output is a result of the thin-film interferometric effect from the bilayer.
  - The oscillations are part of the motivation for investigating the **effect of roughness**

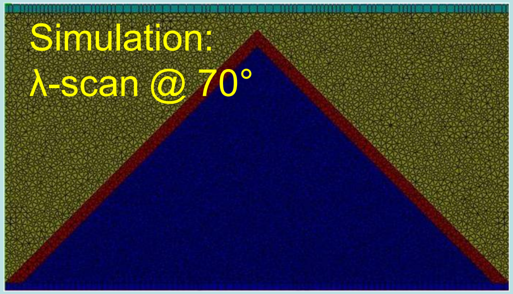




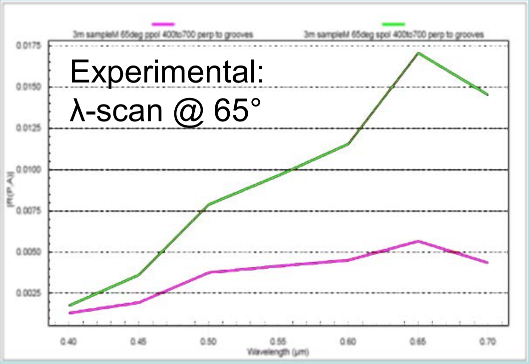
2D FEM vs 2D RCWA model agreement

- **Theory to Experiment Agreement for 3M NSTF CCM**
  - **Simulation data**: 2D Wavelength scan of triangle structure with catalyst layer (in red) set to 0.1 mg Pt/cm^2, incorporating **new Perylene n & k data**
  - **Experimental data**: Wavelength scan of 3M NSTF CCM with 0.1 mg Pt/cm^2 loading using commercial spectroscopic ellipsometer
  - **Promising agreement**, data trends the same as function of λ at illumination angle of incidence of 70° , other angles of incidence give very different reflectivity values

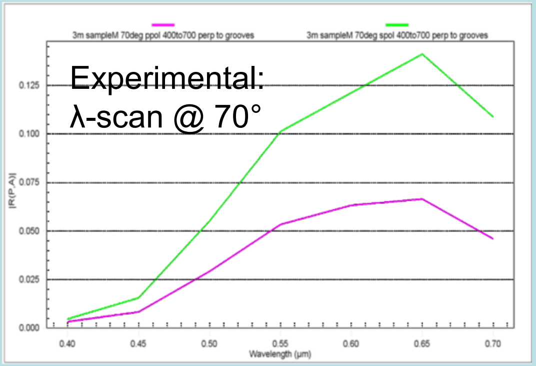




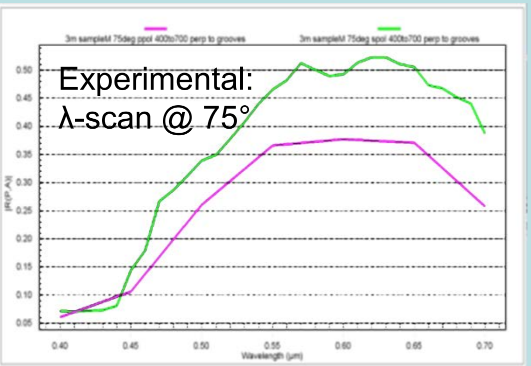
Qualitative Agreement



10X less ←

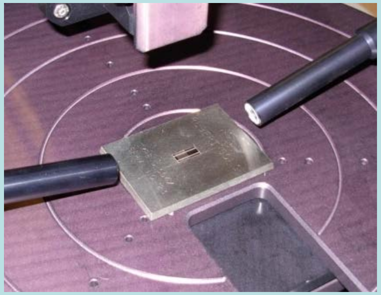
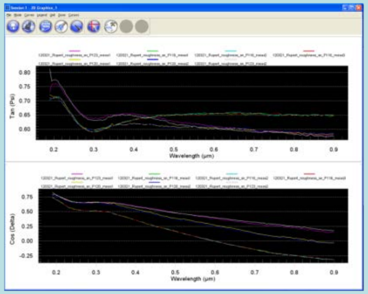


5X more →



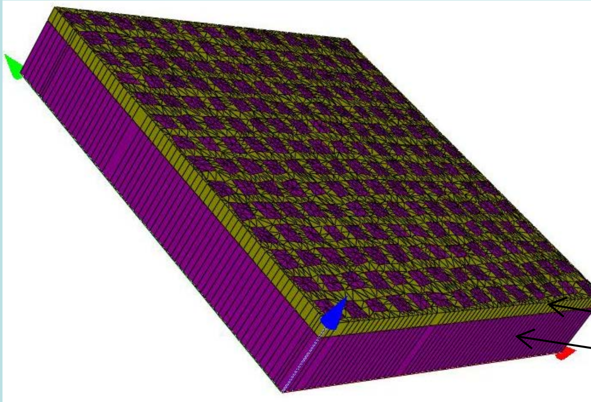
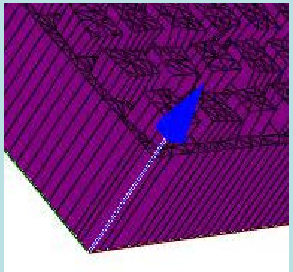
Accomplishments 2011→2012 Roughness Measurements and Simulation

- **2011 Experimental Roughness Measurements**
  - Acquired 3 Rupert electroformed Nickel roughness samples with random roughness profiles. The samples have Ra values of 34.5 nm, 87.9 nm and 129.9 nm.
  - Performed ellipsometric measurements on these samples. Fitting of the data is underway.
  - Completion of this task will aid in **quantifying the effect of roughness** on SE and OSM type measurements of CCMs.

Roughness measurements on Rupert samples

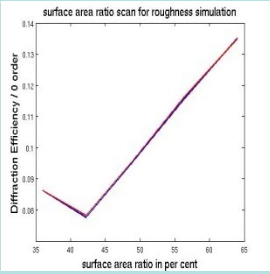
- **2012 Modeling Roughness for CCMs**
  - Built structure to enable simulations for quantifying roughness effect on CCM Scatterfield measurements. Purple is an effective medium approximation (EMA) with Pt, Perylene, Air, and Ionomer. Gold is Air.
  - Ran simulations varying the pillar cross-sectional area and varying illumination angle of incidence. Change in specular reflection observed as a function of these variations.
  - Results are **preliminary** and no quantitative conclusions have been drawn at this point.

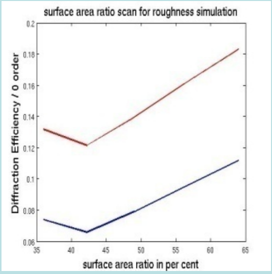
- 50 nm tall pillars
- 200 nm effective medium

Structure to model CCM surface roughness

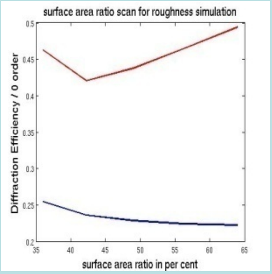
Θ = 0



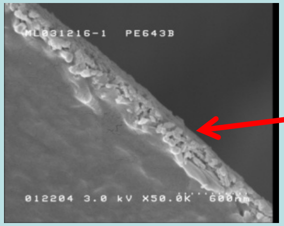
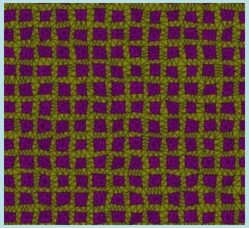
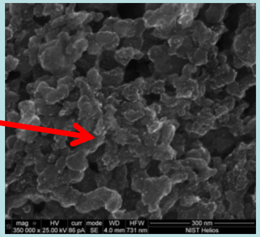
Θ = 30



Θ = 80



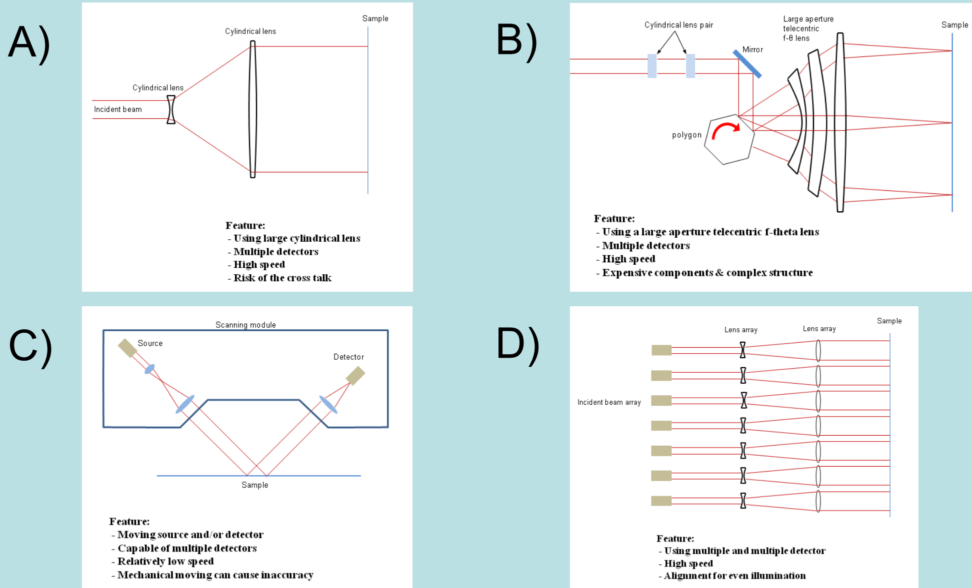
Roughness effect on reflectivity as function of grain size and illumination angle of incidence

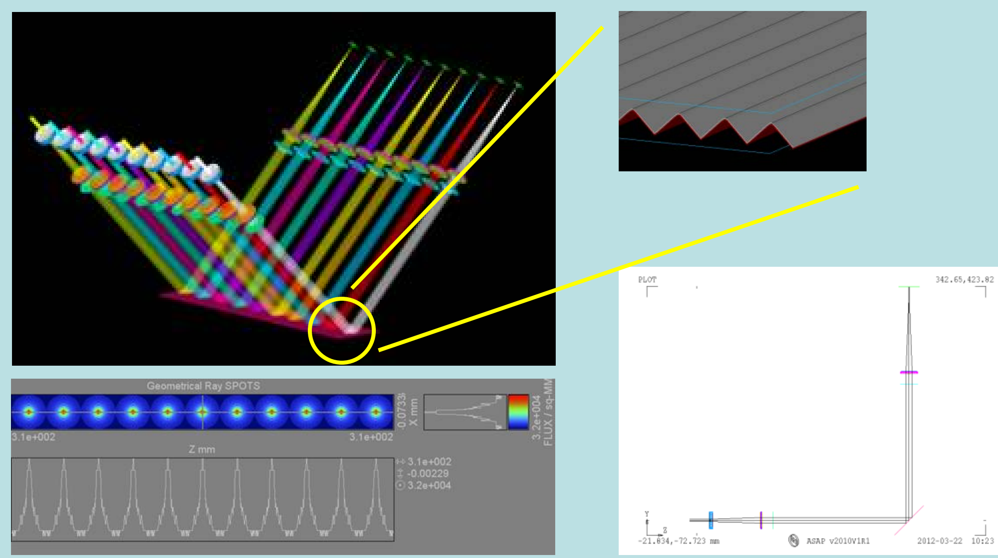
Varying pillar cross-section to simulate CCM roughness

Optical Design of Large Aperture Scatterometry (LAS) system prototype for Fuel Cell CCM Pt Loading Measurements

- **LAS Optical Design**
  - For Pt loading measurement, we are investigating a scatterometric approach (No high-magnification)
  - Still has advantages of acquiring data as function of wavelength, polarization, and angle of incidence
  - Completed design study, arriving at four possible LAS configurations, factoring in field of view, web area of coverage, wavelength, sample reflectance, etc.
    - A) Wide Illumination Beam
    - B) Scanned Illumination Beam
    - C) Single Source and Detector
    - D) Multiple Source and Detector
  - Performed a **complete optical design of** configuration **D)**.
  - Prototype Parts purchased
  - Initial data expected by AMR 2012 meeting. Will perform dynamic Pt loading measurements as a function of web speed (simulating a real web by moving sample on a programmable stage)



Four Possible LAS Design Configurations



Complete Optical Design of LAS configuration D)