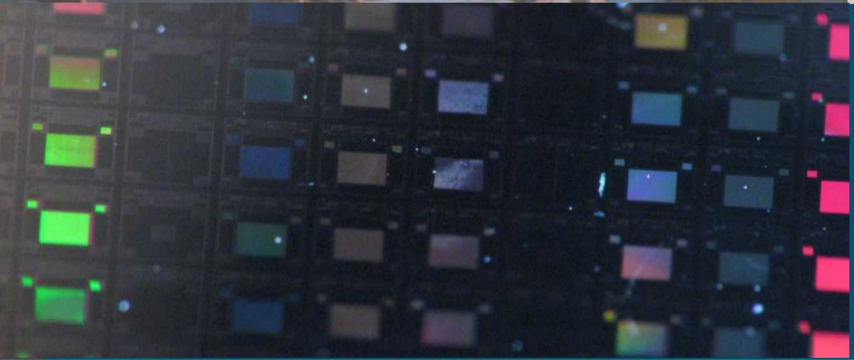
Presenter:
Josefine McBrayer

SAND2020-10388C



Exploring Moiré Interferometry as a Tool to Measure Strain in the Silicon Anode of a Lithium Ion Battery

ECS PRiME Fall 2020: October 4th – October 9th 2020

Poster Presentation: A02-0265

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Department of CHEMICAL ENGINEERING
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NNSA National Nuclear Security Administration
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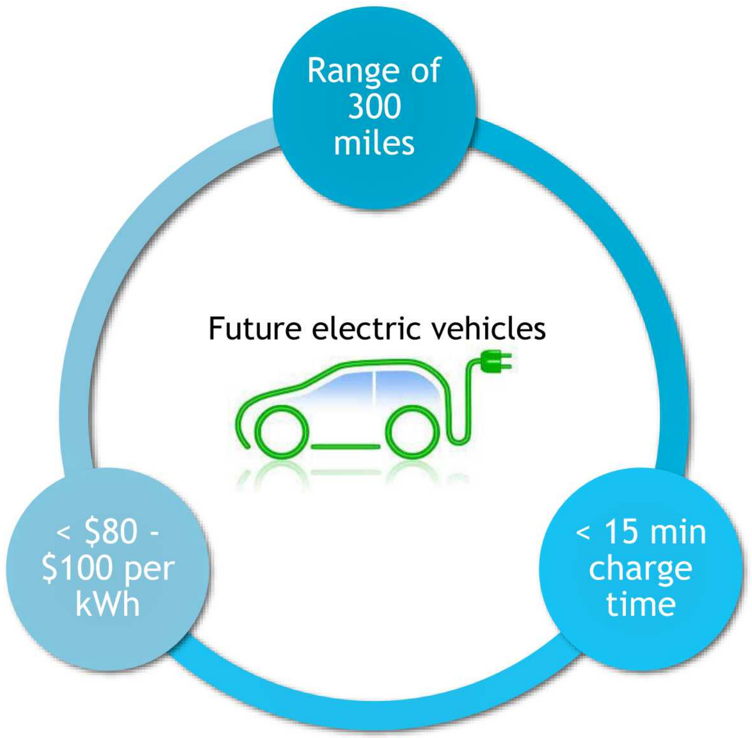
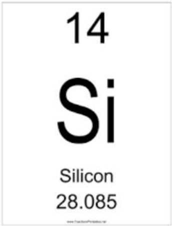
Importance of Lithium Ion Batteries

- Widespread use in personal electronics
- Part of the United States Vehicle Technology Office's goals for electric vehicles
- Current lithium ion battery energy densities are limited by the anode material



https://www.energy.gov/eere/vehicles/batteries-charging-and-electric-vehicles
https://ec.europa.eu/jrc/en/news/fiscal-incentives-how-do-they-impact-electric-vehicle-sales

Silicon Anodes in Lithium Ion Batteries



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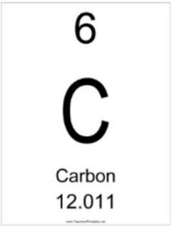
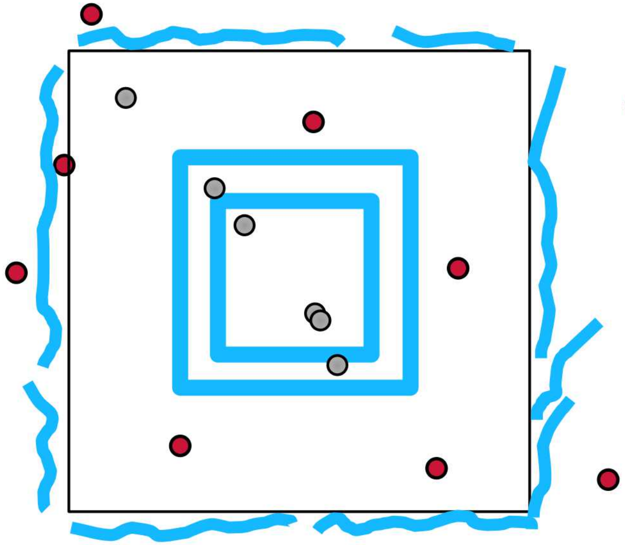


Lithium storage
- 4.4 Li atoms per Si
- 0.17 Li atoms per C

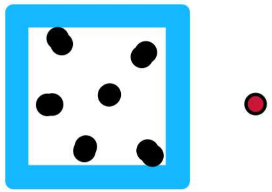
Over 300% expansion upon lithiation
Unstable solid electrolyte interphase (SEI)

High specific energy
Long cycle life
Low self discharge



> 300% expansion

Silicon
3,579 mAh/g



Graphite
372 mAh/g

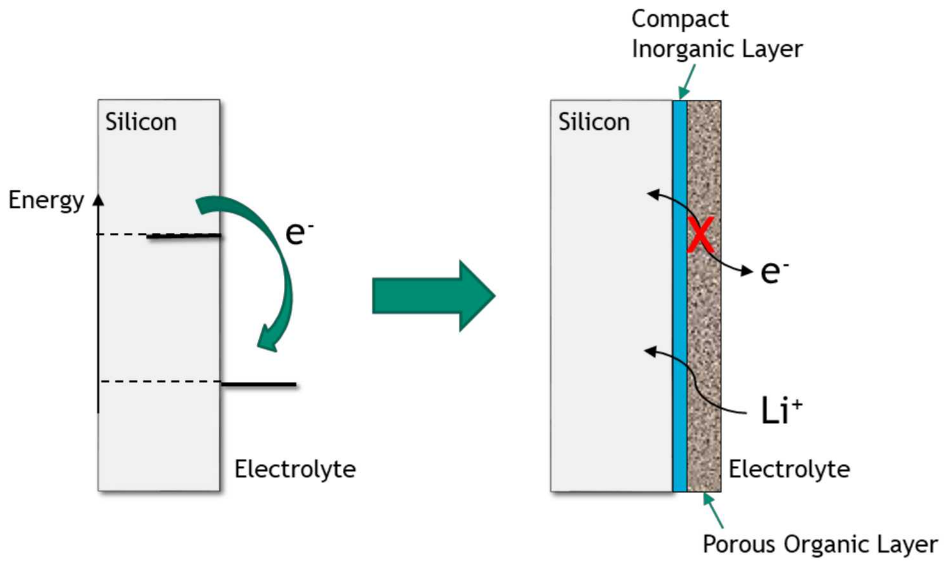
● Carbon
● Lithium
● Silicon

J. Ryu, et al. *Nano Res.*, vol. 10, no. 12, pp. 3970–4002, 2017. J. Lu, et al. *Electrochemical Energy Reviews*, **1**, 35 (2018).
https://www.energy.gov/eere/vehicles/batteries-charging-and-electric-vehicles

Solid Electrolyte Interphase

- Solid electrolyte interphase (SEI): passivating film that forms on the anode of the battery due to the reduction of the electrolyte
  - Ideally, lithium ions can pass through the SEI while electrons cannot
- The SEI on silicon degrades mechanically and chemically resulting in poor battery performance

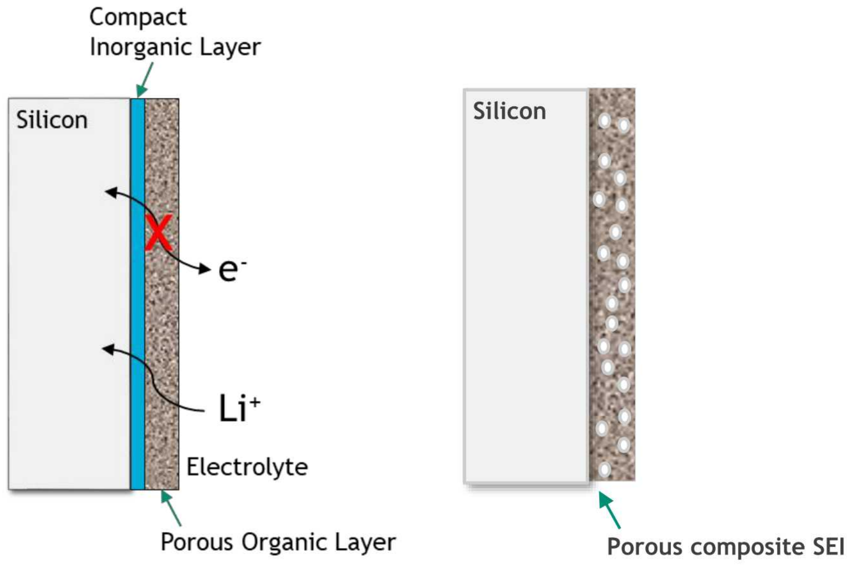
Formation of the SEI due to the reduction of the electrolyte

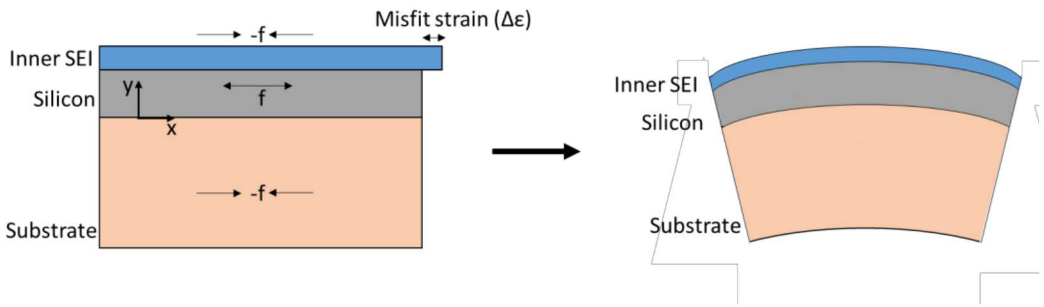


D. Aurbach, et al. *J Power Sources*, **81**, 95 (1999).

SEI Mechanics

- The SEI failure mechanism has not been proven directly
  - Is the current two layer model correct?
- Constraint of the thin film from the current collector drives the stress response, but thin films allow for simpler mechanical analysis
- A common assumption/observation in literature is that silicon expansion as the silicon is lithiated, occurs only in z-direction for thin films
- This won't necessarily be the case as we move towards slurry systems
  - Can we keep a simplified system to study the SEI while preventing or decreasing constraint from current collector for comparison purposes?

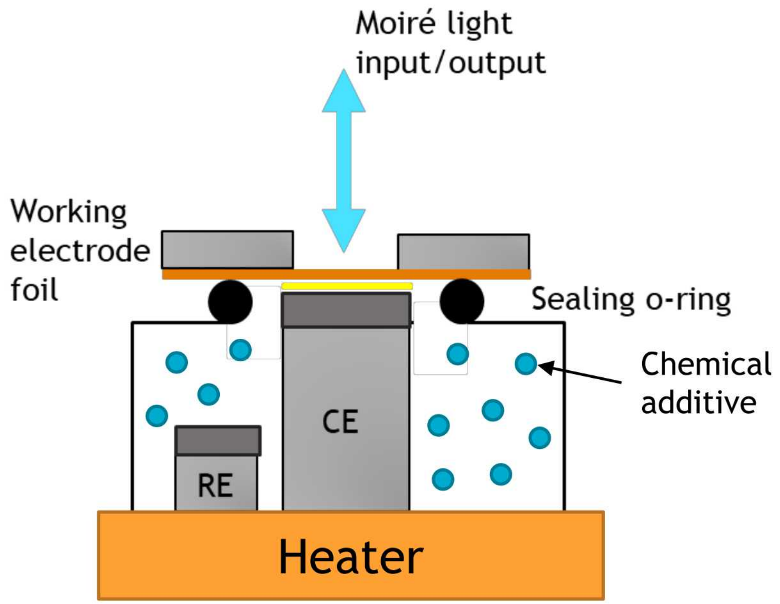




W. Zhang, T. H. Cai and B. W. Sheldon, *The Impact of Initial SEI Formation Conditions on Strain-Induced Capacity Losses in Silicon Electrodes*, *Adv Energy Mater*, **9** (2019).

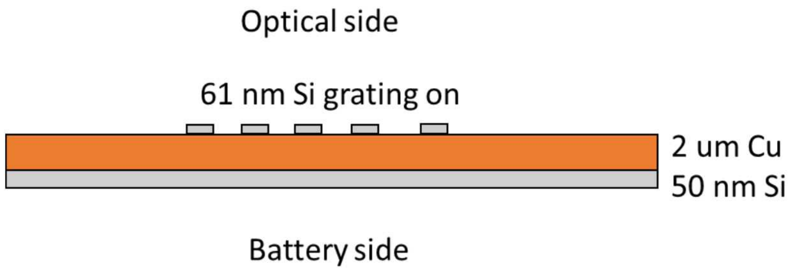
Approach Explored

- By decreasing the thickness of the substrate/current collector, is it possible to more clearly observe strain from the back-side of the current collector due to the SEI?
- Can we develop the ability to see small changes in the strain due to changes in the SEI while maintaining a simplified thin film system?
  - Additives, temperature, initial exposure to electrolyte, etc.
- Can we study the in-plane strain change due to SEI prior to lithiation while out of plane changes will dominate during lithiation



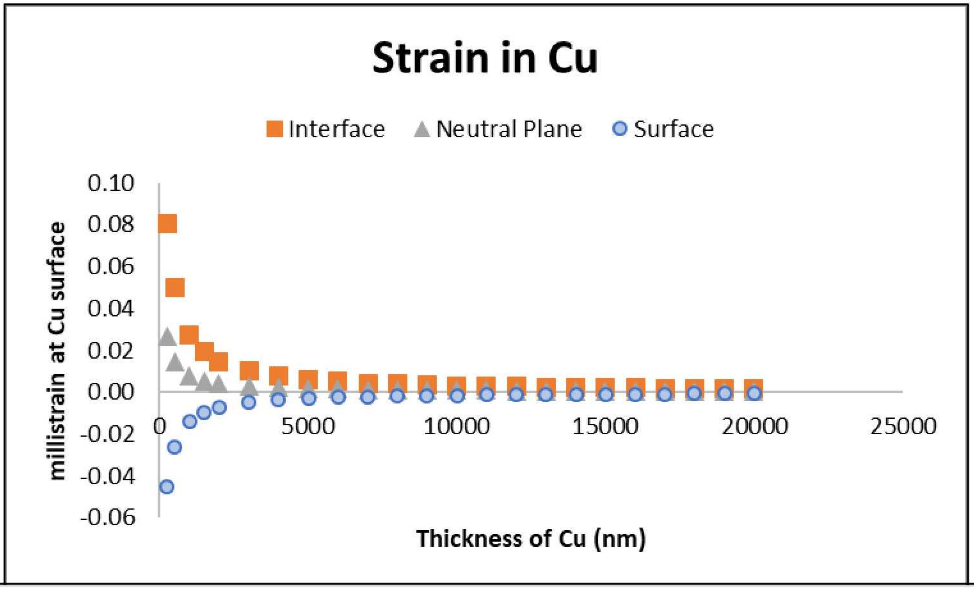
Thin Film Theory: Copper as a Substrate

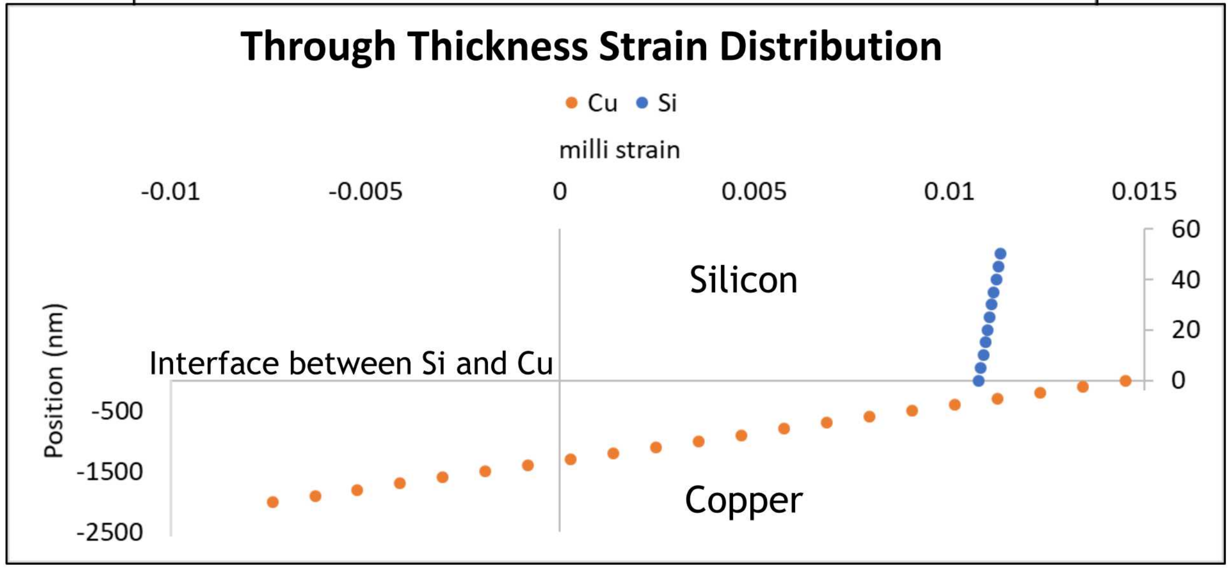
- What level of resolution is required for a back-side technique to be able to see changes due to the SEI?
- With 2 μm thick copper, expect ~ 10 ppm, with 500 nm thick copper, expect ~ 35 ppm strain



Parameters:

misfit strain (Δε)	0.01
E, silicon (GPa)	90
E, Cu (GPa)	128
E, SEI (GPa)	5
h, SEI (nm)	20
H1, silicon (nm)	50
H2, Cu (nm)	2000





K. Guo, R. Kumar, X. C. Xiao, B. W. Sheldon and H. J. Gao, *Failure progression in the solid electrolyte interphase (SEI) on silicon electrodes, Nano Energy*, **68** (2020).

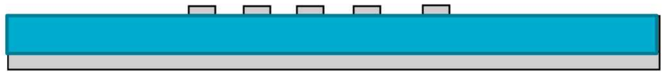
Thin Film Theory: Changing the Modulus of the Substrate

- Alternatively, the substrate modulus can be decreased to enhance the strain observed on the back-side of the electrode

$$\kappa = \frac{6E_s'E_f'(h_f+h_s)h_fh_s\Delta\epsilon}{E_f'^2h_f^4+4E_s'E_f'h_f^3h_s+6E_s'E_f'h_f^2h_s+4E_s'E_f'h_fh_s^3+E_s'^2h_s^4}$$

Optical side

61 nm Si grating on



Substrate
Cu current collector
50 nm Si

Battery side

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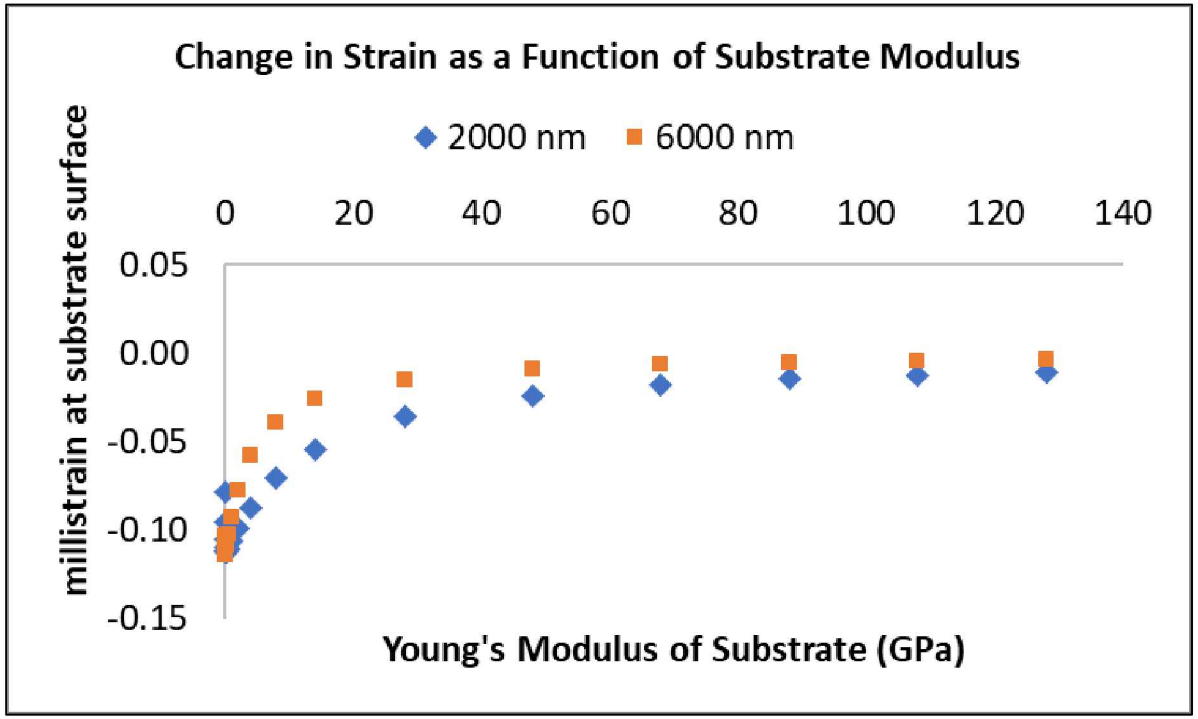


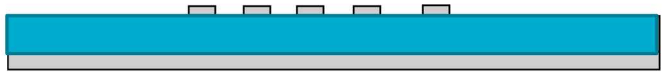
K. Guo, R. Kumar, X. C. Xiao, B. W. Sheldon and H. J. Gao, *Failure progression in the solid electrolyte interphase (SEI) on silicon electrodes*, *Nano Energy*, **68** (2020).

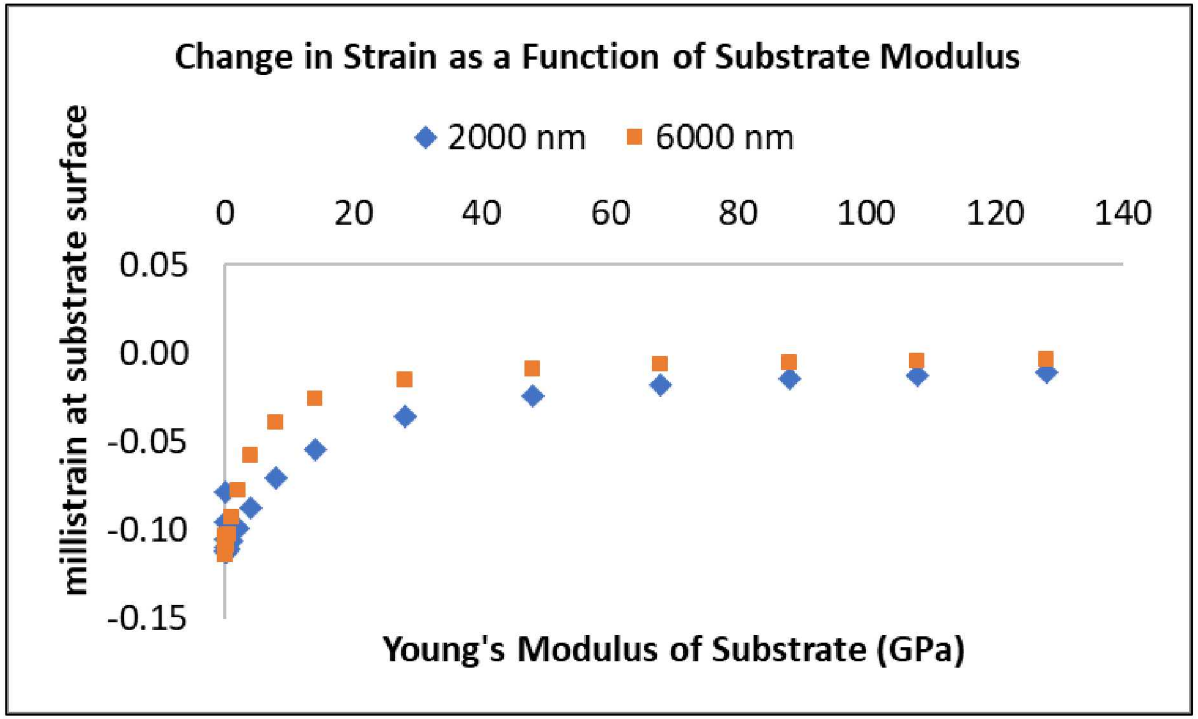
Lambert Ben Freund and Subra Suresh. Thin film materials: stress, defect formation and surface evolution. Cambridge university press, 2004.

Thin Film Theory: Changing the Modulus of the Substrate

- Alternatively, the substrate modulus can be decreased to enhance the strain observed on the back-side of the electrode

Improving sensitivity to back-side measurements can be achieved by using a thinner substrate and is furthered by decreasing substrate modulus





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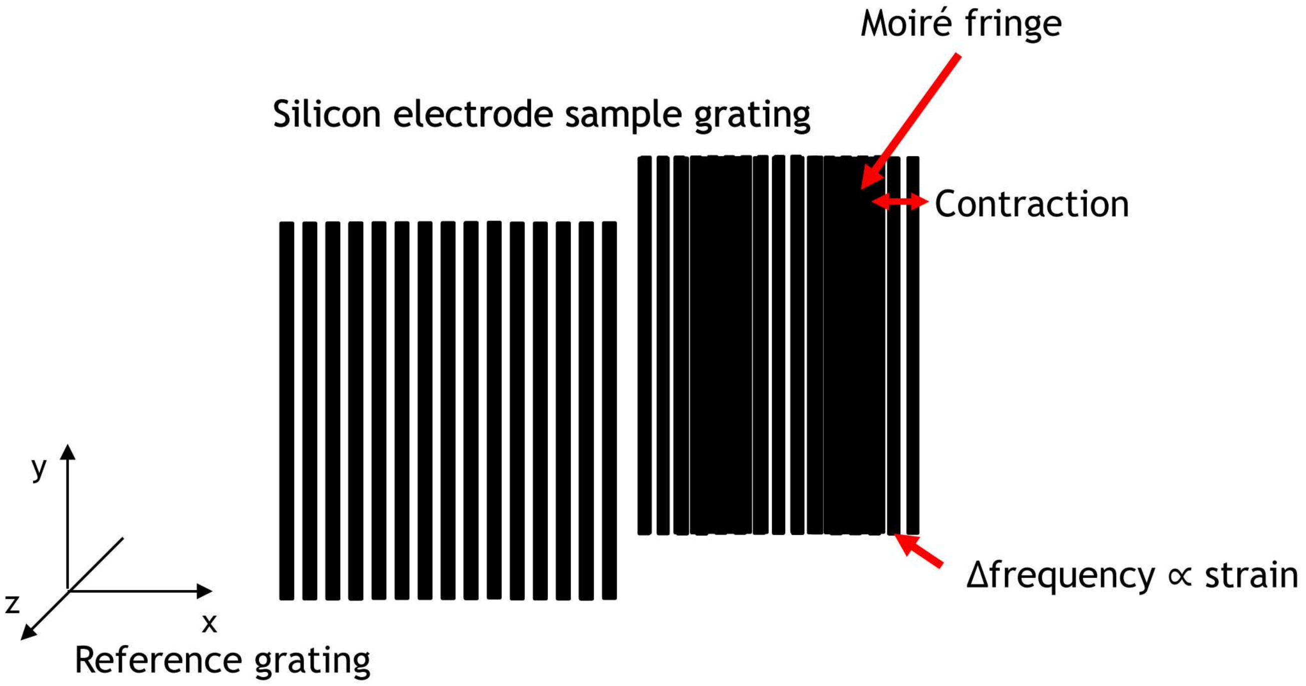
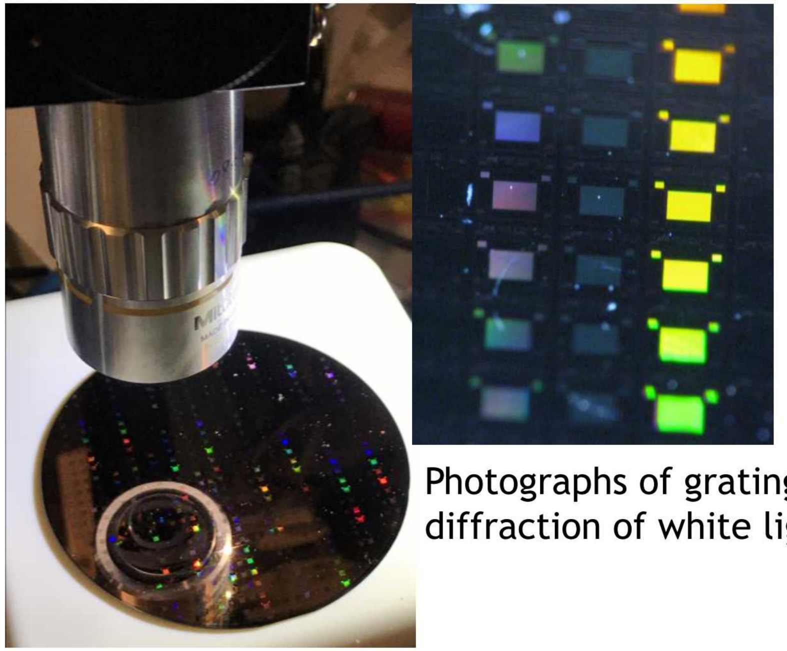
How Moiré Microscopy Works

- Moiré fringes are formed when two similar gratings are overlaid and are offset
- Why use moiré microscopy?
    - Minimal change to the system
    - Simple instrumentation
    - Direct measurement of in-plane strain as compared to curvature measurements
    - Strain resolution beneath the diffraction limit of light

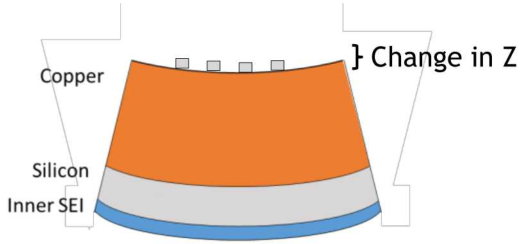




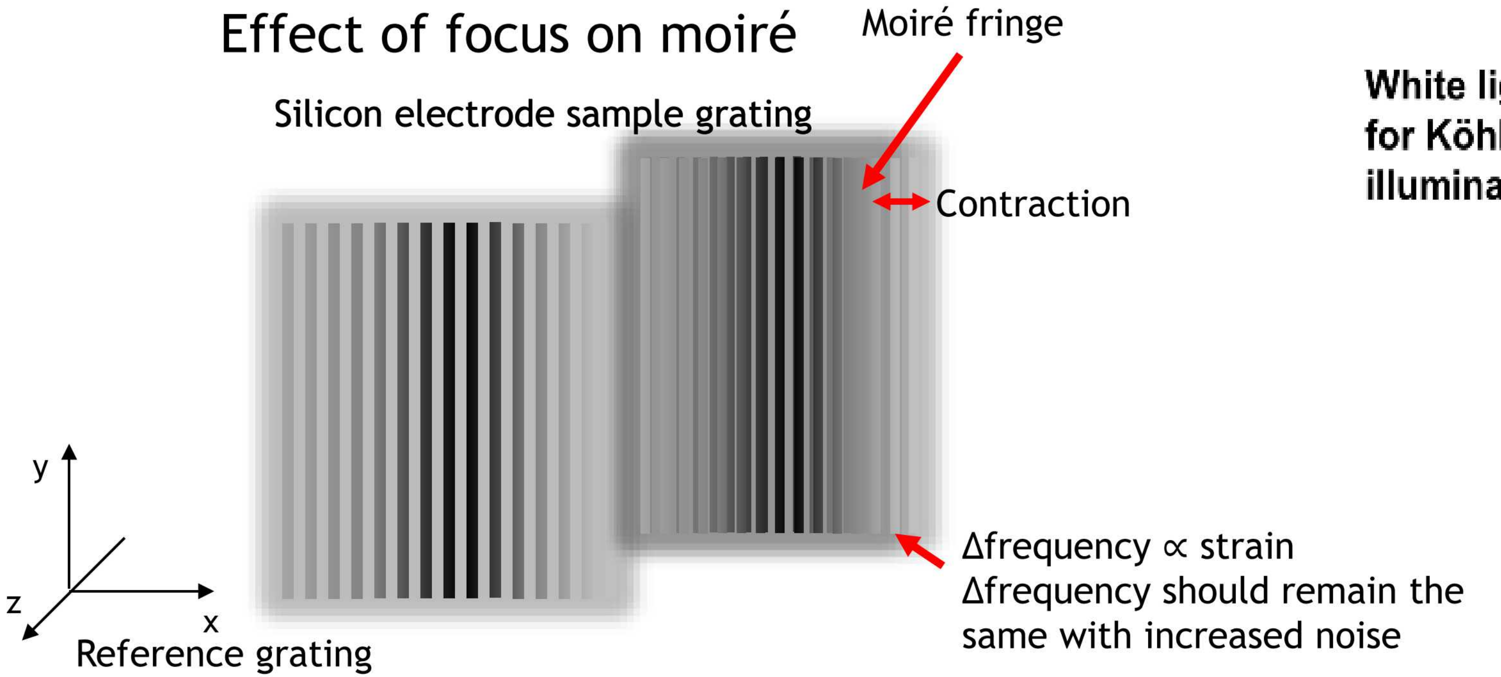
Photographs of gratings showing diffraction of white light

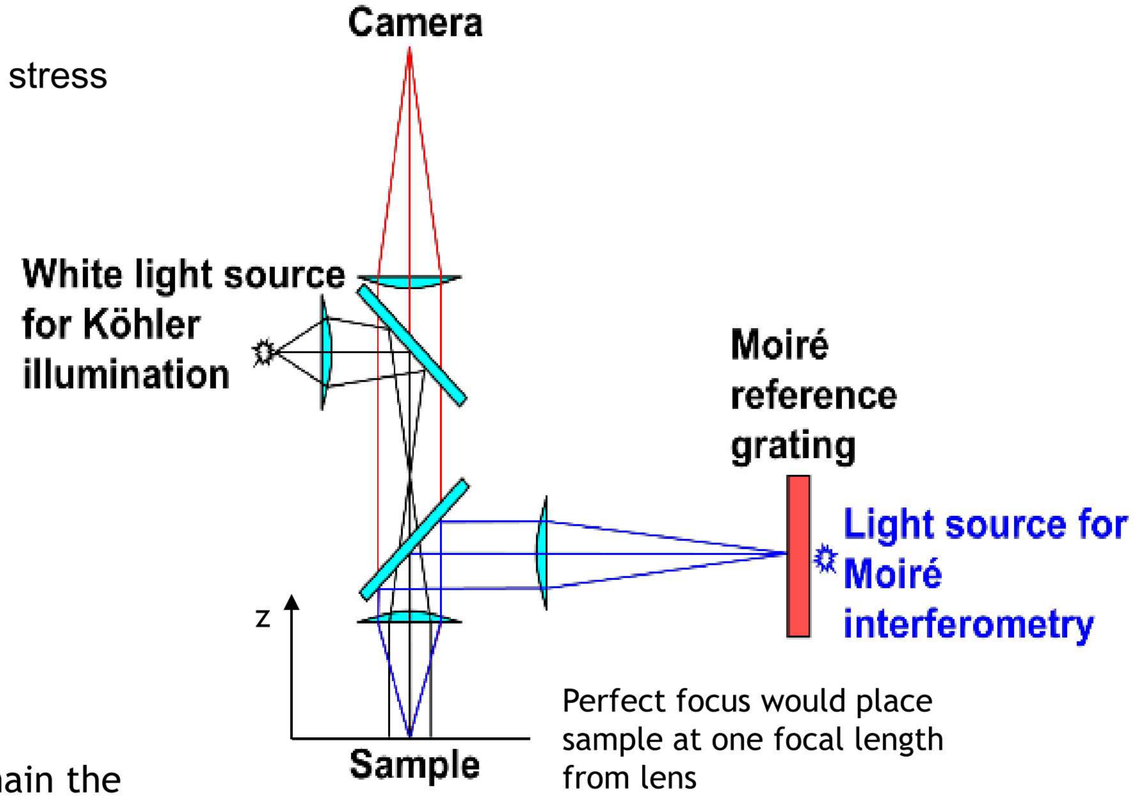
How Moiré Microscopy Works

- In this presentation, Z focus will be discussed
  - Synonymous terms: focus, Z position
- Z position is the direction normal to the sample surface
- A change in focus is expected
  - Thin membrane, gassing during SEI formation, curvature due to stress

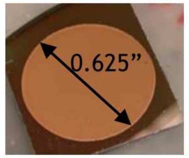


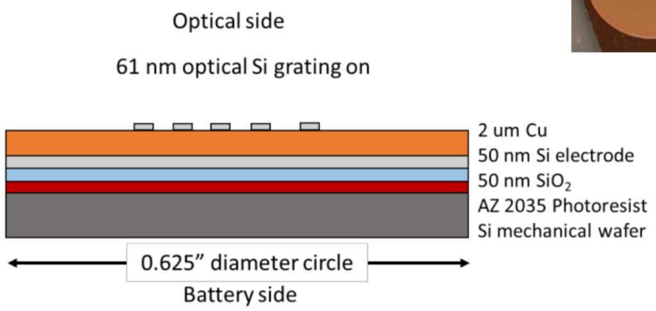
Effect of focus on moiré





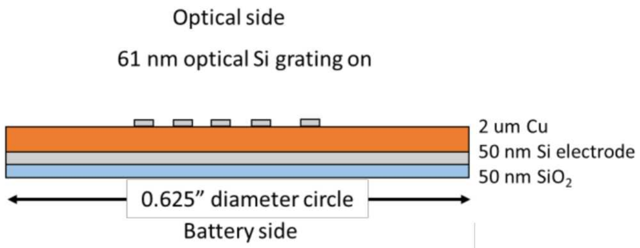
Experimental Setup

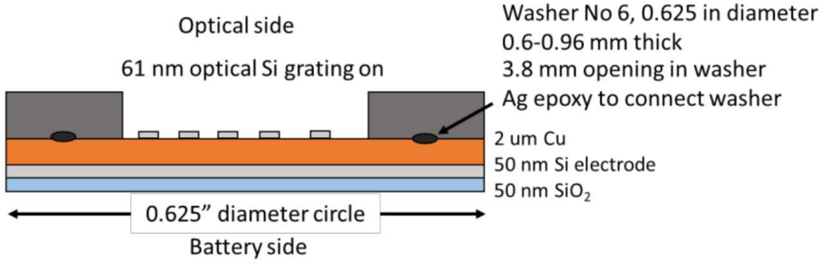


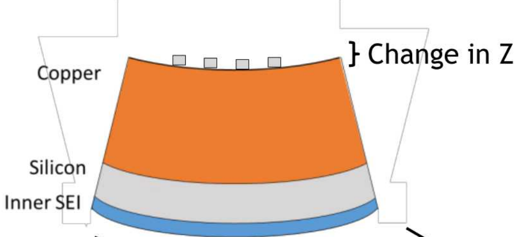


Schematic of foil electrode pre-release

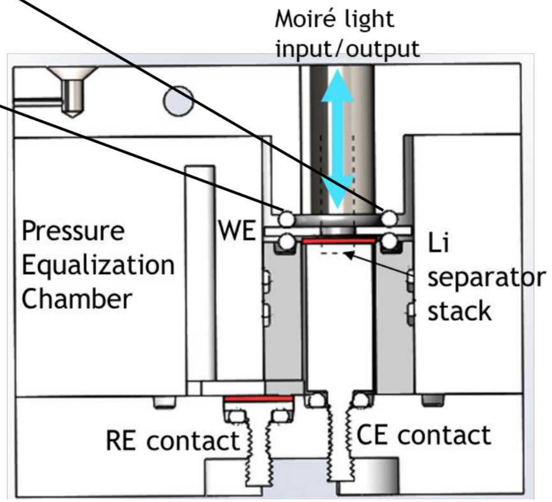
Cu side with grating post-release



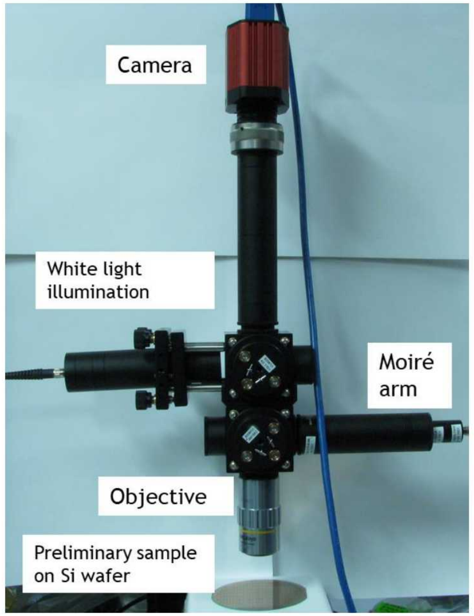


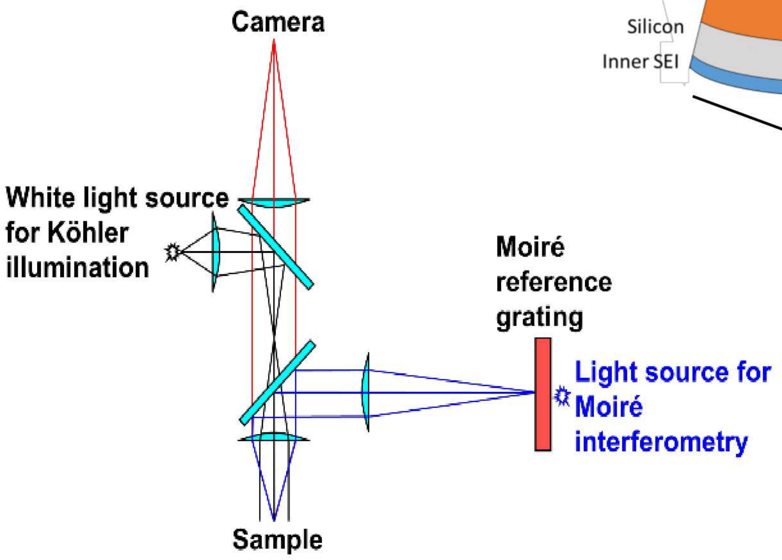


O_2 plasma clean and removal of SiO_2 with HF (little to no native oxide)



Time sensitive transfer of sample and building of cell (in glovebox within ~10 min and built within the hour)

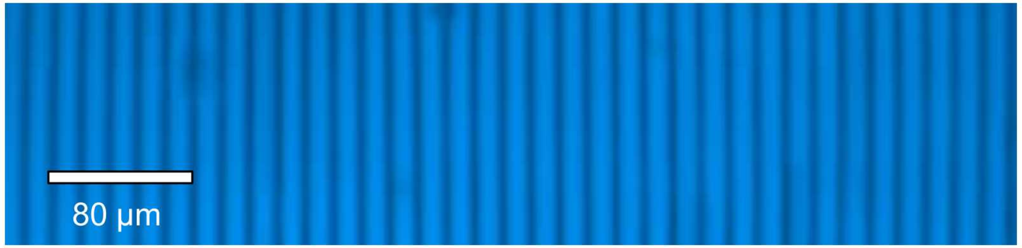


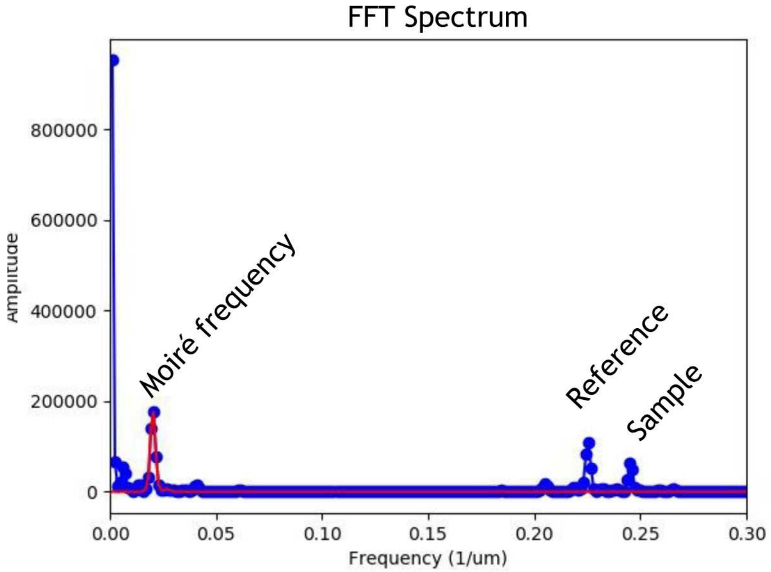


Schematic of the moiré microscope

Python Data Analysis

1. Every 50 sec, scan over Z, taking images every 5 µm with x averages using C#
2. Open image as matrix of pixels in python
3. Average rows of pixels in range of interest, normalize to light and dark standards
4. Discrete Fourier Transform (DFT) using Fast Fourier Transform (FFT) algorithms
5. Brick wall filter to isolate frequencies expected for sample, reference, and moiré fringes
6. Inverse FFT for sample, reference, and moiré
7. Find zeros by looking for negative to positive transition. Linear fit to find zero
8. Plot zeros as a function of zero number. 1/slope gives moiré frequency
9. Calculate strain
   $\varepsilon = (f_{Moire\ Ref} - f_{Current})/f_{Sample}$
10. Take specific value or fit strain or moiré signal to take in-focus value





Python Data Analysis

Every 50 sec, scan over Z, taking images every 5 µm with x averages using C#

Open image as matrix of pixels in python

Average rows of pixels in range of interest, normalize to light and dark standards

Discrete Fourier Transform (DFT) using Fast Fourier Transform (FFT) algorithms

Brick wall filter to isolate frequencies expected for sample, reference, and moiré fringes

Inverse FFT for sample, reference, and moiré

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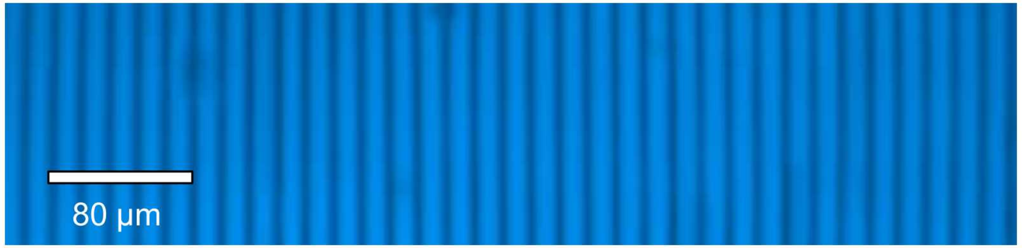
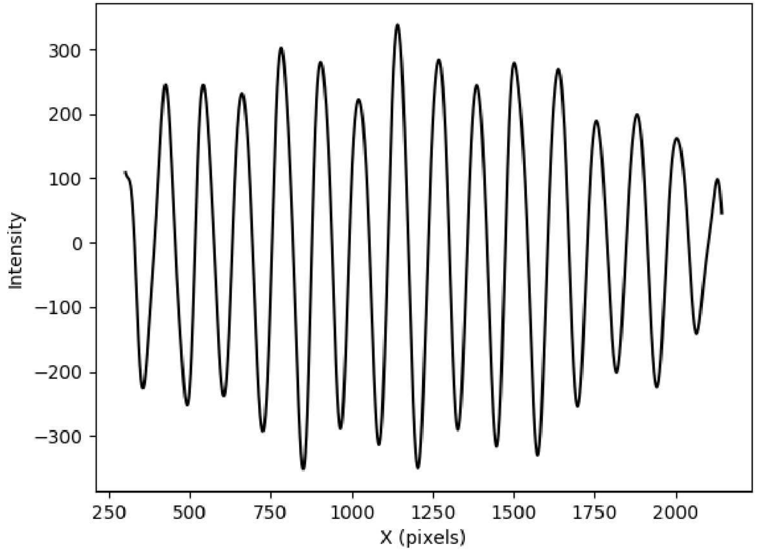
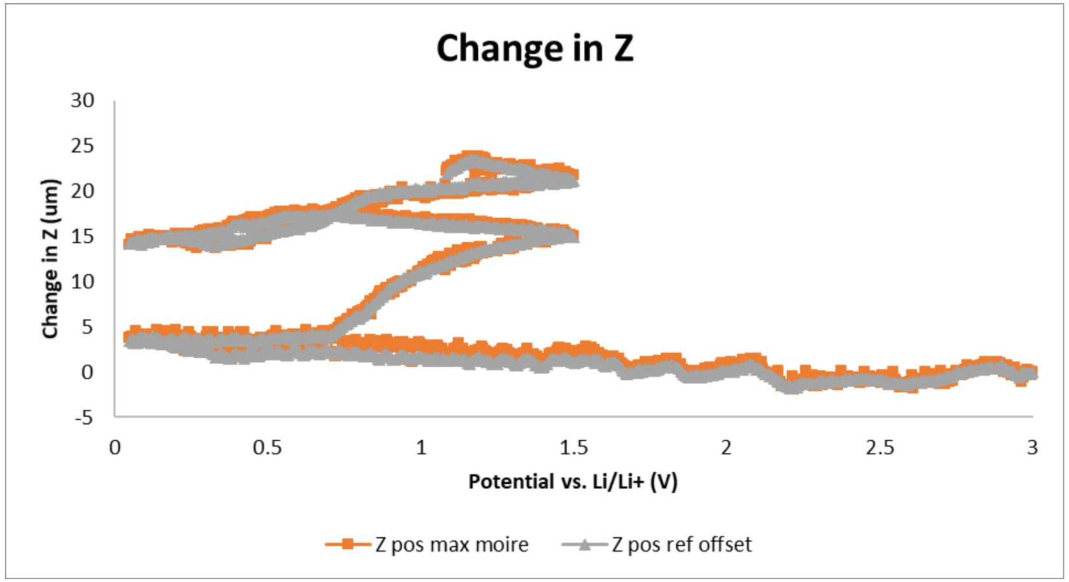


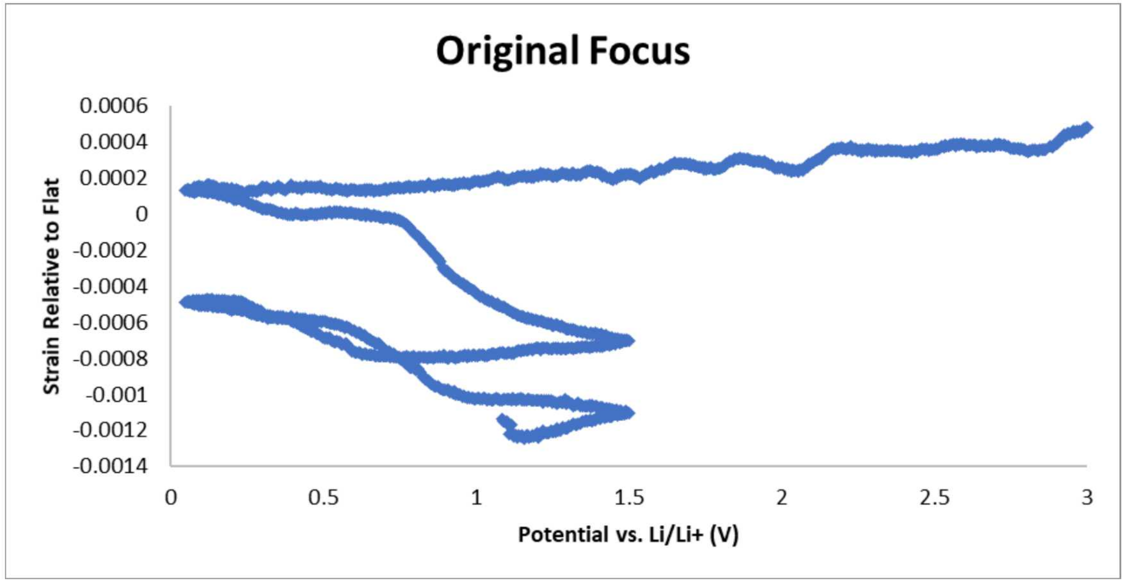
Post FFT and Filter Moiré Periodic Structure

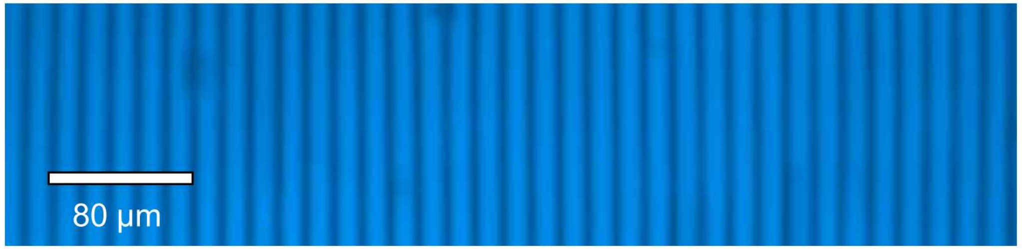


First Setup was not Insensitive to Focus Position

- Observed “strain” was erroneous and tracked perfectly with changes in Z during cycling







Old Setup: Structured Illumination for Reference

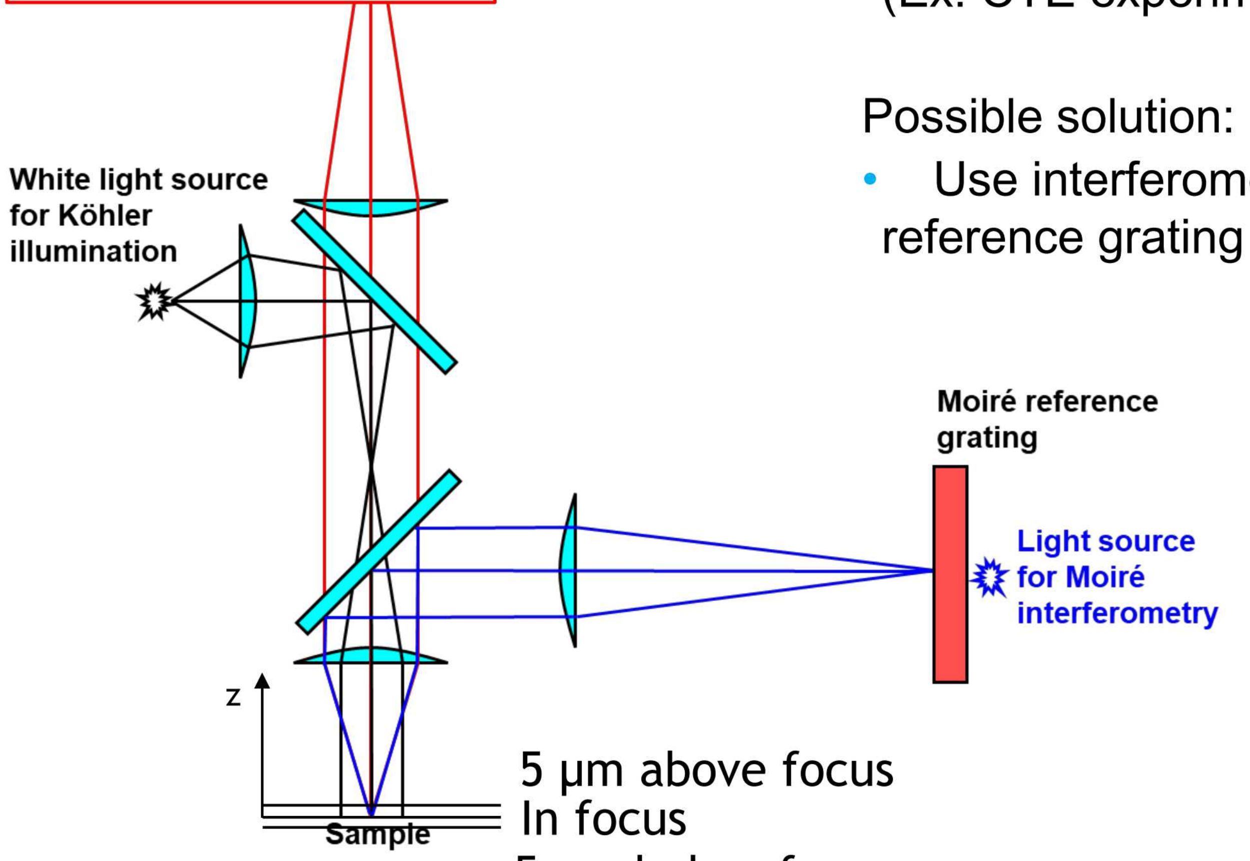
Over 200 ppm of strain change when move 5 µm out of focus when looking for 35 ppm change in strain

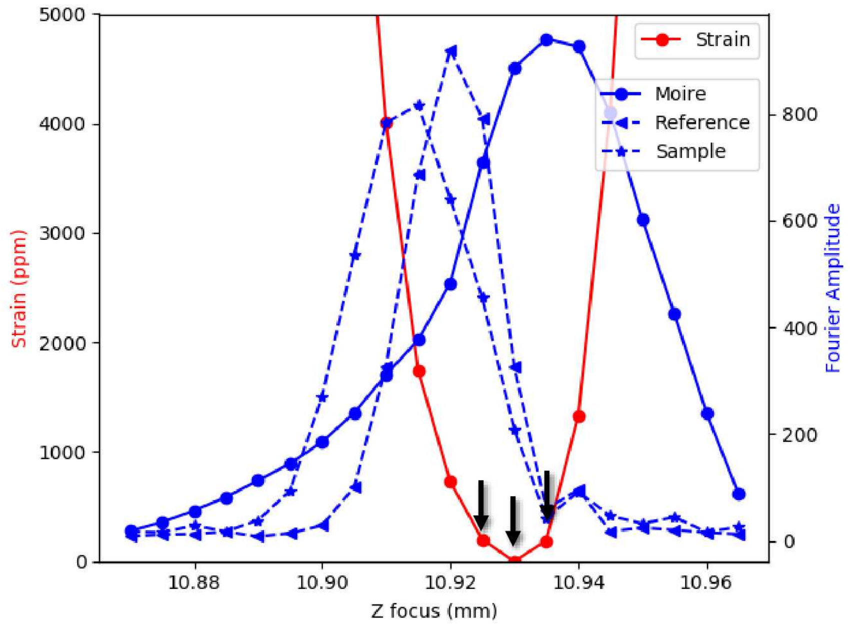
PROBLEM:

- Strain changes drastically as a function of Z position
- Noisy and hard to reproduce
- Can get consistent data on static sample, but as soon as it moves in Z (Ex. CTE experiment) cannot get consistent data

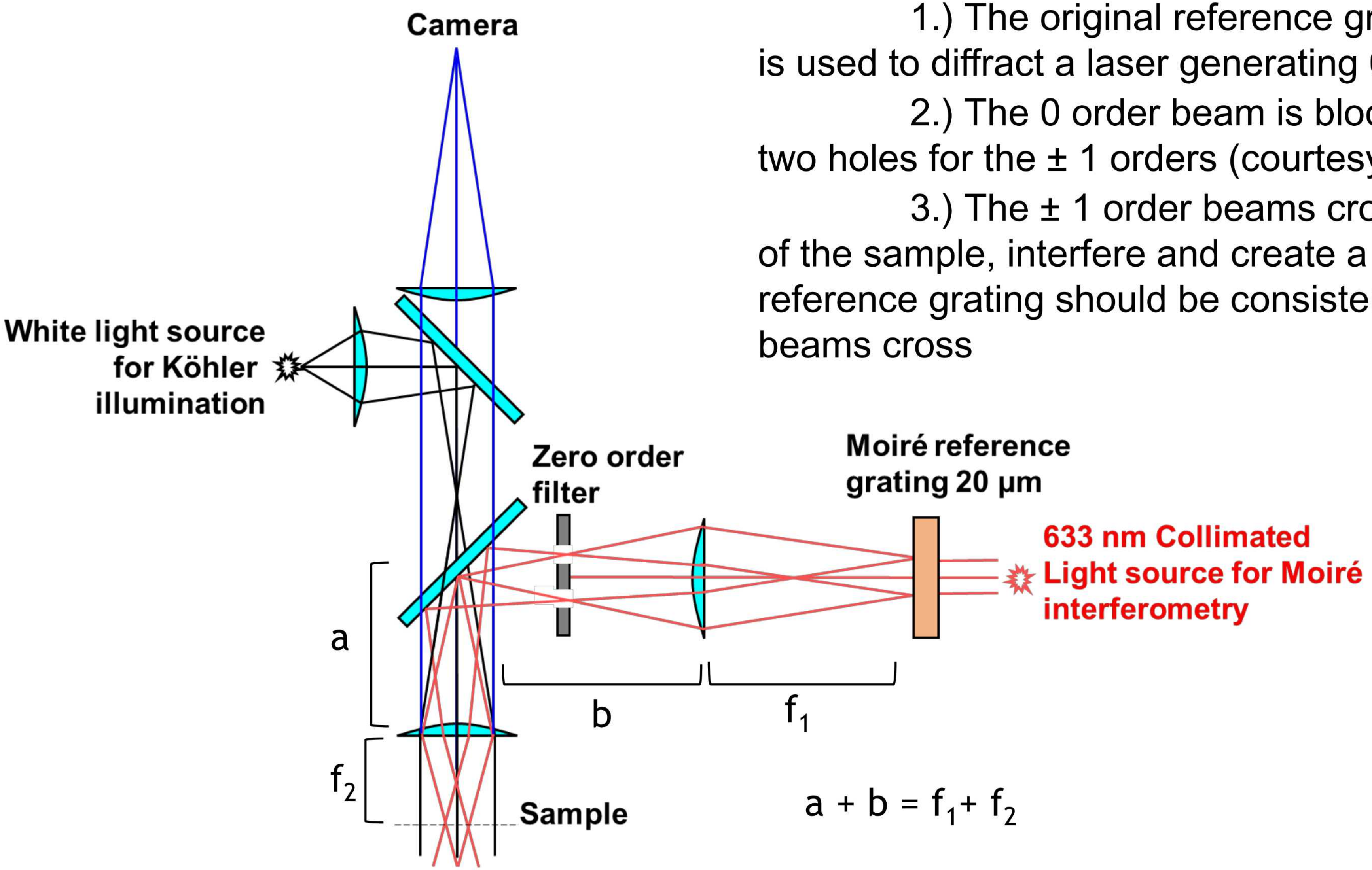
Possible solution:

- Use interferometry rather than structured illumination to create the reference grating





New Setup: Interference of ±1 Orders for Reference



Method:

1.) The original reference grating from the previous setup is used to diffract a laser generating 0 and ± 1 orders

2.) The 0 order beam is blocked by a 3D printed filter with two holes for the ± 1 orders (courtesy of Ted Morin)

3.) The ± 1 order beams cross each other near the plane of the sample, interfere and create a reference grating. The reference grating should be consistent over region that the two beams cross

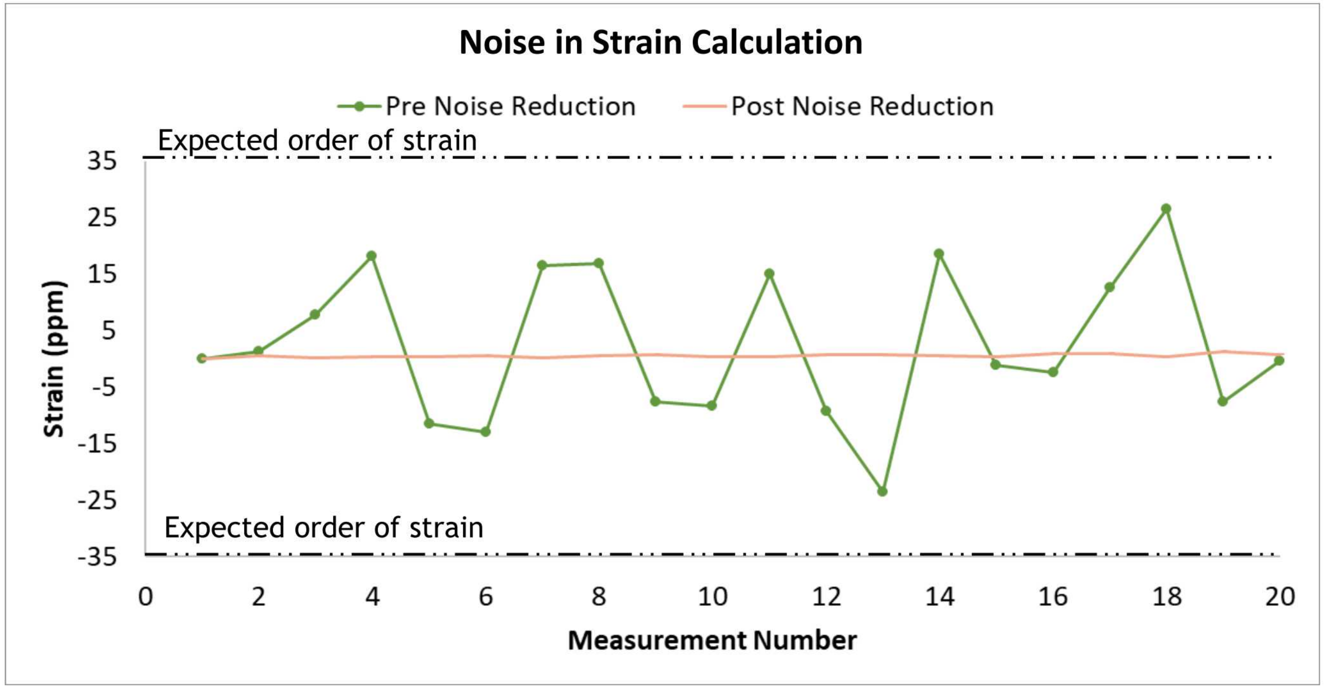
$a + b = f_1 + f_2$

f_1 = 80 mm

f_2 = 35 mm

Noise in Static Imaging Reduced

- Noise was on the order of the measurement we are expecting to make – on order of 50 ppm of strain
- Have decreased noise in static imaging to less than 2 ppm
  - Increased averaging
  - Changing to a monochromatic camera
  - Improving AR coating



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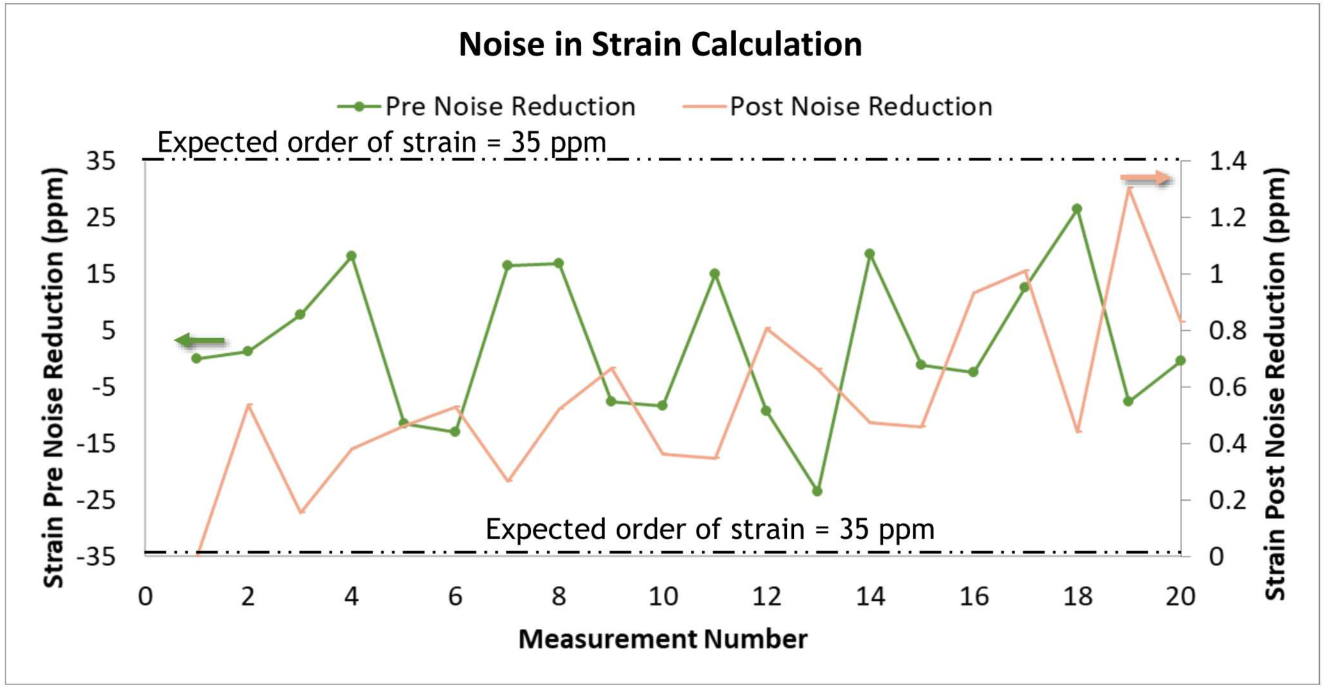
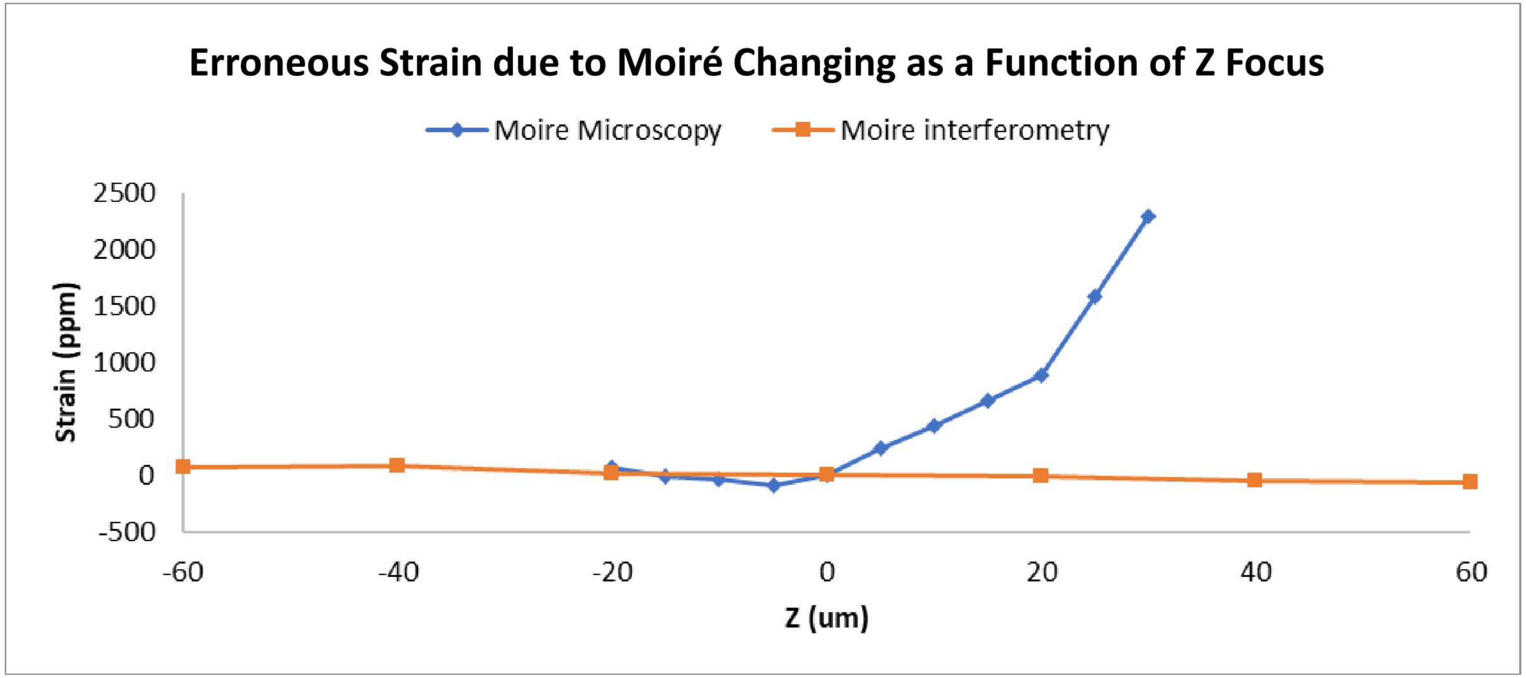


Decrease in Z Sensitivity Achieved

- Switching methods greatly reduced the effect of changes in Z
  - ± 30 µm change in Z before reach ~ 35 ppm of strain



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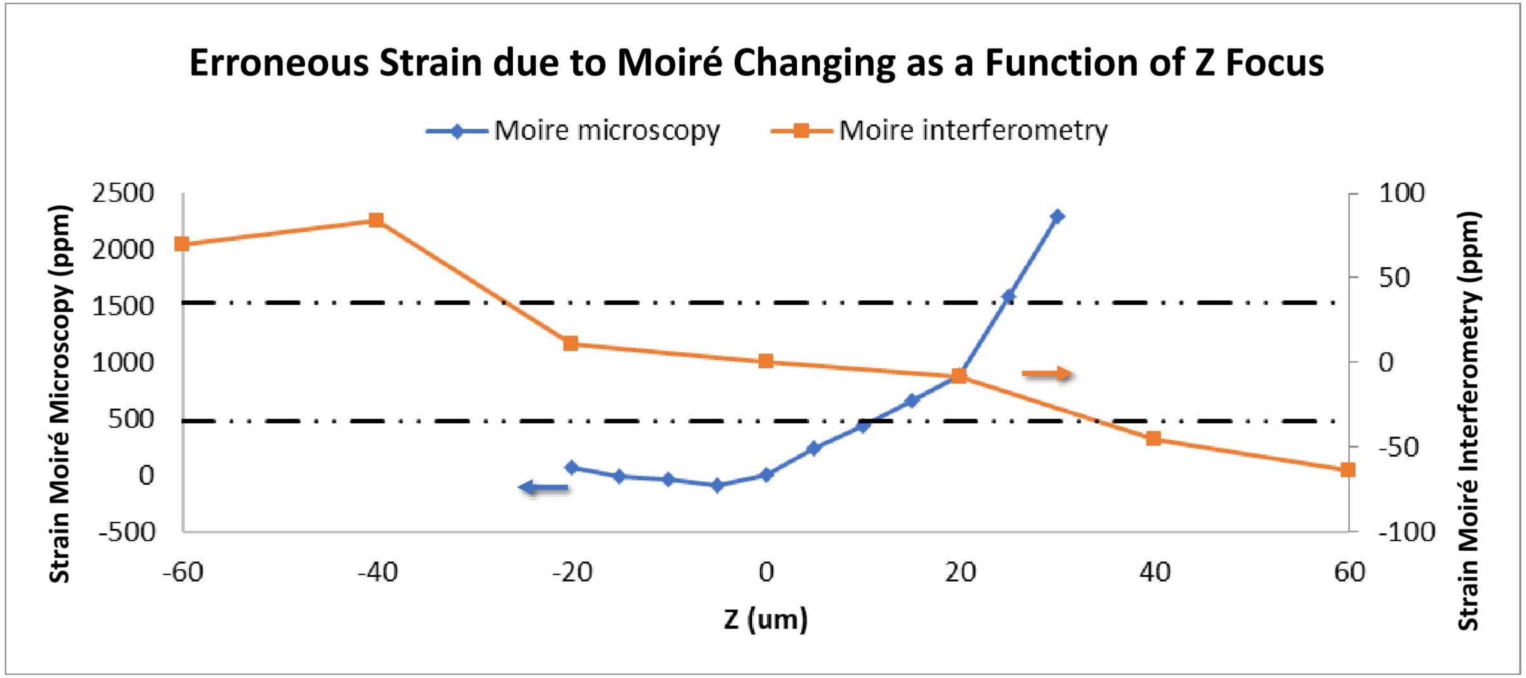
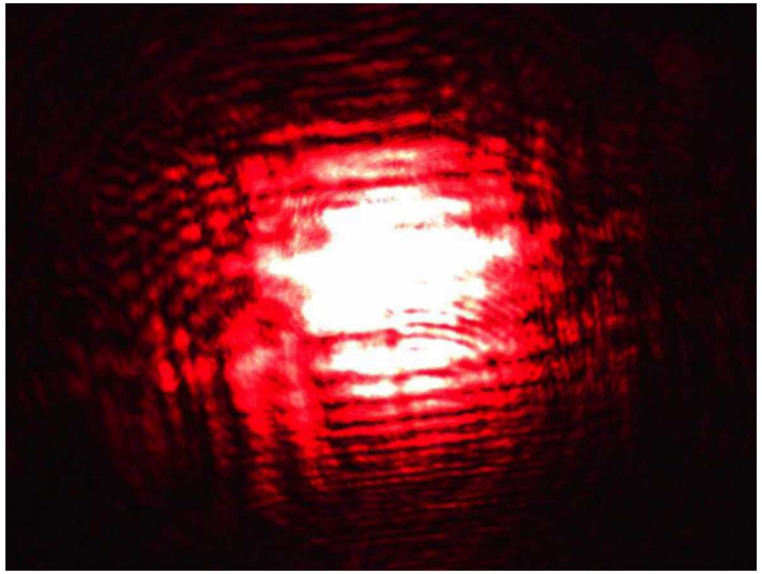


New Difficulties

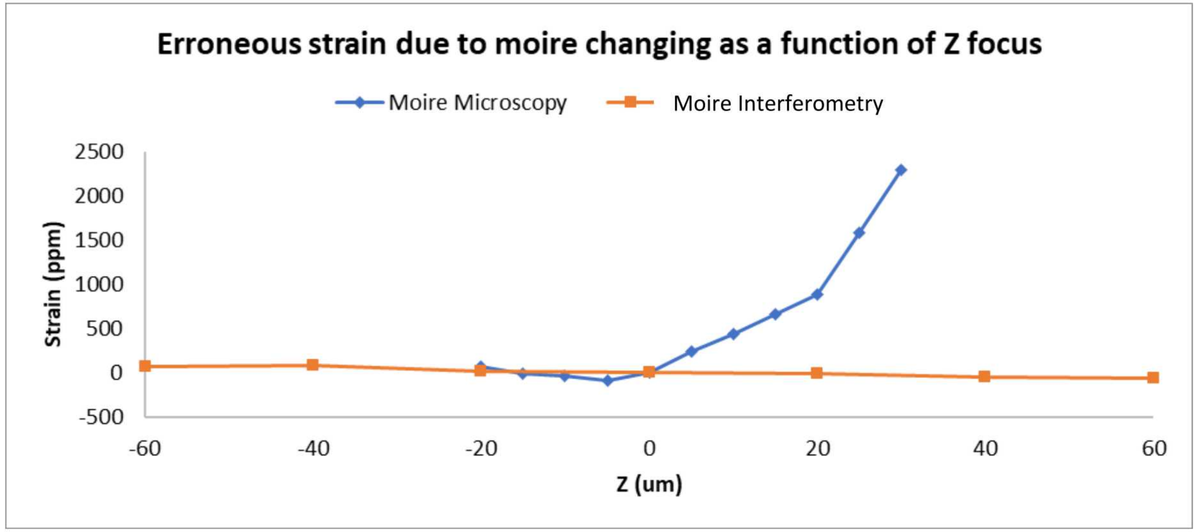
- Did achieve large decrease in Z sensitivity
- Now have sensitivity in tip/tilt of the sample which may be difficult to keep well aligned during an *in situ* test
  - Small instabilities could also be playing a role as observed during alignment of the microscope
    - Air currents, thermal fluctuations, vibrations, etc.

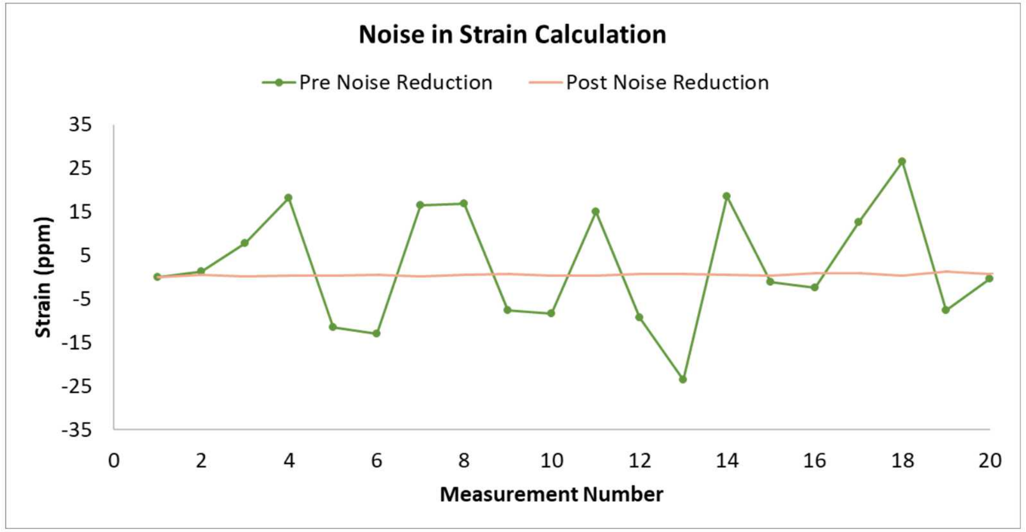
Alignment of Sample Tilt



Summary

- Determined previous *in situ* results to be incorrect because of convolution of the moiré signal due to changes in Z in addition to actual changes in strain
- Changed approach to moiré by forming a reference grating via interference rather than structured illumination
- Reduced noise in static imaging and reduced observed “strain” dependence on Z
- Future work
  - Use developed technique to measure high strain electrochemical processes
  - Despite improvements in noise and sensitivity to Z focus, keeping alignment during in situ operation is difficult, therefore new techniques will be explored





Thank you!

Solid electrolyte interphase stabilization (SEISta) research consortium and Vehicle Technologies Office

Dr. Shelley Minteer and Minteer research group at the University of Utah

Power Sources and Technology Group at Sandia National Laboratories

Dr. Kyle Fenton

Dr. Chris Apblett

Dr. Darwin Serkland

Dr. Chris Orendorff

Victoria Sanchez

My committee

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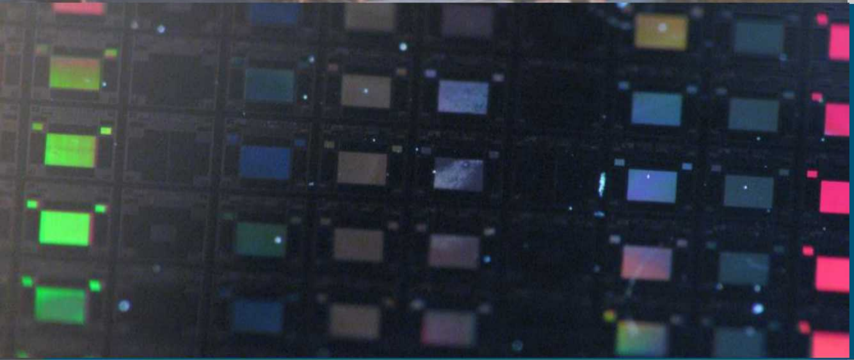

Presenter:
Josefine McBrayer

Exploring Moiré Interferometry as a Tool to Measure Strain in the Silicon Anode of a Lithium Ion Battery

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Poster Presentation: A02-0265

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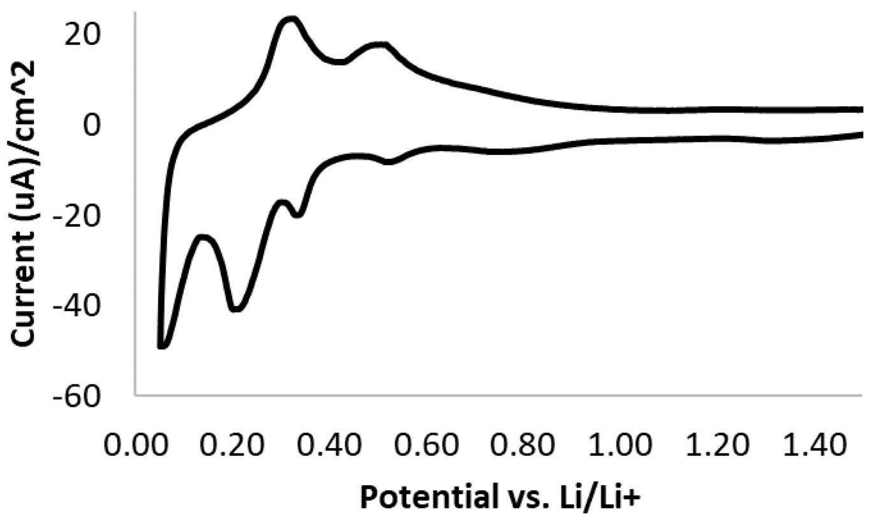
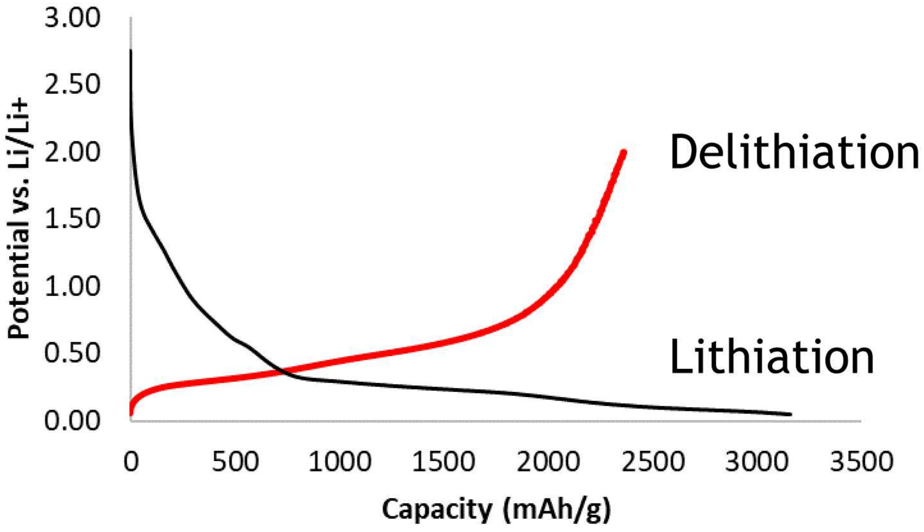
Evaporated Foil Electrochemistry

Cyclic voltammetry and constant current discharge shows lithiation and delithiation of the silicon thin film on the evaporated foil electrode

Cyclic voltammogram of Si foil



C/20 constant current lithiation and delithiation



Coin cell half cell configuration
WE: Si evaporated foil
CE/RE: Li metal
Electrolyte: 1.2 M $LiPF_6$, 3:7 Ethylene carbonate: ethyl methyl carbonate
Scan rate: 0.1 mV/s
Environment: Built under argon, RT