In-Situ Spectroscopic Ellipsometry of Lithium Ion Intercalation in GLAD Three-Dimensional Nanostructure Films

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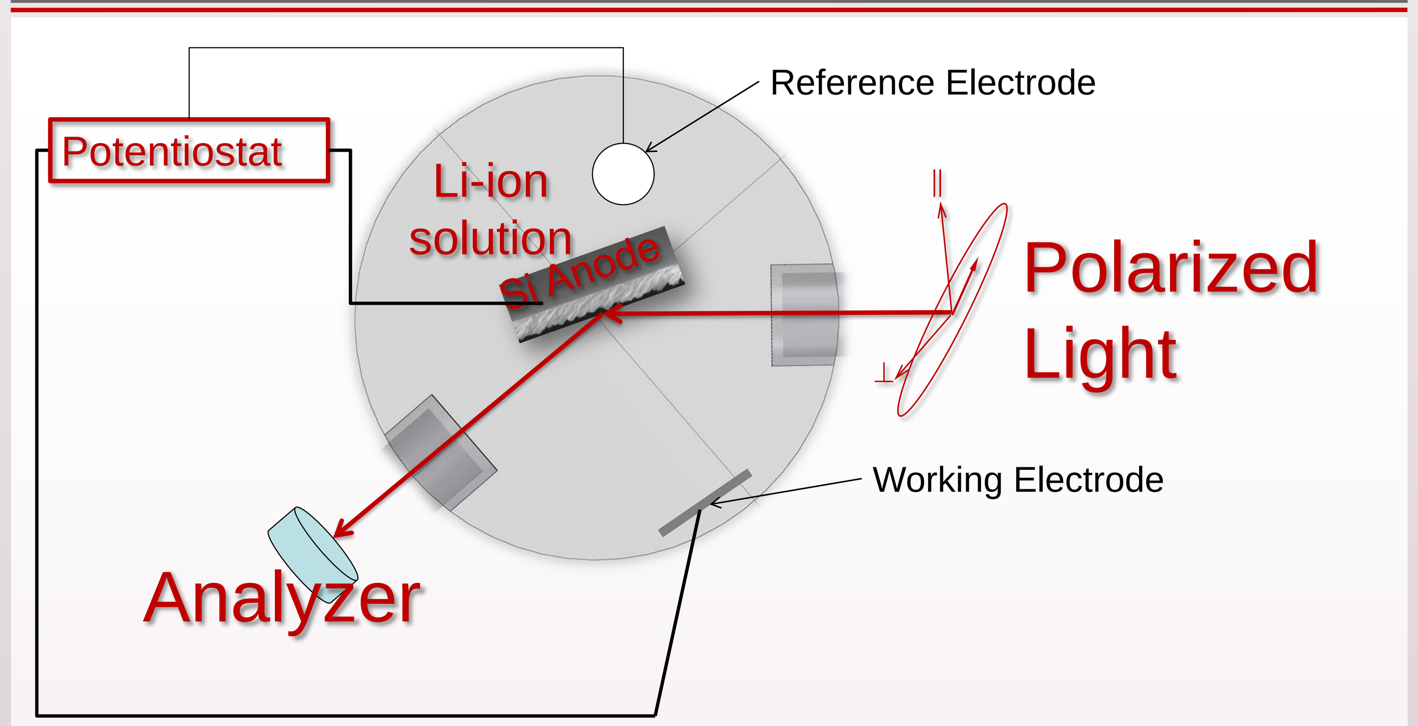
Our message

- **Rechargeable lithium ion batteries are the backbone of the today's portable electronics industry.**
- **Improved electrode materials with higher capacity and longer life cycles are still needed.**
- **Thin structured films of silicon (Si) are employed to increase surface area, and reduce stress caused by the intercalation of lithium into the films.**
- **The charge capacity of the films can be observed as a change of index of refraction using ellipsometry.**

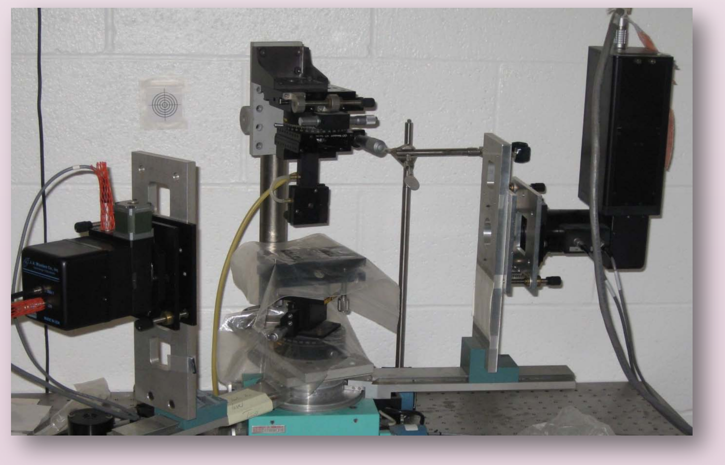
In-Situ Electrochemistry - Experimental Setup



Cyclic Voltammetry experiments are used to investigate the half cell reactivity of an analyte (Li solution) with the Si Anode. The experiments control the potential of an anode in contact with the analyte while measuring the resulting current (amperes).

The working electrode must apply the desired potential with respect to the reference electrode, which has a known reduction potential. In this setup a Saturated calomel electrode (SCE) is used that has a built in potential of +0.2415V. No current is passed through the SCE. All current and therefore charge is passed through the Si Anode.

During the Cyclic Voltammetry in-situ Mueller Matrix ellipsometry is preformed, to optically monitor the change during the redox reactions occurring on the Silicon Anode.



Motivation:

- To increase the specific energy of lithium-ion batteries, alternative anode materials with higher charge capacity are needed.
- Si stands out because of its high capacity to accommodate li-ions into its lattice structure.

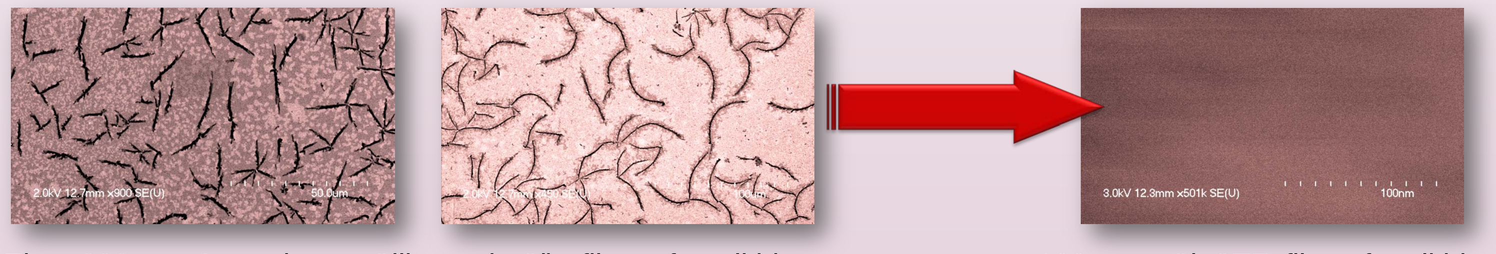
a-Si

- Uptake of $Li_{4.4}Si$, corresponds to 4200 mAh/g of Si.
- This volume change presents great lattice strain which leads to cracking.

a-Si STF

- Nano sized Silicon structures can relieve this stress. Making higher capacity longer lasting batteries.

a-Si after intercalation / **a-Si Nano-rods after intercalation**



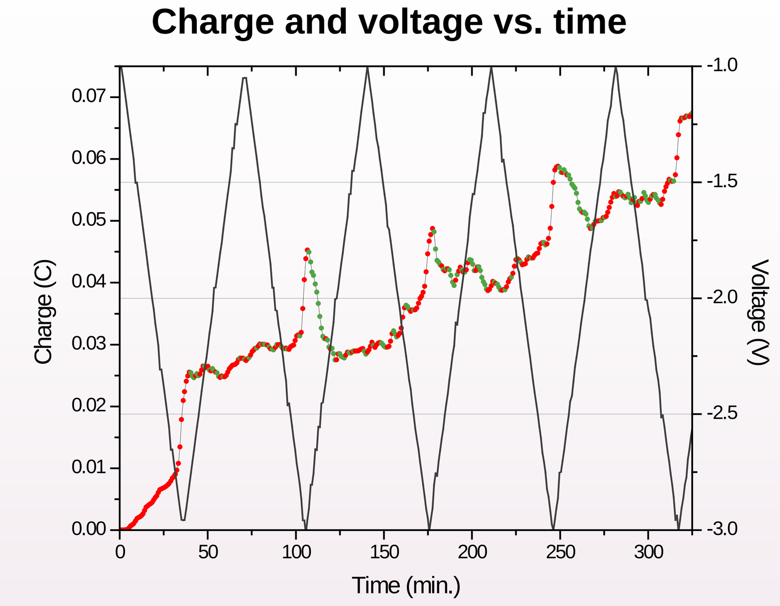
The 200nm Amorphous Silicon (a-Si) film after lithium intercalation shows cracks from the cyclic charging .

120nm a-Si STF film after lithium intercalation shows no signs of stress from the cyclic charging .

Amorphous vs. STF Silicon

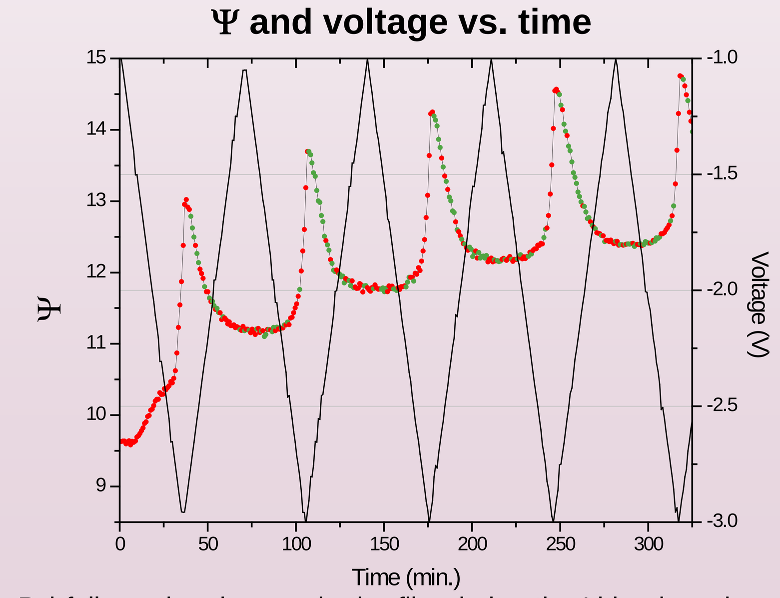
Amorphous Silicon

Charge and voltage vs. time



A 200nm thick film of a-Si intercalated with Li-ions. Red/green circles correspond to positive/negative current respectively

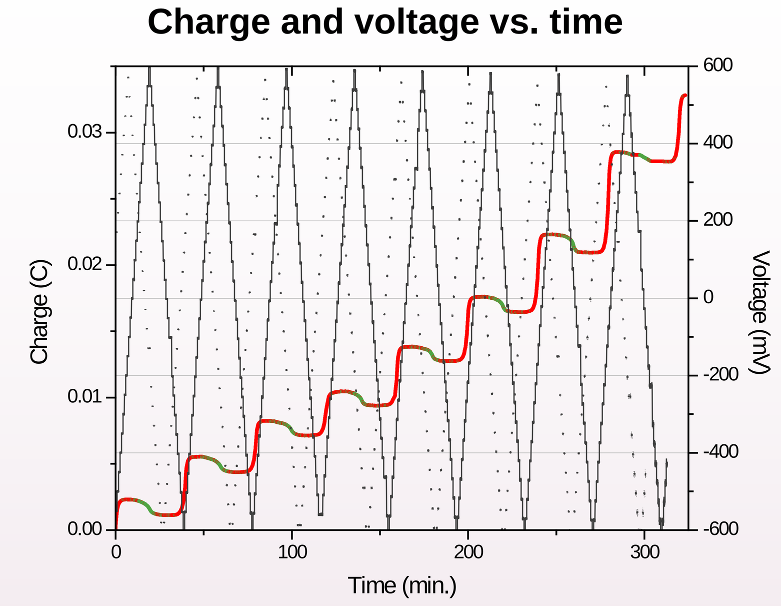
Ψ and voltage vs. time



Psi follows the changes in the film during the Li-ion insertion and removal. Red/green circles correspond to positive/negative current respectively

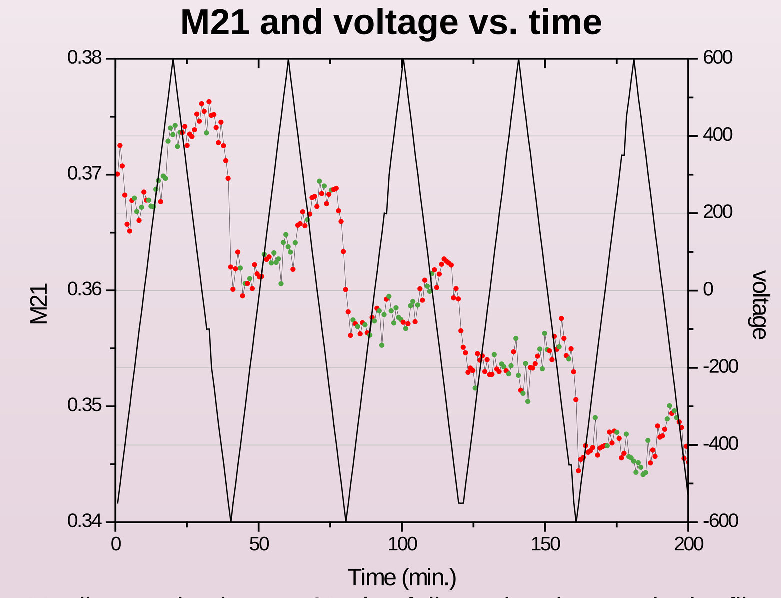
Amorphous-STF Silicon

Charge and voltage vs. time



A 120nm thick film of a-Si nano rods intercalated with Li-ions. Red/green circles correspond to positive/negative current respectively

M21 and voltage vs. time

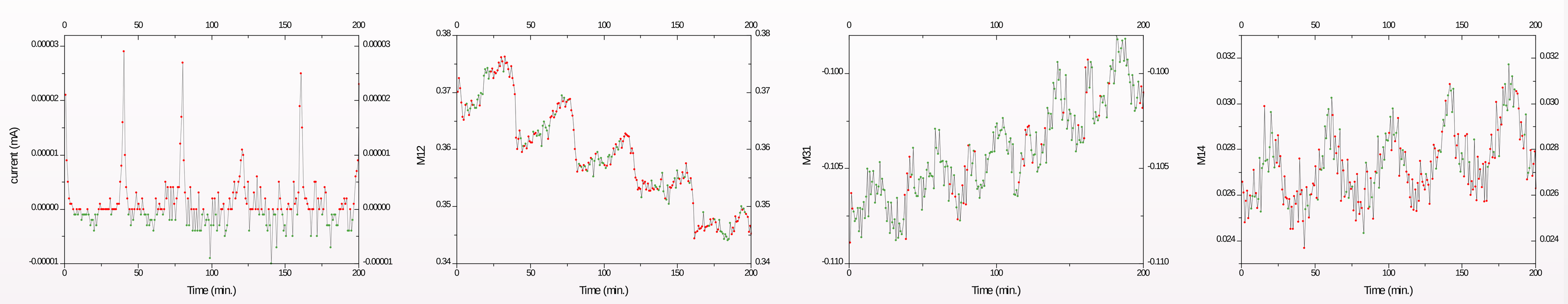


Mueller matrix element 21 also follows the changes in the film during the Li-ion insertion and removal. Red/green circles correspond to positive/negative current respectively

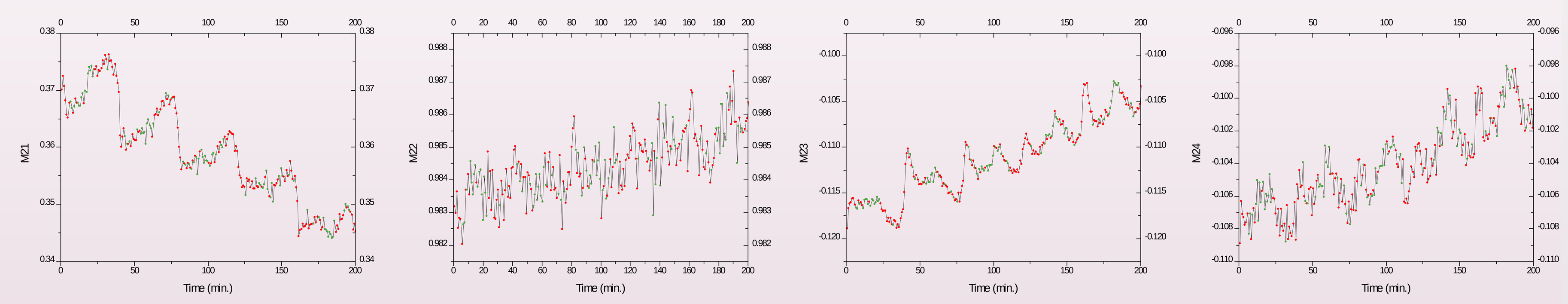
Silicon Nano-Rods

Optical Characterization of Li-ion Intercalation in Si-Nano Rods

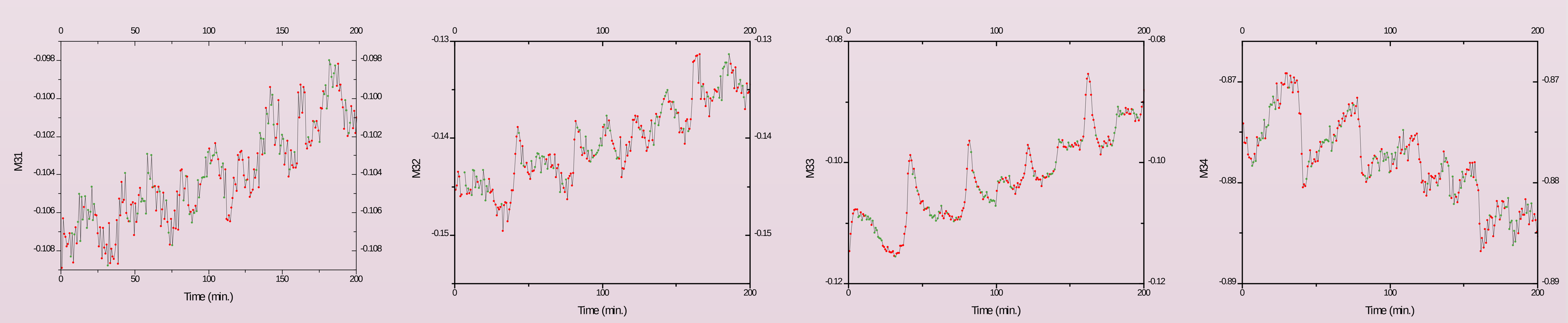
In-Situ Mueller Matrix elements



• Positive Current • Negative Current



• Positive Current • Negative Current



We see that the off diagonal matrix elements show birefringence that are changing over time, and follow the cell current flow that follows Li-ion flow into and out of the Si-Nano Rods.

Future work

- Relate the Mueller Matrix data directly to the amount of Li-ion's being intercalated by the Si, giving an optical technique to characterize and understand the physical changes that occur to the Nano-Rods during the Li-ion insertion process.
- Find a suitable separator to allow full discharge of the samples.
  - Electronic insulator
  - Minimal electrolyte (ionic) resistance
  - Mechanical and dimensional stability
  - Sufficient physical strength to allow easy handling
  - Chemical resistance to degradation by electrolyte, impurities, and electrode reactants and products
- Optically characterize other structured thin films, e.g. chiral structures