Thin Film & Small Scale Mechanical Behavior
Gordon Research Seminar
Colb SAND2012-5104C ille, ME

9:00 - 9:20 a.m. 7/22/2012

Direct Observation of Deformation and Fracture of Si Electrodes in the Nano-sized Lithium Ion Batteries

Xiaohua Liu

Center for Integrated Nanotechnologies (**CINT**)
Sandia National Laboratories*, Albuquerque, New Mexico

*Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

ACKNOWLEDGMENT

Financial Support

This work was supported by a Laboratory Directed Research and Development (LDRD) project at Sandia and by the Dept. of Energy Office of Basic Energy Science as part of an Energy Frontier Research Center (The NEES Center). This work was performed, in part, at the Sandia-Los Alamos Center for Integrated Nanotechnologies (CINT).

Collaborators

CINT, Sandia N.L.	**Jian Yu Huang, Yang Liu**
	John P. Sullivan, Nicholas S. Hudak, Arunkumar Subramanian
	Hongyou Fan
CINT, Los Alamos N.L.	**Tom S. Picraux, Shadi A. Deyah, Jeong-Hyun Cho, Jinkyoung Yoo**
Georgia Inst. Tech.	**Ting Zhu, Shan Huang, Feifei Fan**
M.I.T.	**Ju Li, Akihiro Kushima, Liang Qi**
Univ. Pittsburg	**Scott X. Mao, He Zheng, Li Qiang Zhang, Jiang Wei Wang, Li Zhong**
Penn State Univ.	**Sulin Zhang, Wen Tao Liang, Xu Huang**
Pacific Northwest N.L.	**Chongmin Wang, Wu Xu**

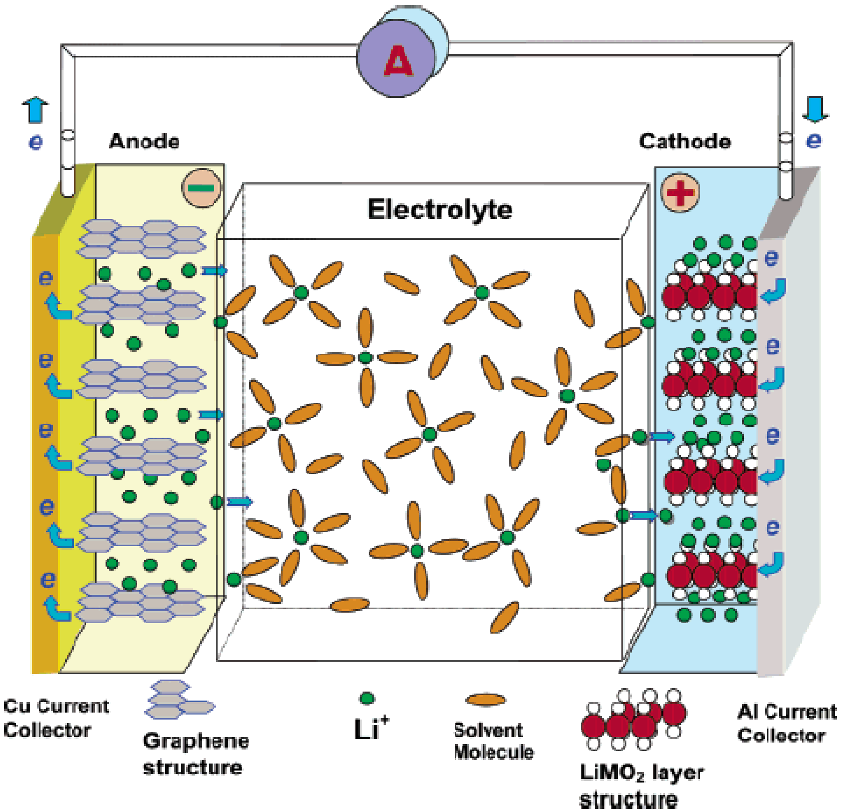
OUTLINE

1. Motivation: Why Si? Why TEM?
2. Approach: TEM + nano-LIB
3. Results
   3.1 Anisotropic Swelling of Crystalline Si
   3.2 Size-Dependent Fracture of Si Nanoparticles
4. Conclusions

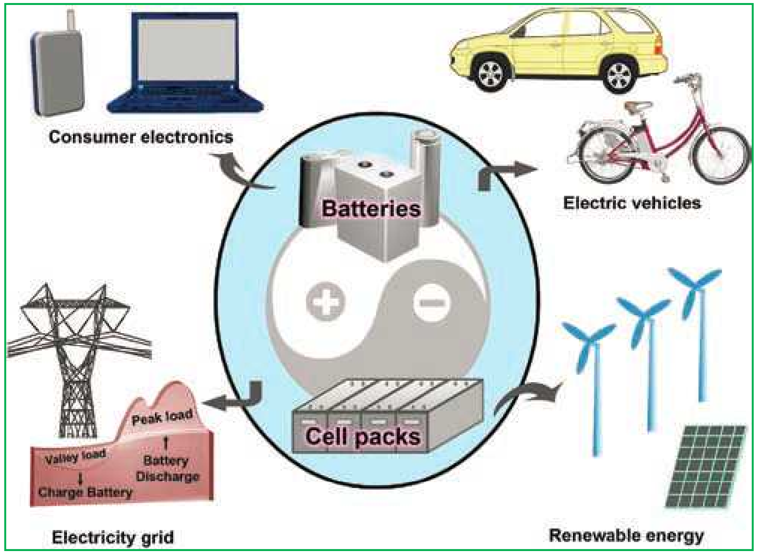
1. Motivation

Lithium ion battery (LIB):

A complex system involves multiple phases, interfaces, charge and mass transport processes. Commercialized for > 30 years, having many applications, but not well understood.



A LIB during discharging



Prevailing and potential applications

1. Motivation

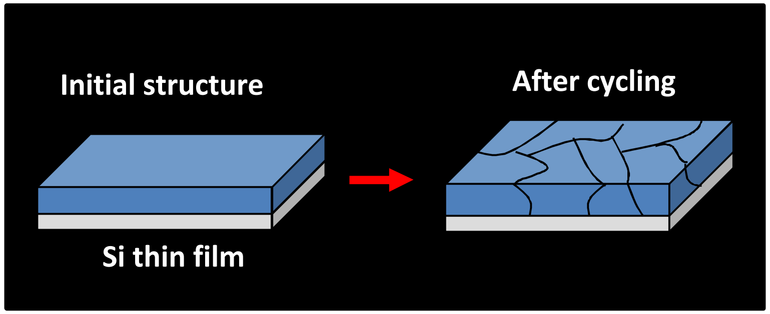
Global efforts are ongoing to improve LIB performance, targeting higher energy/power density, higher safety, and longer durability.
Mechanical degradation is one of the major problems of those high-energy LIBs under development.

$C + xLi \rightarrow Li_xC \; (0 \leq x \leq 1/6)$ 372 mAh/g

$Si + xLi \rightarrow Li_xSi \; (0 \leq x \leq 4.4)$ 4200 mAh/g

Capacity of various anode materials for LIBs

Si electrodes crack and fracture after only a few cycles. There is an urgent need of understanding the mechanical responses upon electrochemical reactions.



Larcher, *et al.* ***J. Mater. Chem.***, **17**: 3759 (2007).

1. Motivation

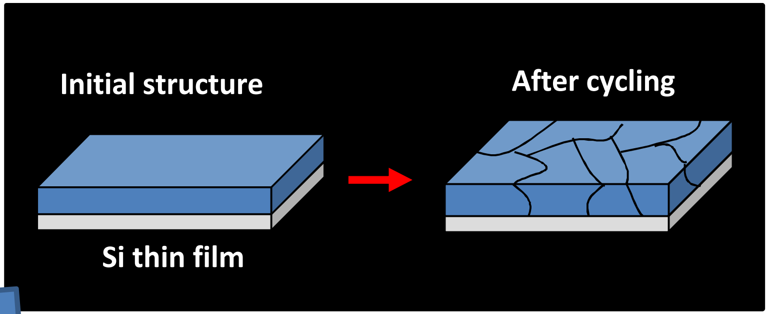
Large volumetric expansion is intrinsic to the high-energy anodes such as Si and Ge.
But how does it actually occur accompanying the electrochemical reactions?

Nano-battery + TEM

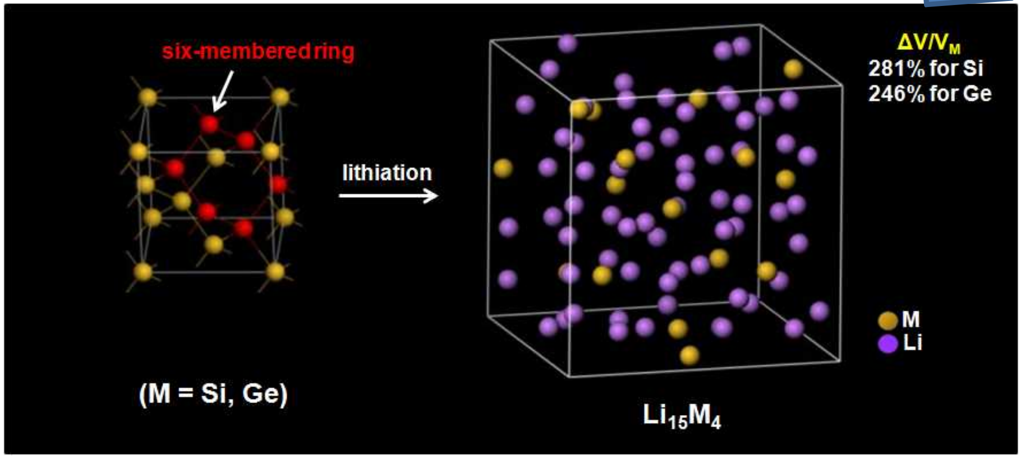
Microscopically: ??

How is fracture initiated? Developed? Finalized?

(length scale: Å ~ nm ~ μm)



Macroscopically: Crack and fracture (length scale: mm and up)



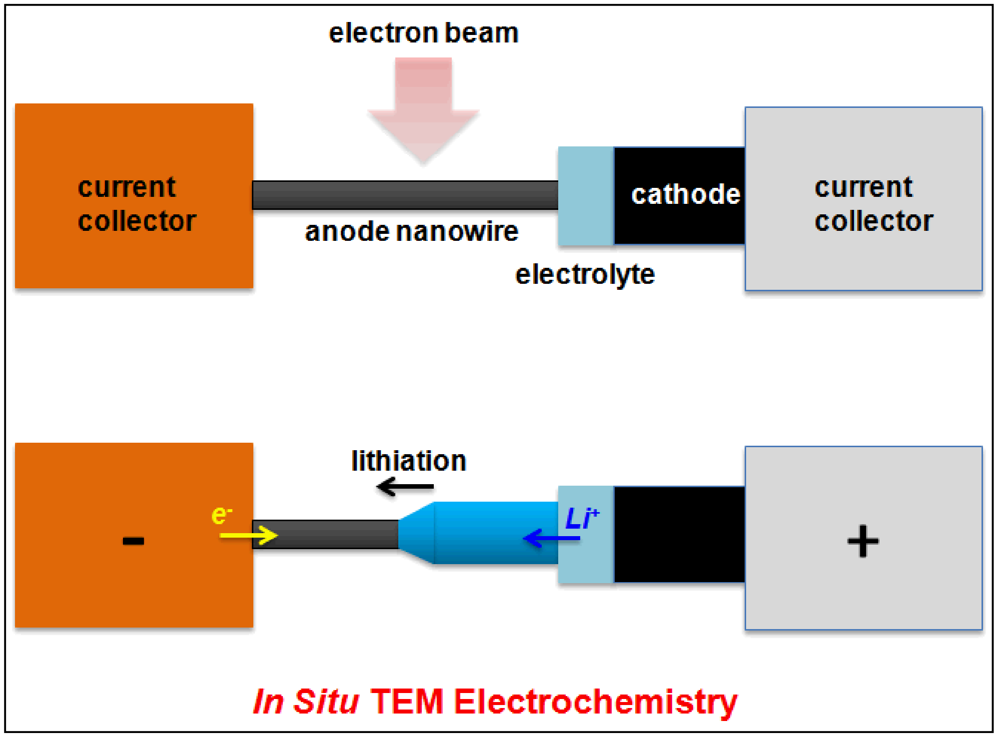
Atomically: intrinsic volumetric changes and dilution of Si atoms by Li (length scale: sub Å ~ 1 nm)

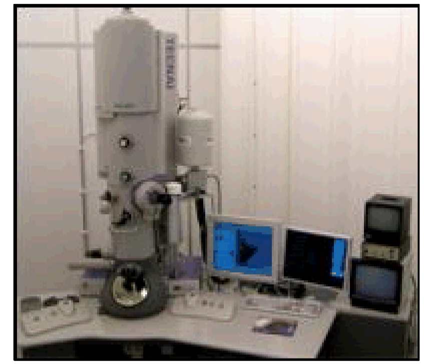
Liu, *et al*. ***Adv. Energy Mater.***, DOI: 10.1002/aenm.201200024 (2012).

2. Approach

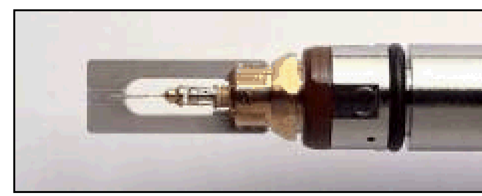
Building a nano-battery compatible for TEM observation

→ Understand deformation at the atomic to micrometer length scale





FEI Tecnai™ F30 TEM
Image of TEM of the same model obtained from http://lims.msl.angstrom.uu.se/WebForms/Equipment/EquipmentView.aspx?toolId=135



Nanofactory™ STM-TEM holder

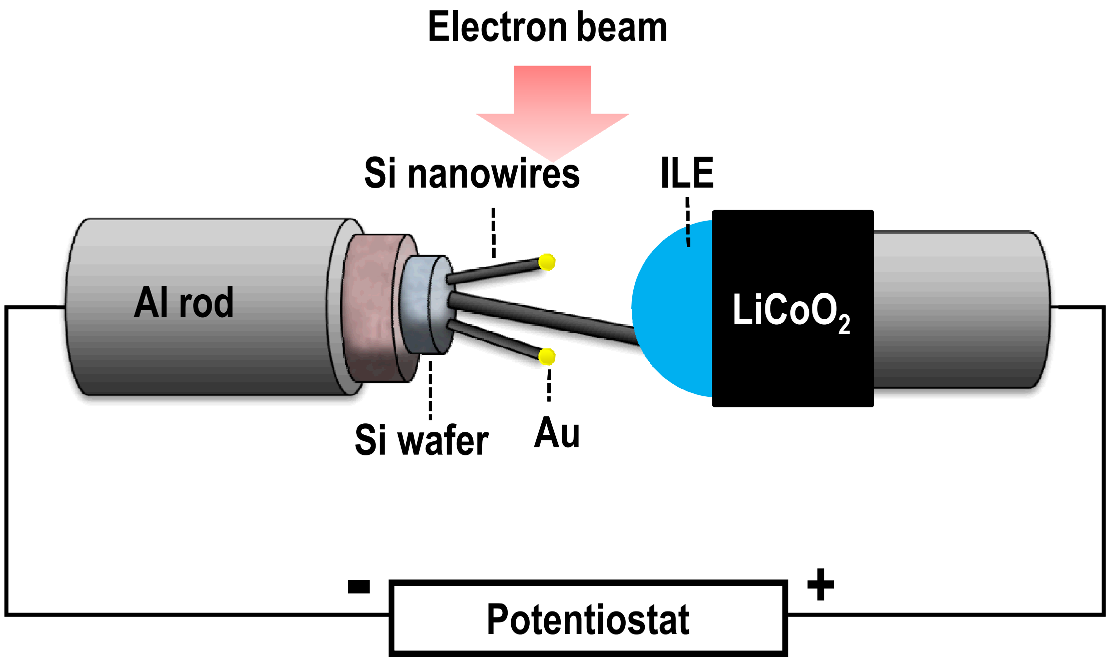
Schematic illustration

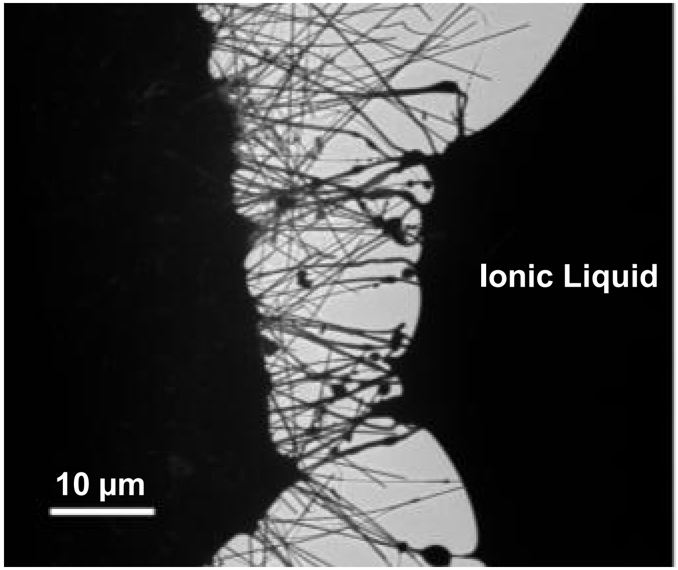
Instrumentation

Liu, *et al*. ***Adv. Energy Mater.***, DOI: 10.1002/aenm.201200024 (2012).

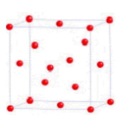
(1) Liquid Cell

Using vacuum-compatible ionic liquid electrolyte (ILE)

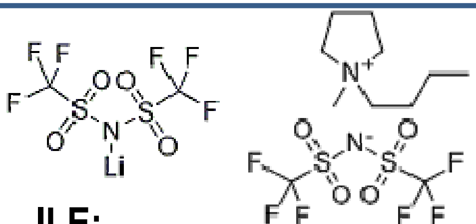




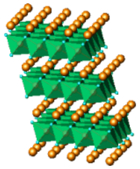
A low-magnification view in TEM



Anode: Si



ILE:
LiTFSI (10wt%) in P_{14}TFSI

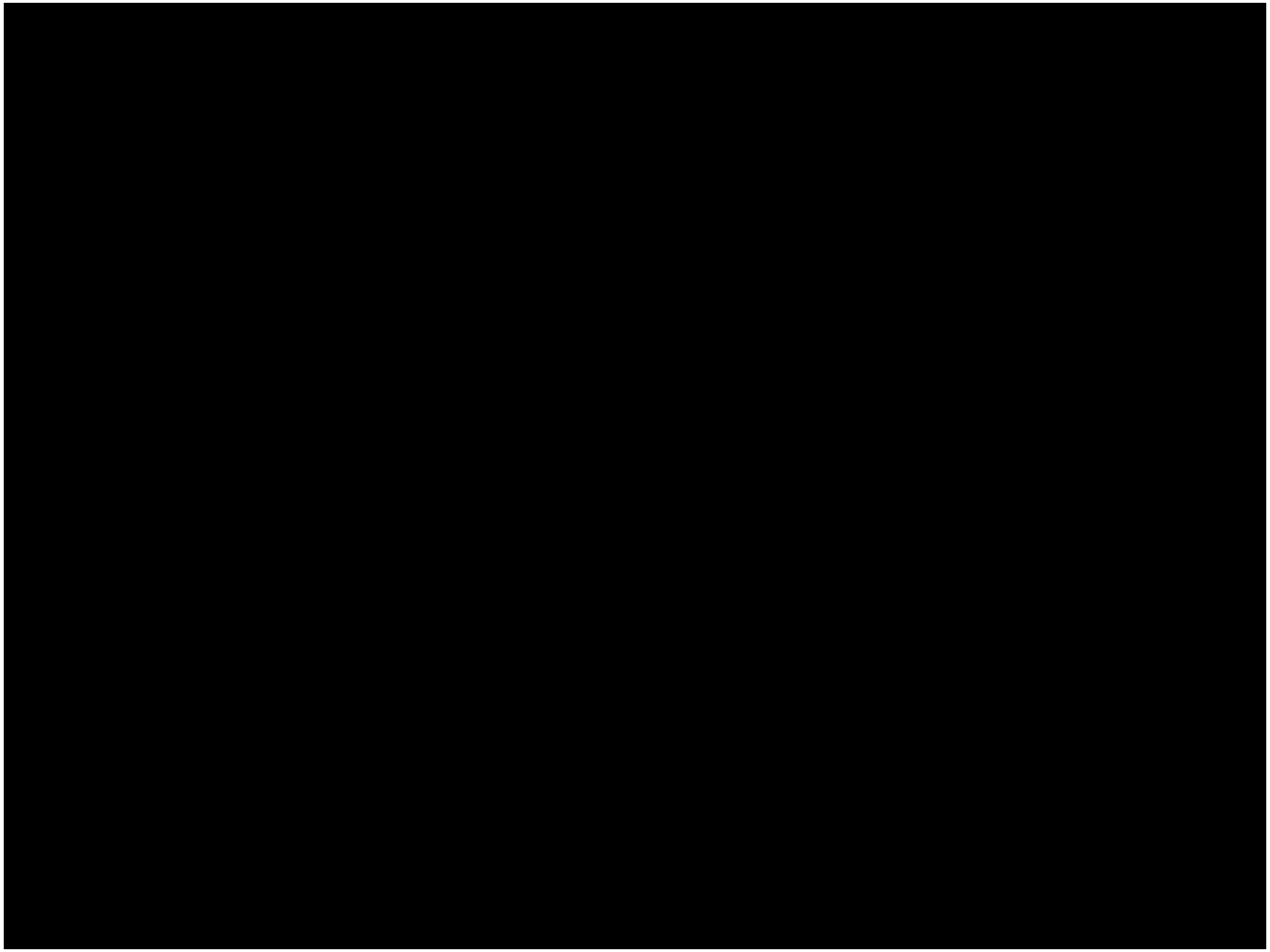


Cathode: $LiCoO_2$

Huang, *et al.* ***Science***, 330: 1515 (2010); Liu, *et al.* ***Nano Lett.***, 11: 2251(2011).

(1) Liquid Cell

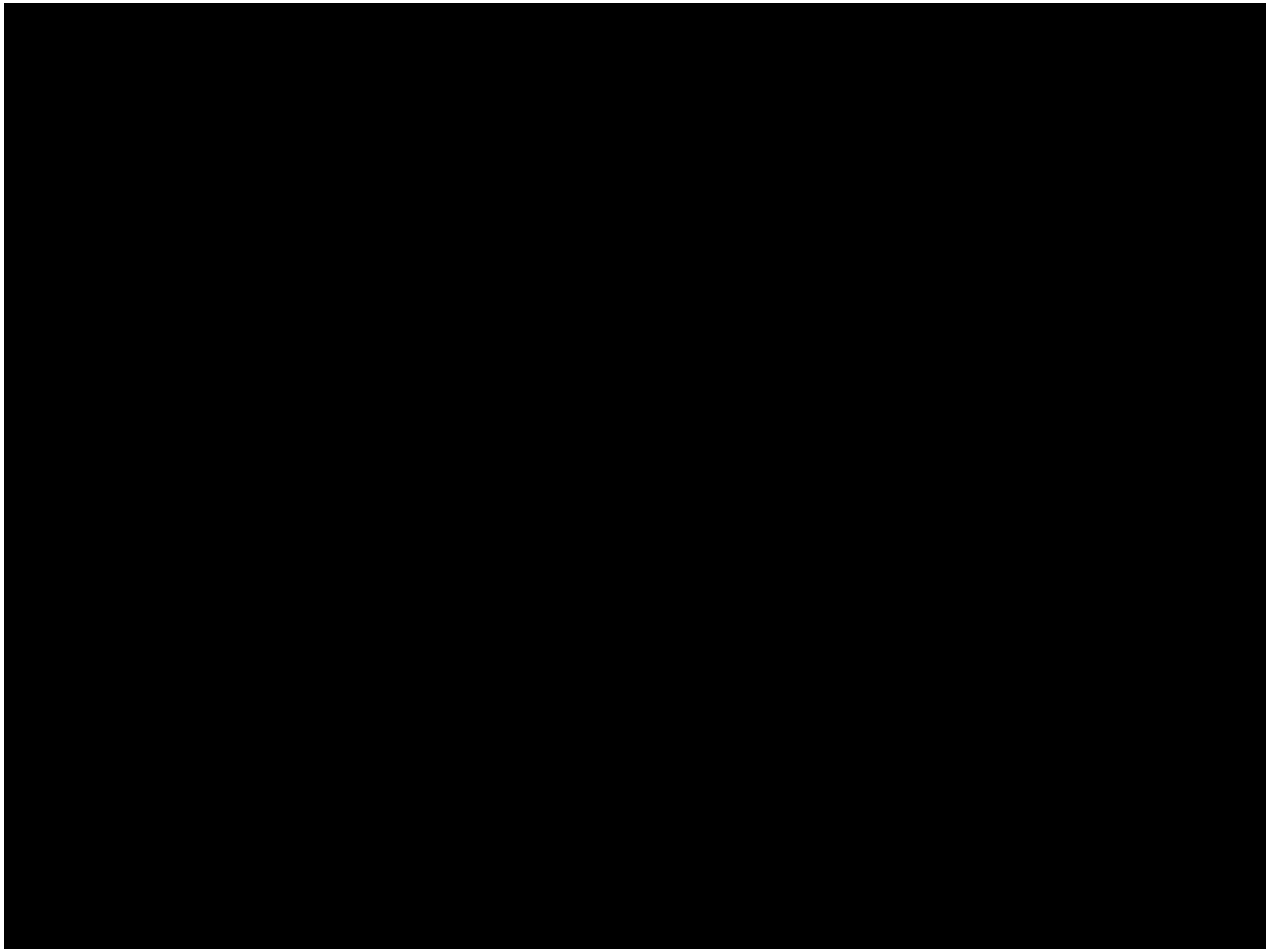
Lithiation of a SnO_2 nanowire showing instant elongation and swelling



Huang, *et al.* ***Science***, 330: 1515 (2010).

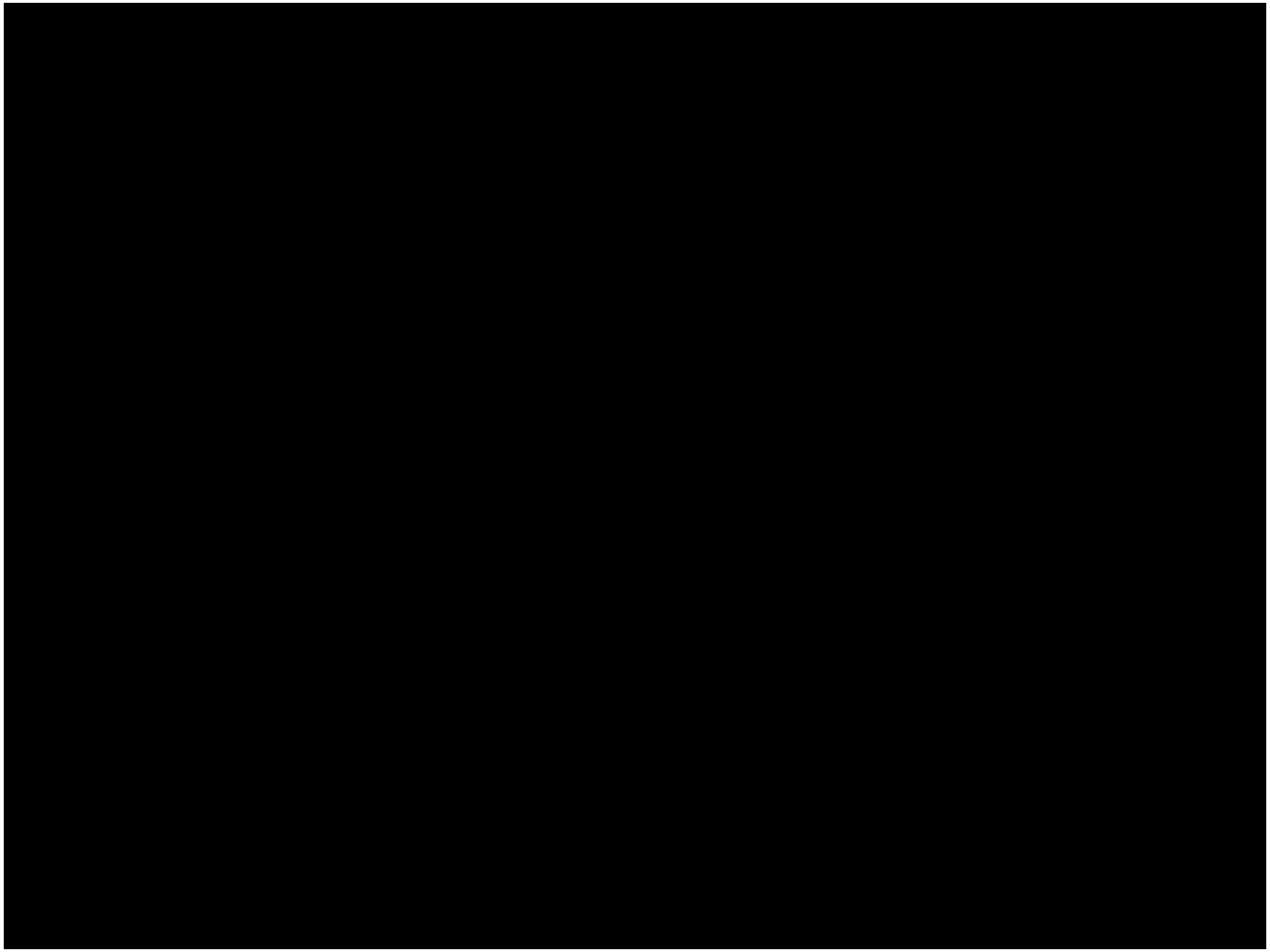
(1) Liquid Cell

Lithiation of SnO_2 - dislocation clouds and amorphization



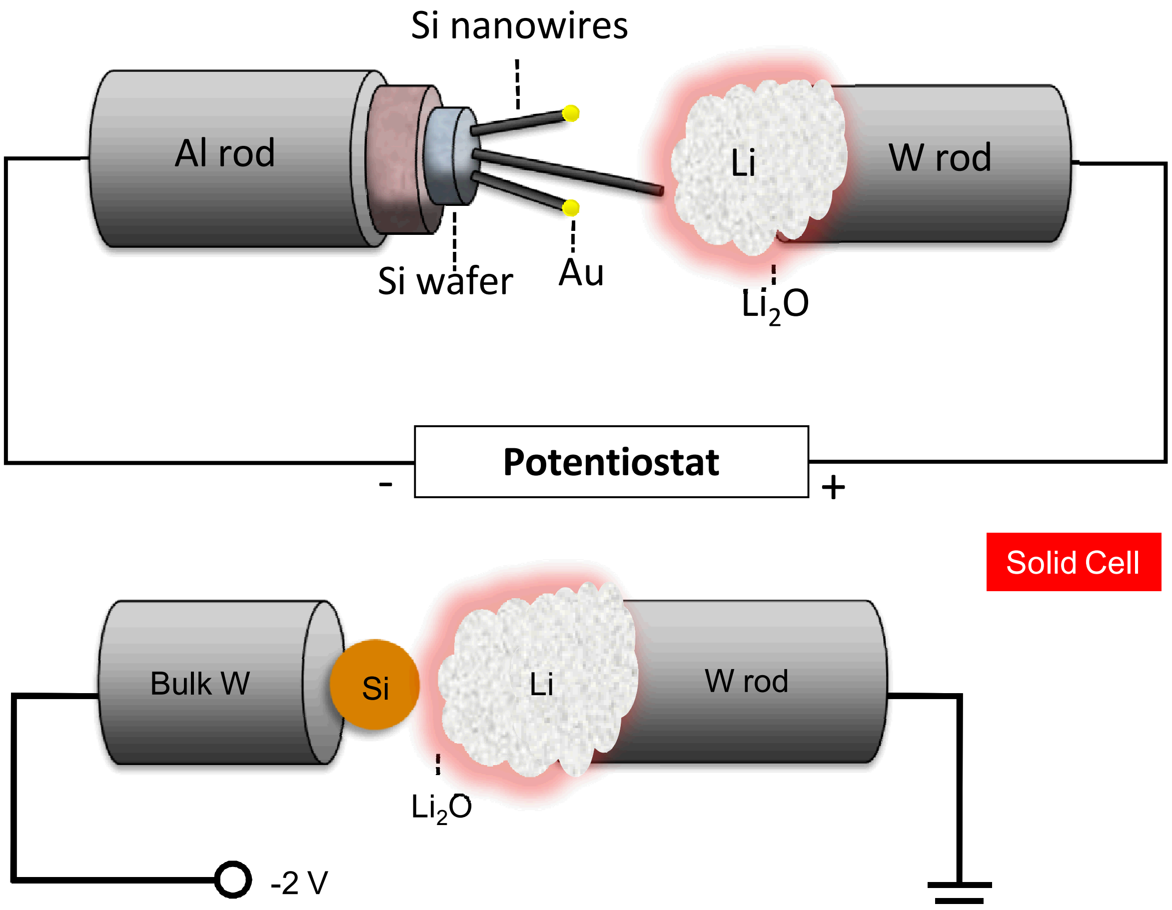
(1) Liquid Cell

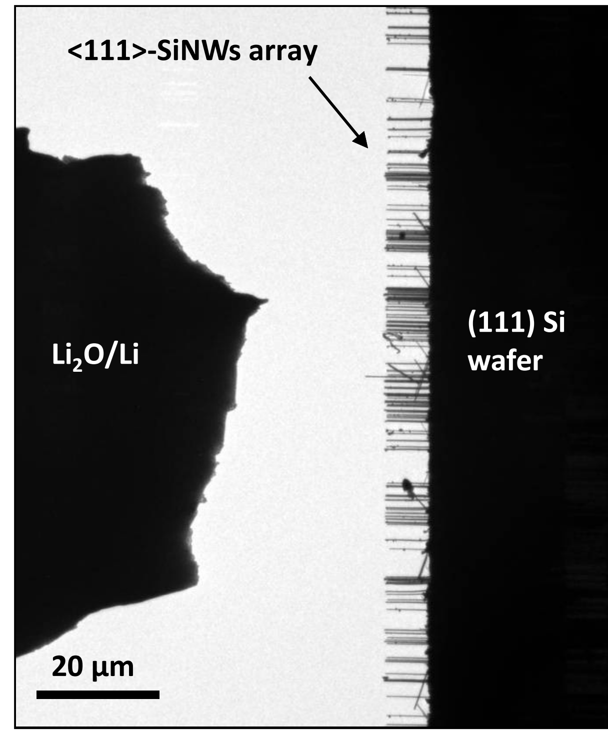
Ultrafast charging of a phosphorus-doped and carbon-coated Si nanowire



(2) Solid cell based on Li_2O/Li

Half cell; Li counter-electrode; Li_2O solid-state electrolyte





A low-magnification view in TEM

Advantages over the “liquid cell” configuration:

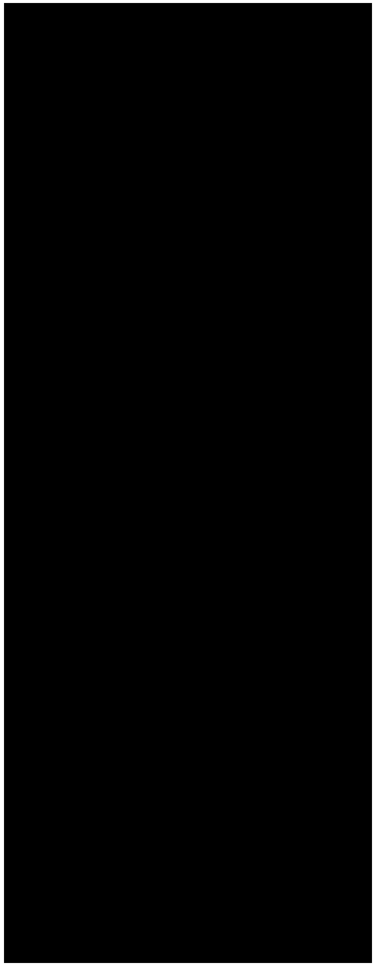
(1) observation from the beginning;

(2) sample size down to a few nanometers.

Liu, *et al.*, ***Energy Environ. Sci.* 3**, 3844-3860 (2011);
Liu, *et al.*, ***ACS Nano* 11**, 6: 1522-1531 (2012);
Liu, et al., ***Nano Lett.* 11**, 3312-3318 (2011).

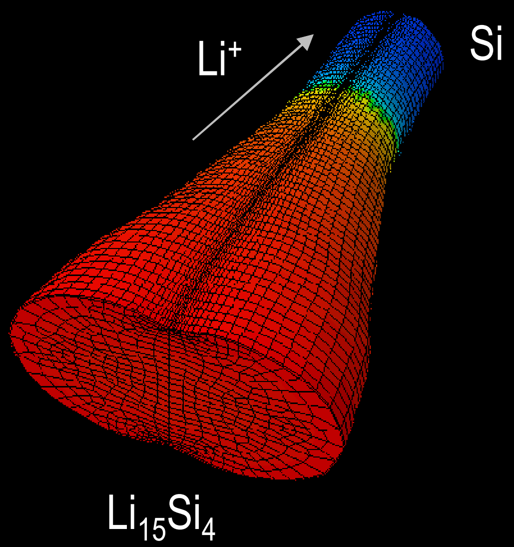
(2) Solid Cell

Lithiation of a crystalline Si nanowire



Liu, *et al.* ***Nano Lett.*** **11**, 3312-3318 (2011).

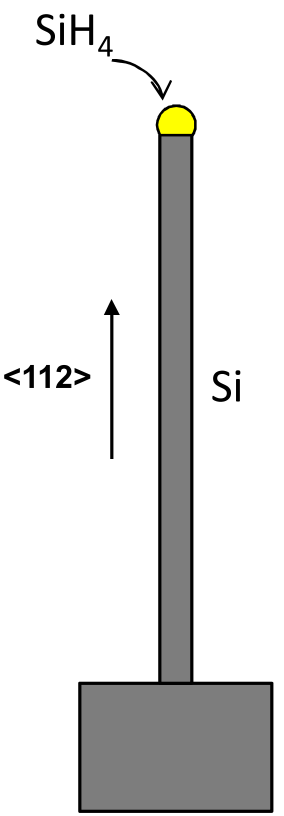
Part 3.1
Anisotropic Deformation of Crystalline Si during Lithiation



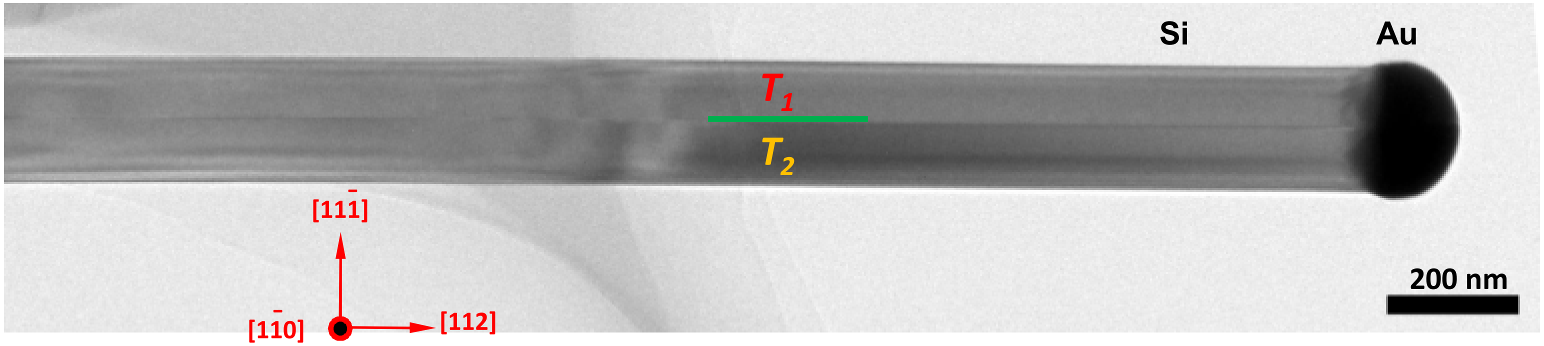
Pristine <112>-Si nanowire

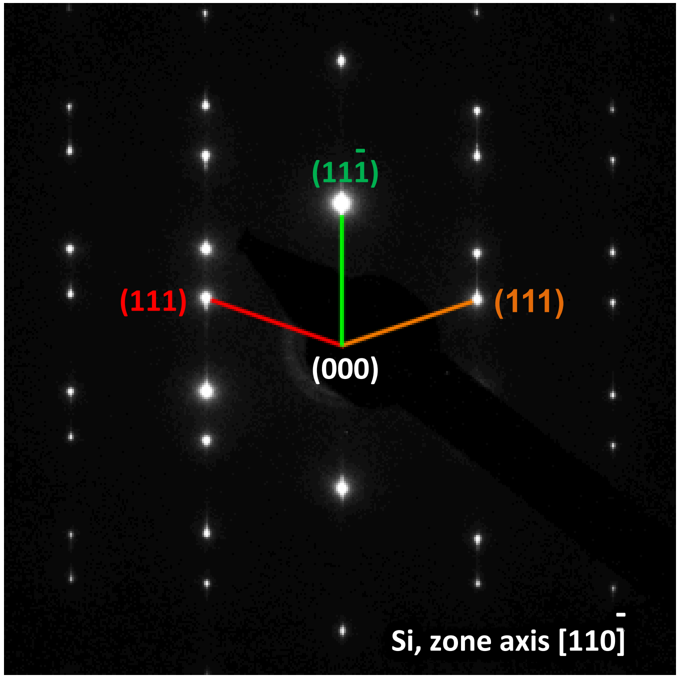
Perfect cylinder shape defined by the liquid droplet of Au catalyst

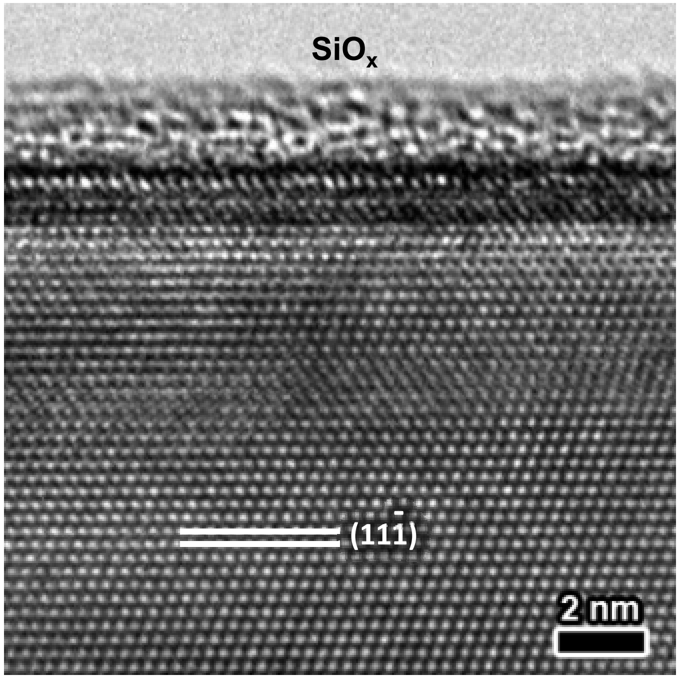
Straight Si nanowires with a few twinning defects and a thin SiO_x layer



Vapor-liquid-solid (**VLS**) growth in a chemical vapor deposition (**CVD**) furnace catalyzed by Au



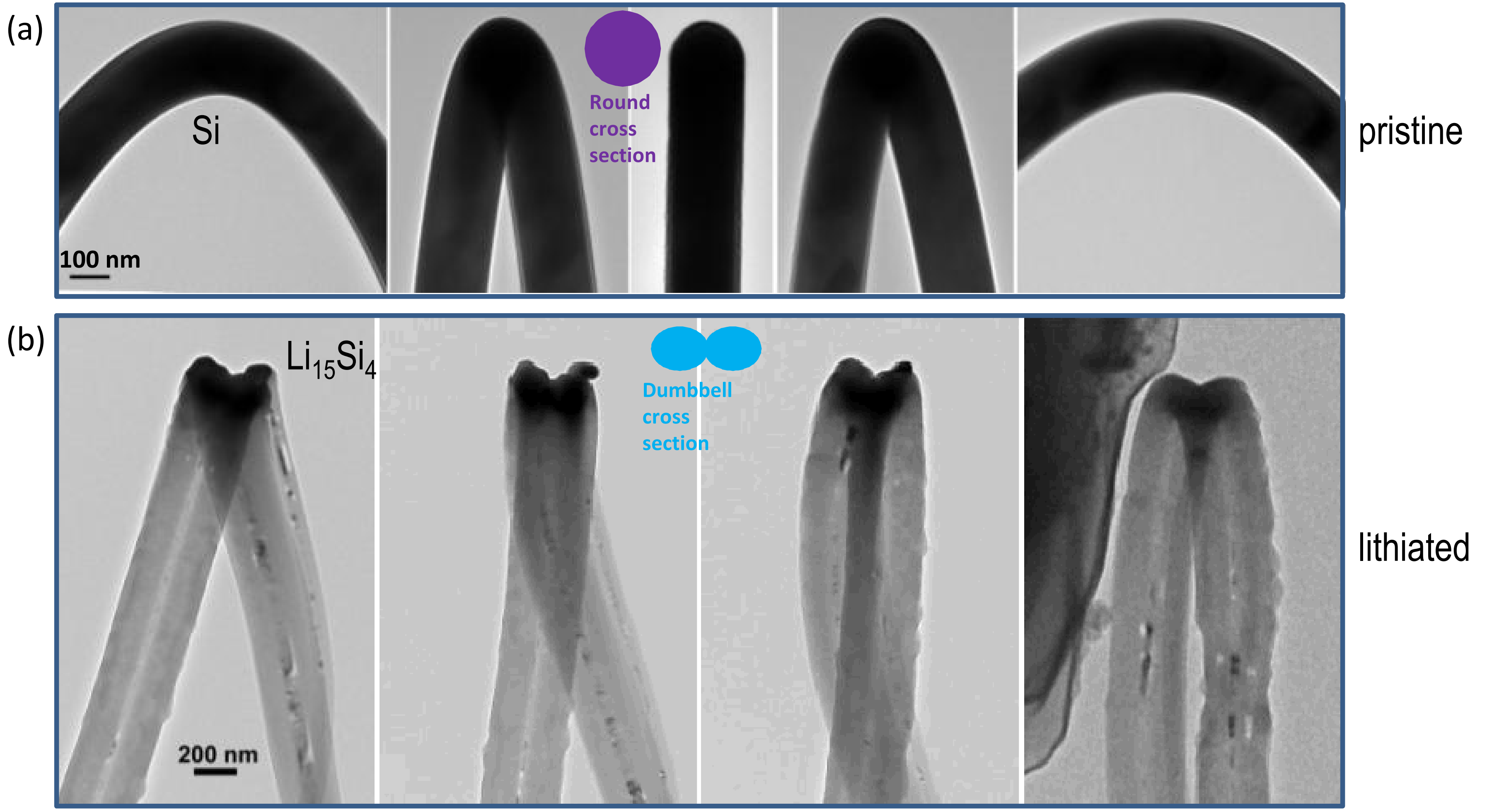




Liu, *et al.* ***Nano Lett.* 11**, 3312-3318 (2011).

Dramatic shape change after lithiation

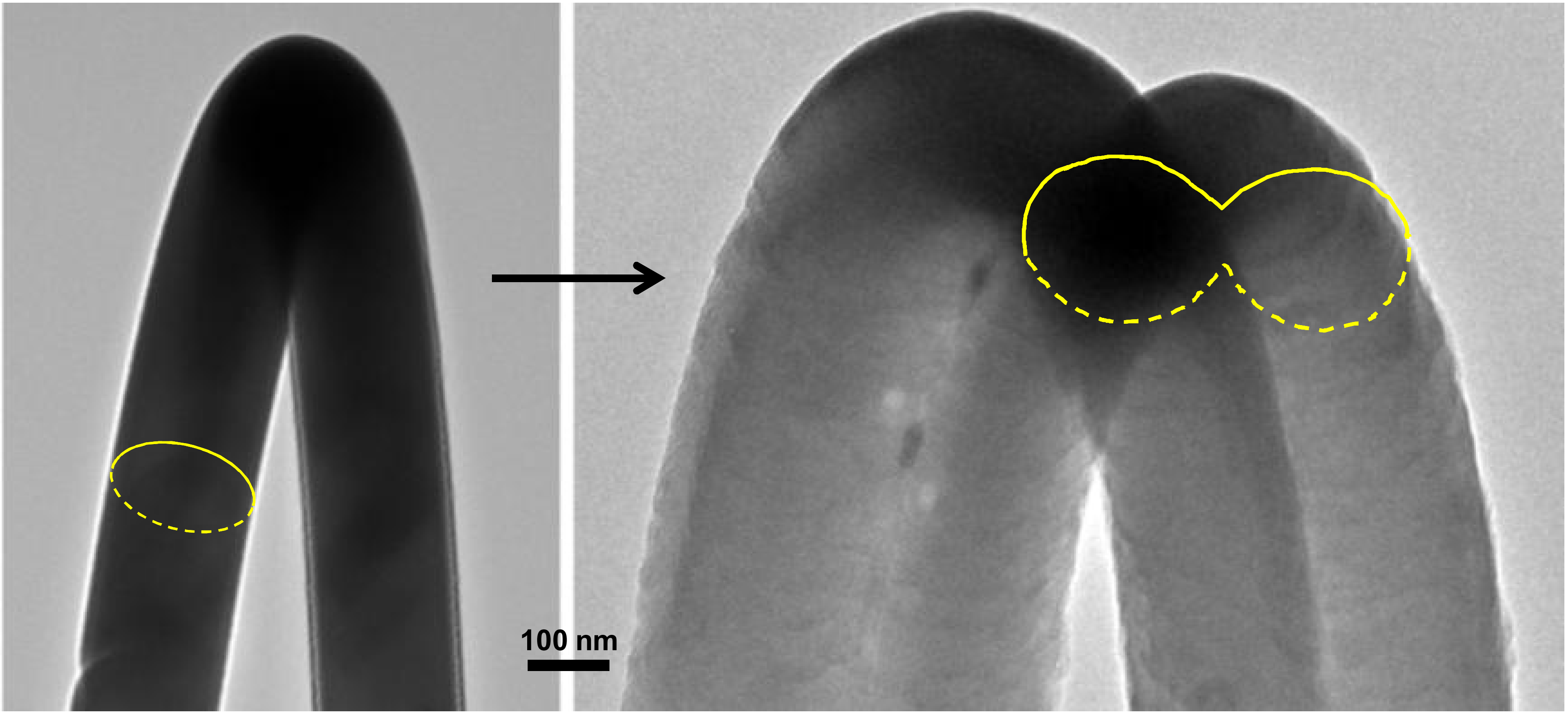
Perfect cylinder → dumbbell cross section



Tilted series showing the shapes of the nanowires before and after lithiation.

Lithiated Si nanowire

Dumbbell shaped cross section

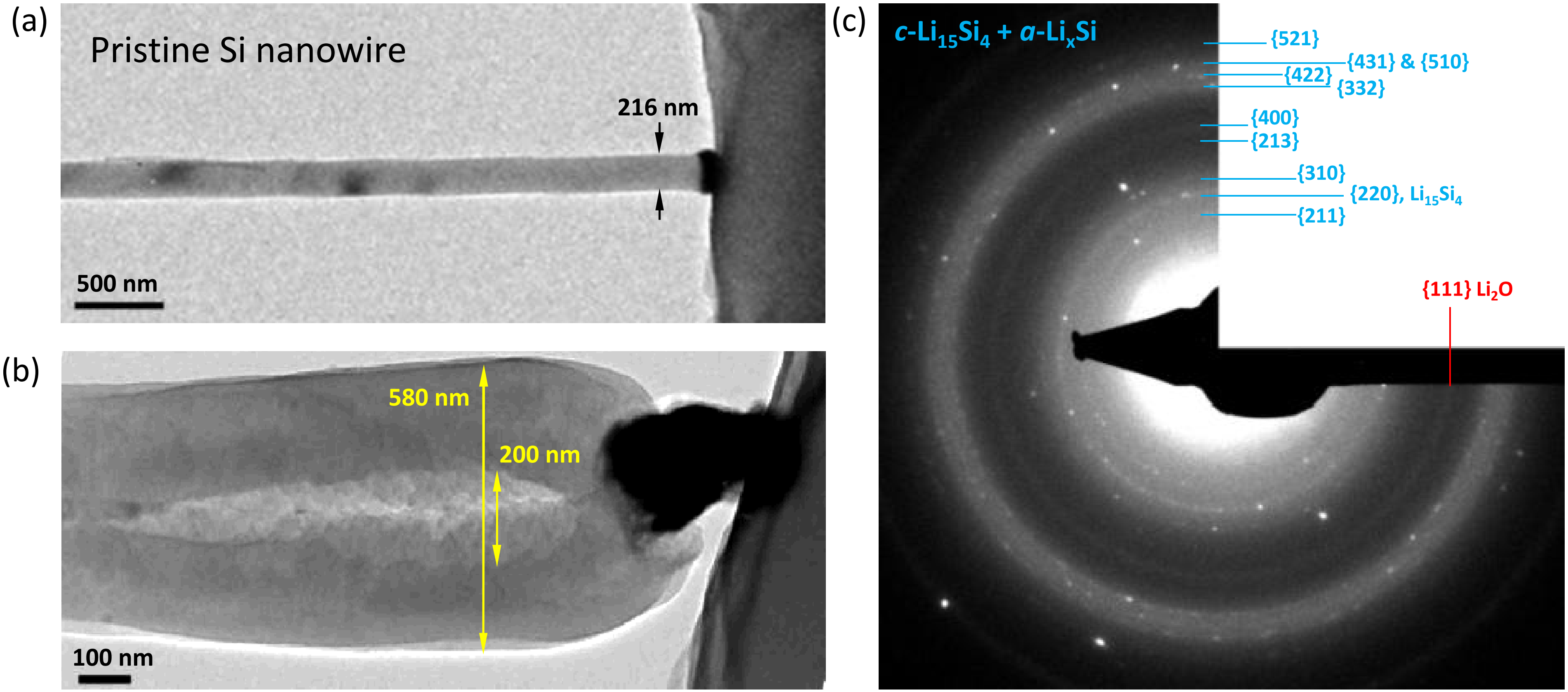


pristine lithiated

Liu, *et al.* ***Energy Environ. Sci.*** **3**, 3844-3860 (2011).

Microstructure change

Center crack running along the axis of the nanowire due to uneven radial swelling

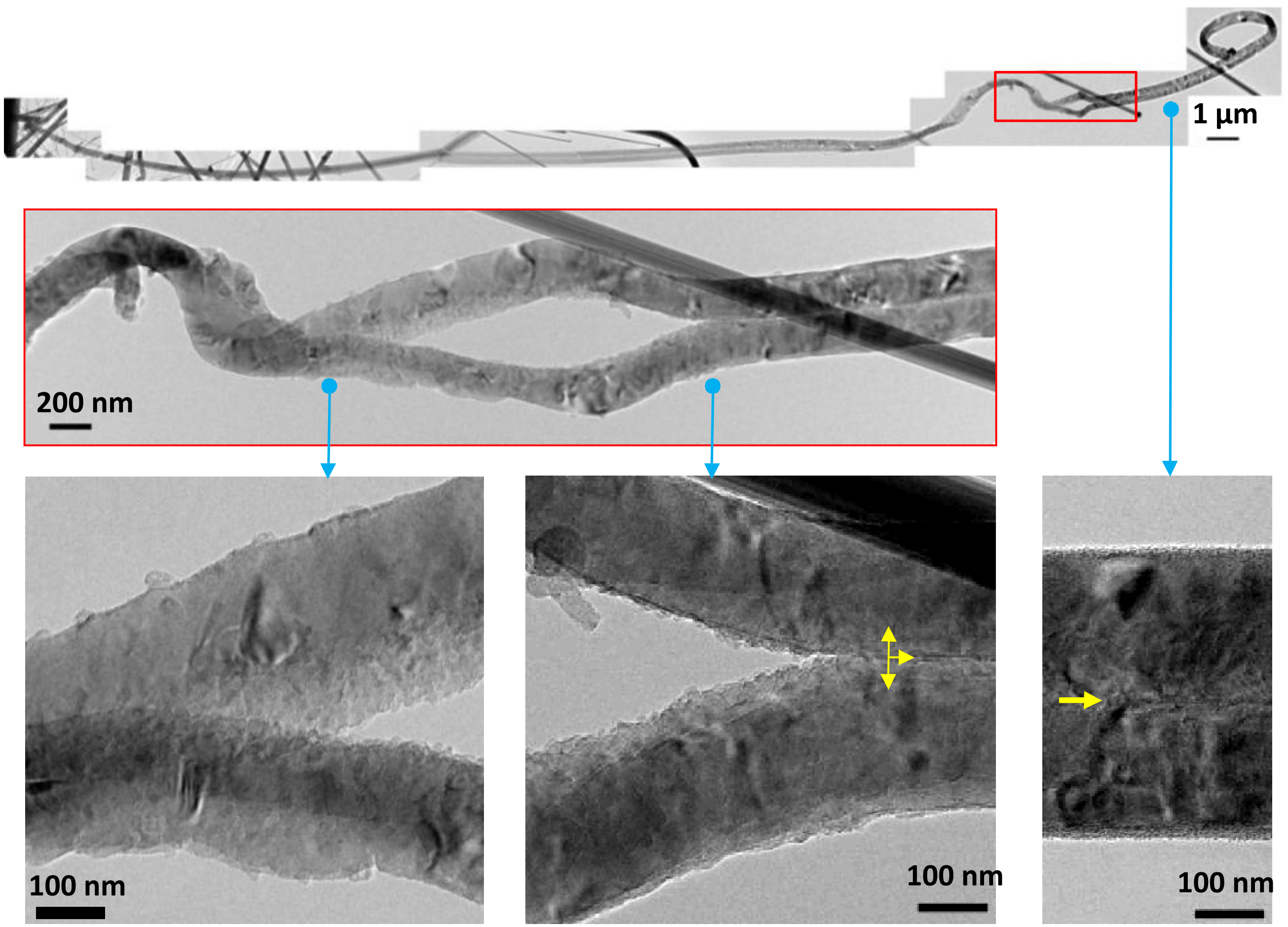


Lithiated Si nanowire with a central crack

Converted to polycrystalline $Li_{15}Si_4$

Self-splitting

Anisotropic radial swelling sometimes split the nanowire into two sub-wires



Anisotropic lithiation

↓

Cracking along the axis

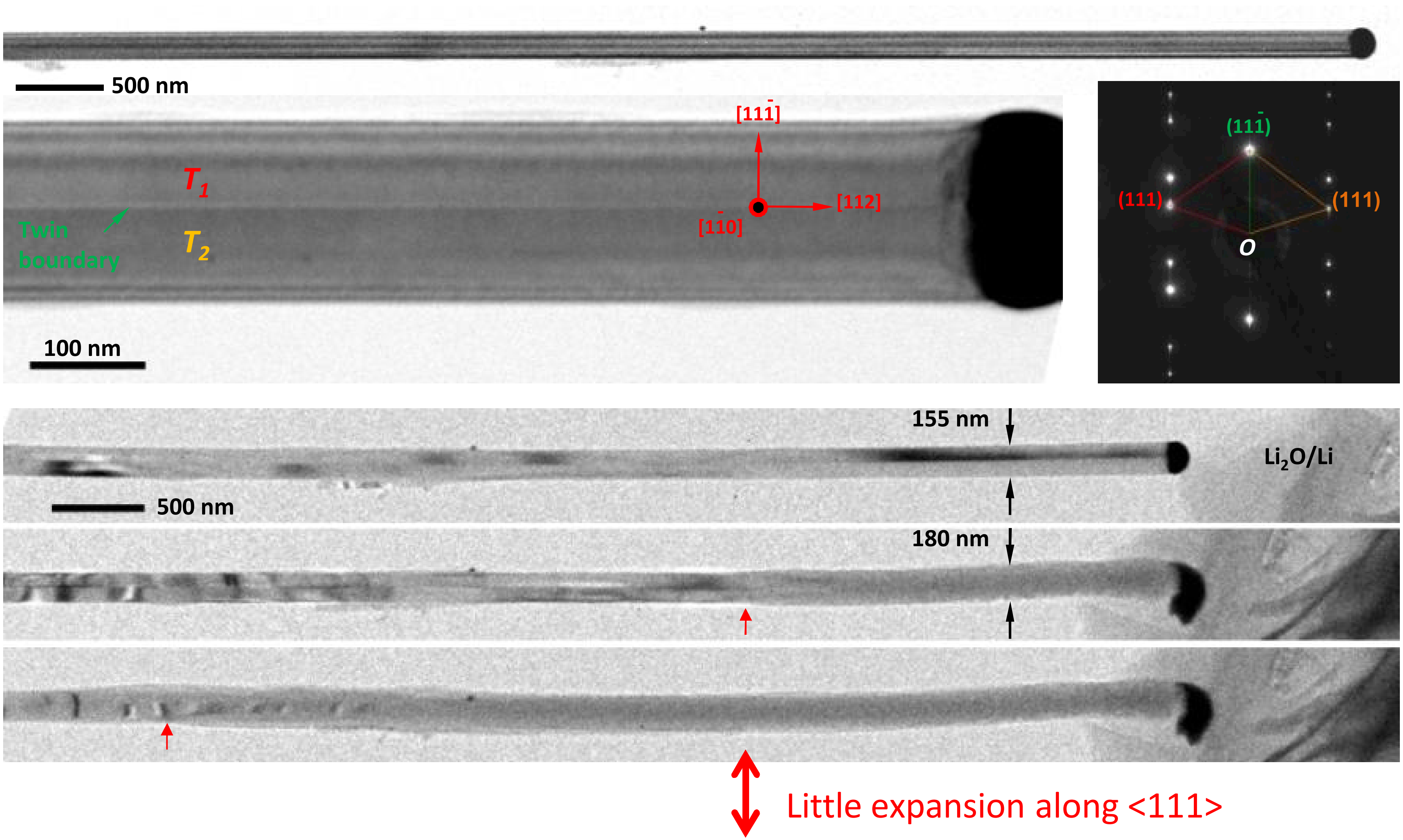
↓

Self-splitting

Liu, *et al.* ***Nano Lett.*** **11**, 3312-3318 (2011).

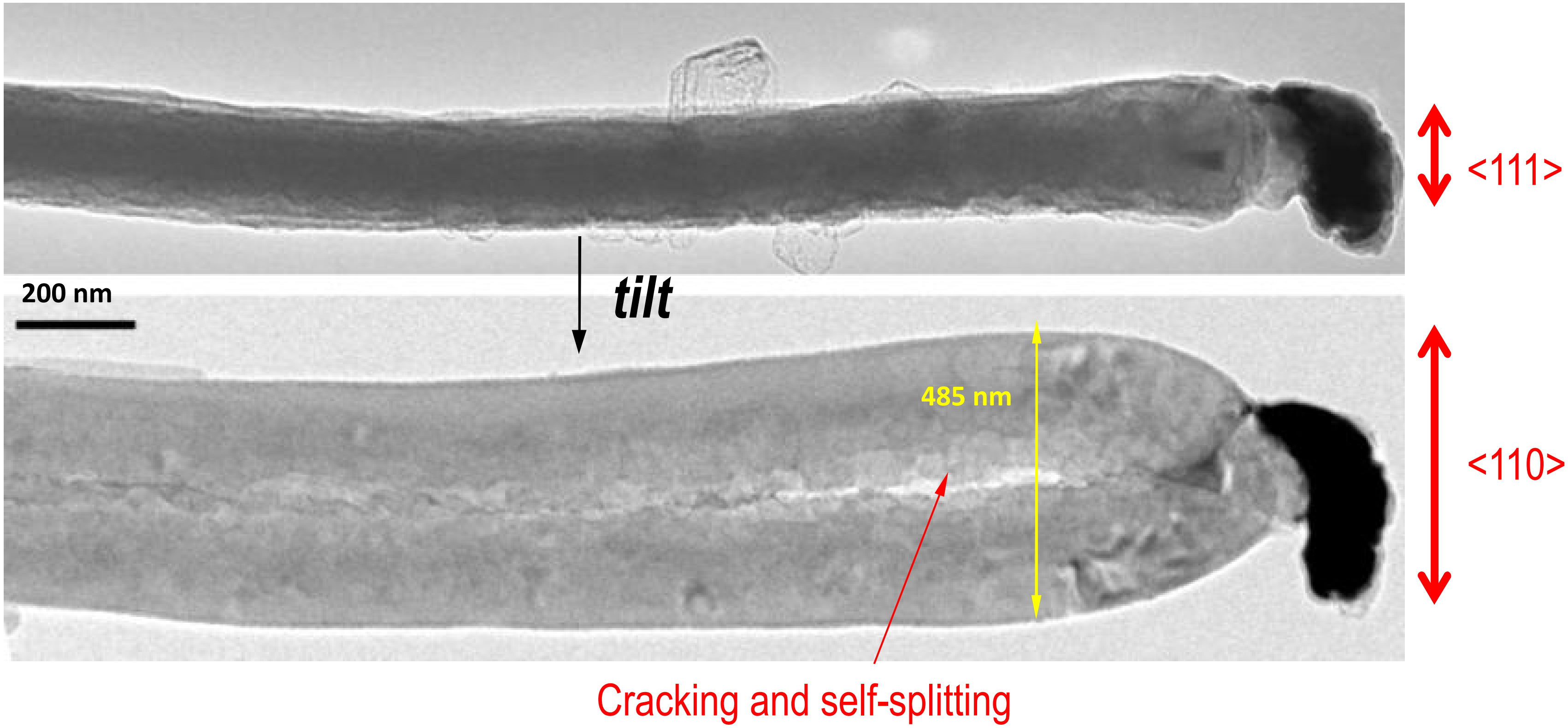
Crystallography of the anisotropic lithiation of <112>-Si nanowires

Little volume expansion was seen along <111>



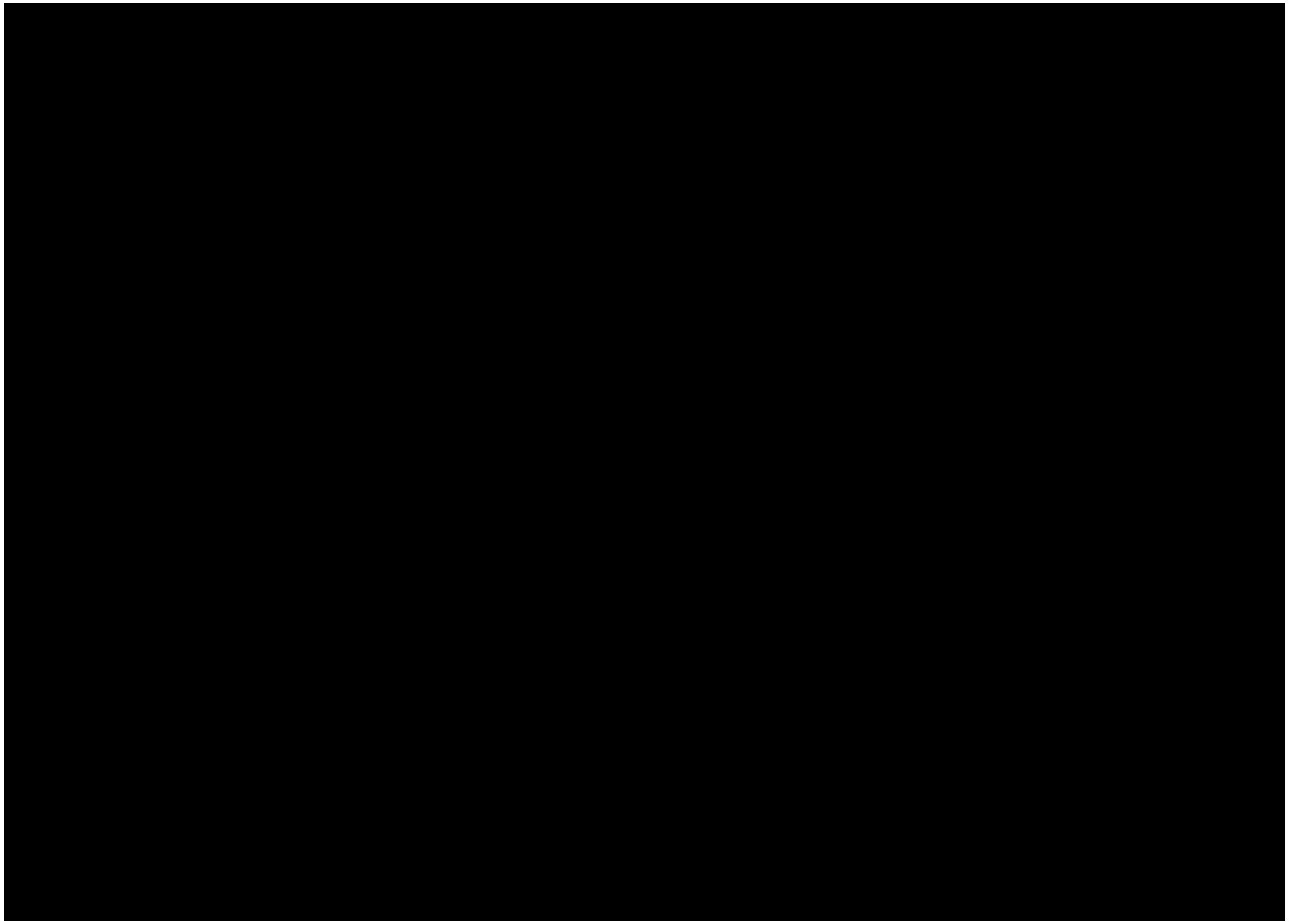
Liu, *et al.* ***Nano Lett.*** **11**, 3312-3318 (2011).

Tilted images showing different views



Finite element simulation

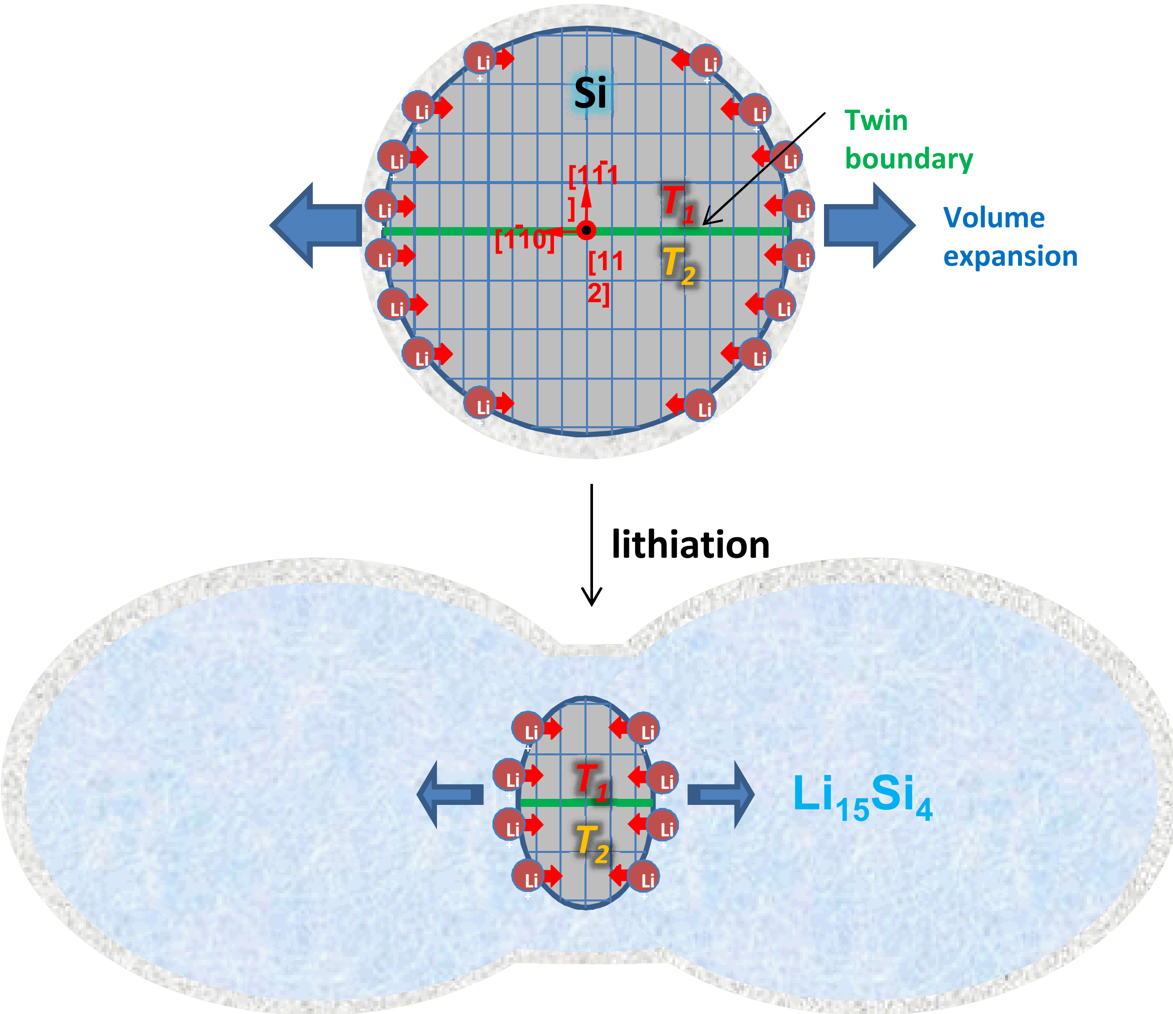
Reproducing the anisotropic swelling of <112>-Si nanowires

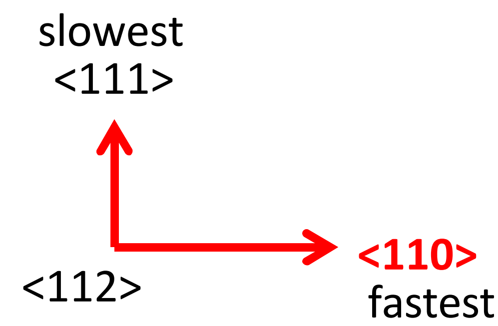


Liu, *et al.* ***Nano Lett.*** **11**, 3312-3318 (2011).

Crystallography of the anisotropic lithiation of <112>-Si nanowires

Much faster lithiation and swelling along the radial <110> directions than that along <111>





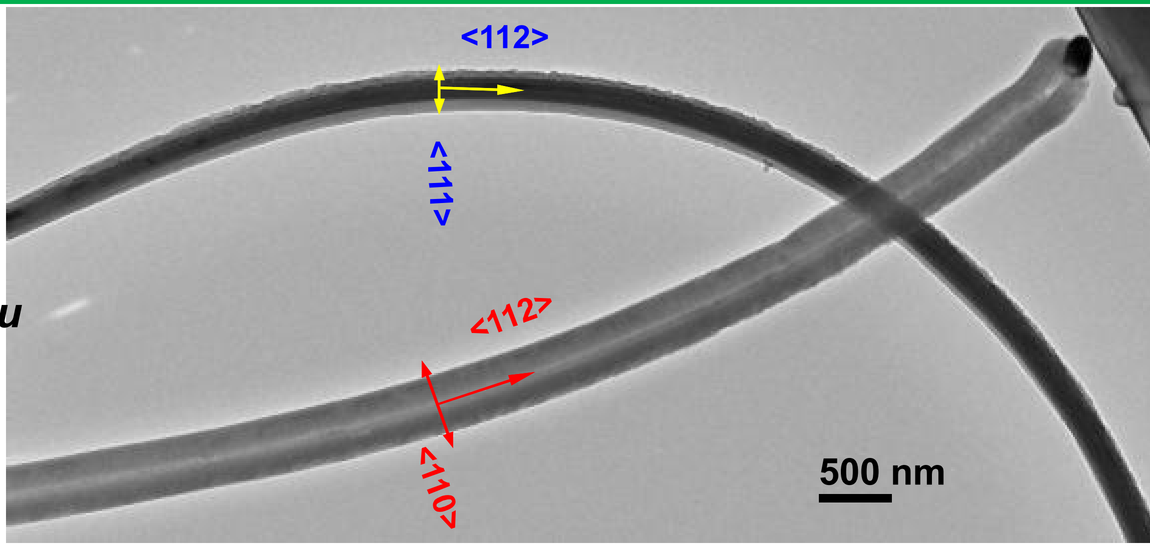
Lithiation occurred preferentially along the radial <110> directions, and the lithiated products ($Li_{15}Si_4$ nanocrystals) swelled along the opposite directions to release the stress generated by huge volume expansion.

Liu, *et al.* ***Energy Environ. Sci.*** **4**, 3844-3860 (2011).

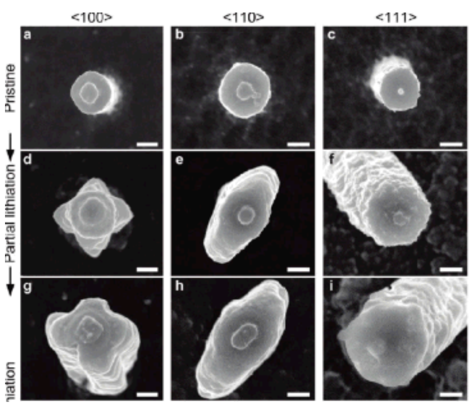
Comparison of *in-situ* and *ex-situ* studies

Both showing fast lithiation along Si <110> directions

in situ

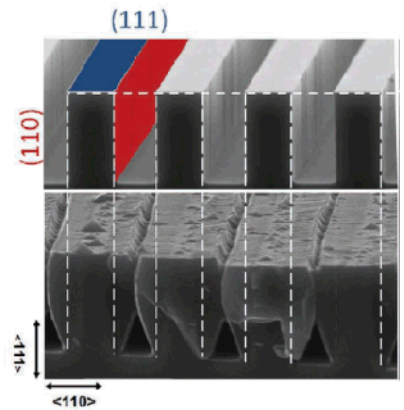


ex situ



Anisotropic shapes of Si pillars with different orientations.

Lee, *et al.* ***Nano Lett.* 11**, 3034-3039 (2011).



Si microslabs swell on the {110} faces but not on {111}.

Goldman, *et al.* ***Adv. Func. Mater.* 21**, 2412-2422 (2011).

The consistency between the *in-situ* and *ex-situ* studies also verifies the powerfulness of in-situ TEM and its relevance to real battery studies.

Liu, *et al*. ***Adv. Energy Mater.***, DOI: 10.1002/aenm.201200024 (2012).

A brief summary

on anisotropic lithiation of crystalline Si

1. For a <112>-oriented Si nanowires with a cylinder shape, lithiation and swelling occur predominately on the radial <110> directions;

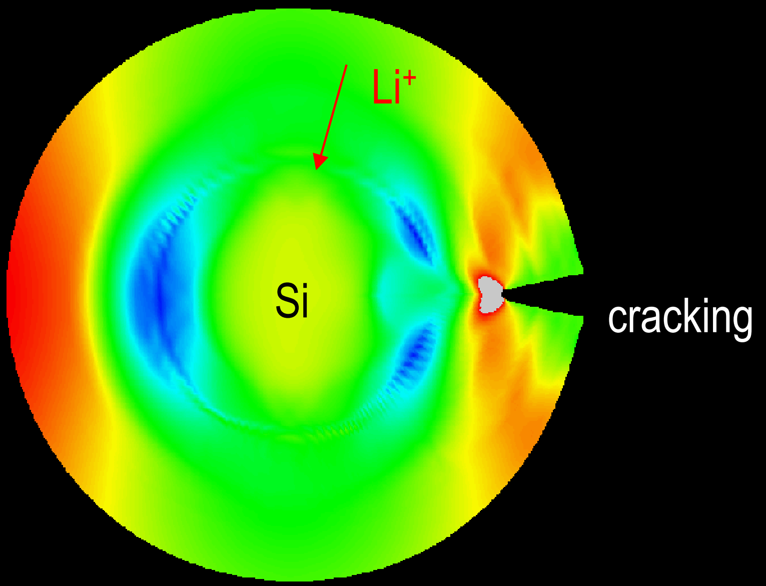
2. Such anisotropic swelling leads to cracking and sometimes self-splitting;

3. Anisotropic lithiation should be considered in the design of Si electrodes.

Liu, *et al.* ***Nano Lett.*** **11**, 3312-3318 (2011).

Part 3.2

Size dependent fracture of Si nanoparticles during lithiation

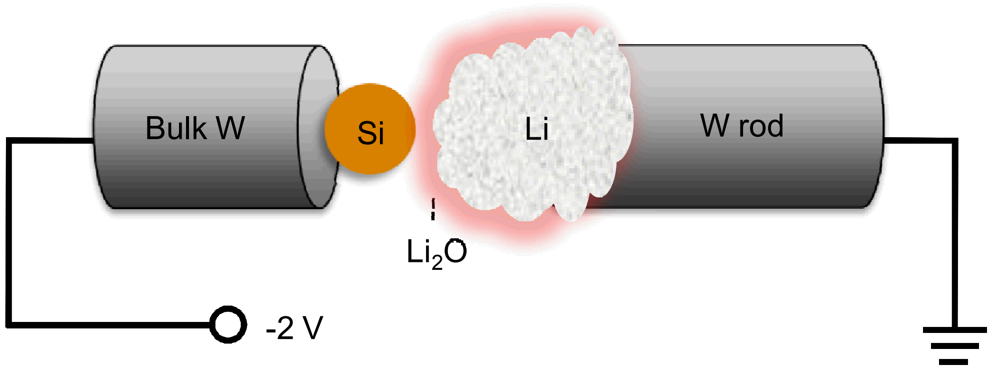


D > 150 nm

Experimental method

Si nanoparticles with various sizes were lithiated

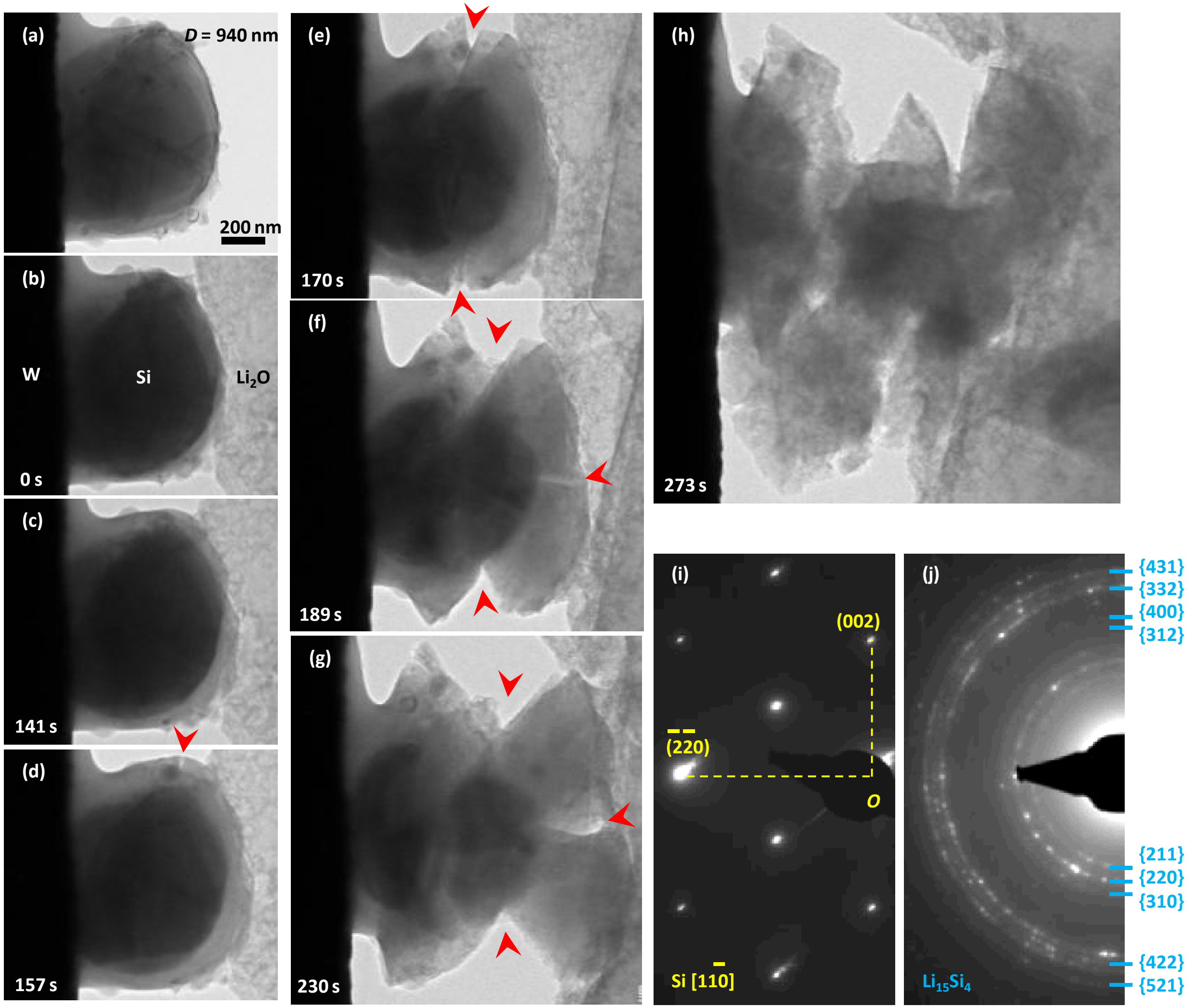
1. Solid cell configuration using Li_2O/Li electrolyte/counter-electrode
2. Individual Si nanoparticles with nm ~ μm sizes



Solid Cell

Large Si nanoparticles

Always crack and fracture upon the first lithiation



Core-shell lithiation

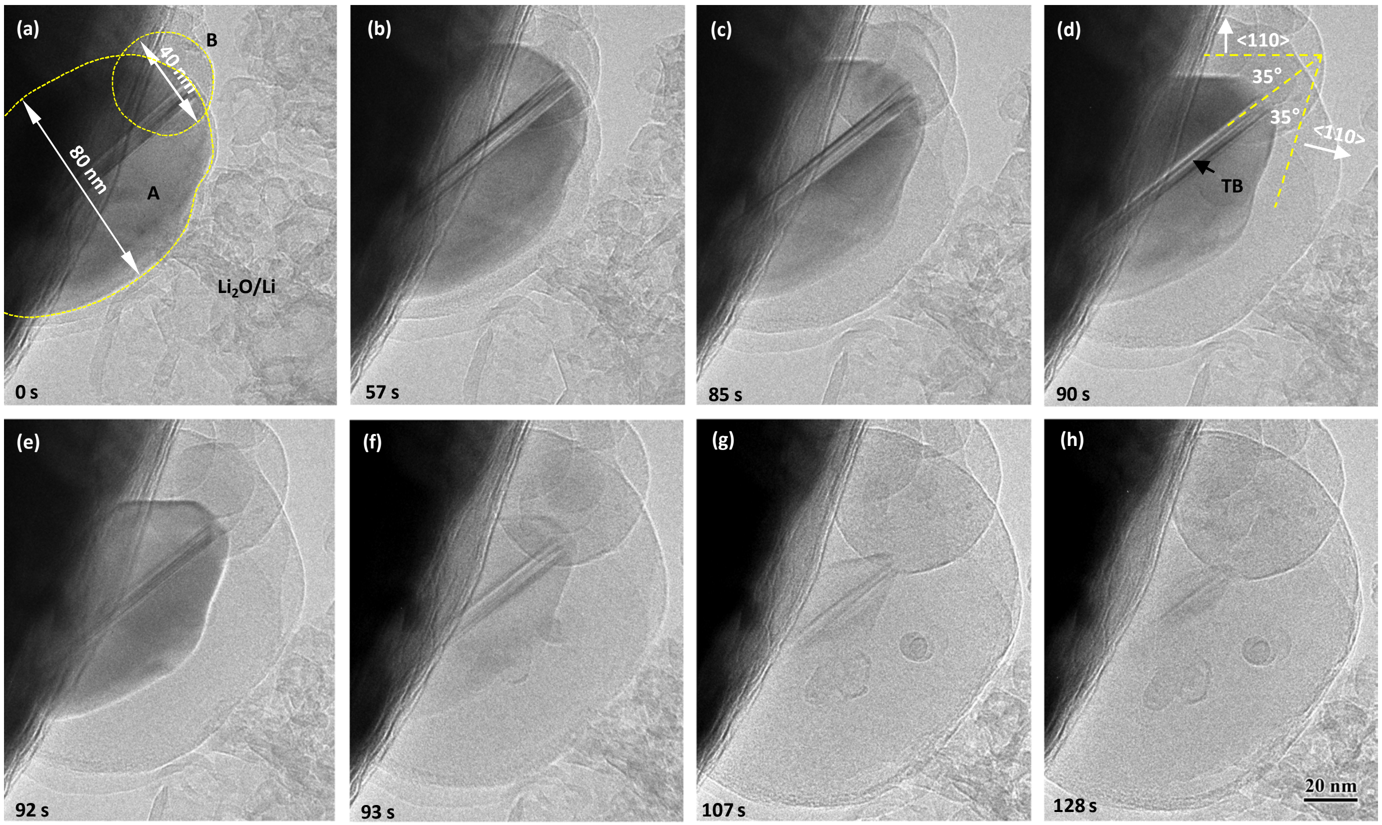
Two-phase (Li_xSi/Si) mechanism

Broken into pieces after lithiation

Fully lithiated to $Li_{15}Si_4$

Small Si nanoparticles

Not cracking



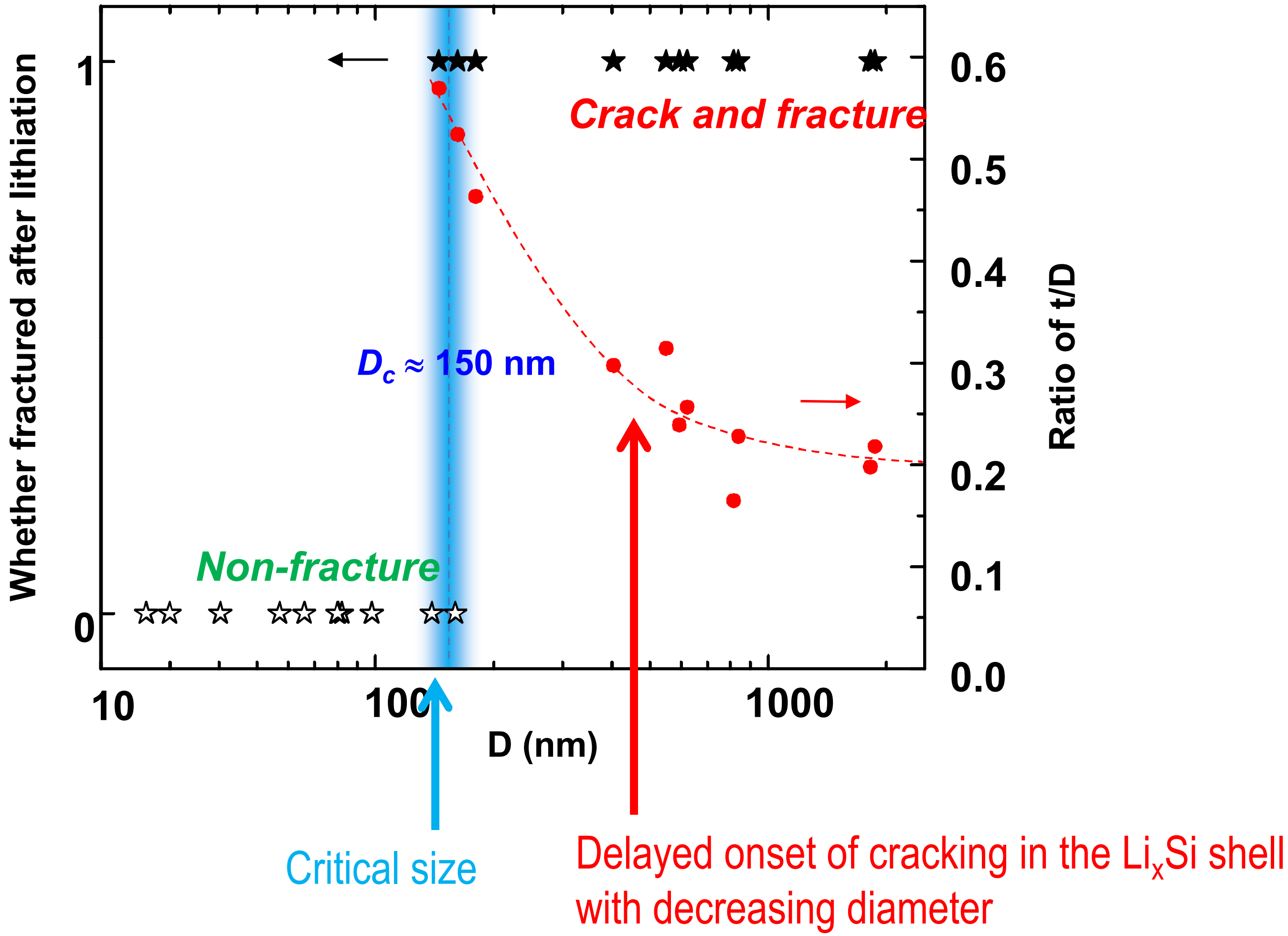
Also forming a core-shell structure

Like an inflating balloon

Strong size dependence of fracture behavior

Critical size ~ 150 nm

Statistics showing very reproducible size-dependent fracture behavior of Si nanoparticles upon first lithiation:

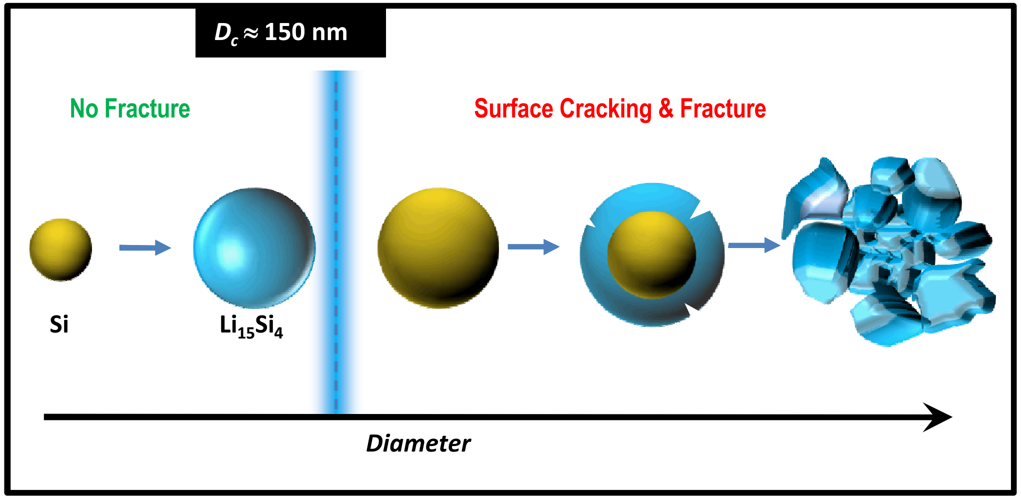


Strong size dependence of fracture behavior

Critical size ~ 150 nm

Fracture of large Si nanoparticles

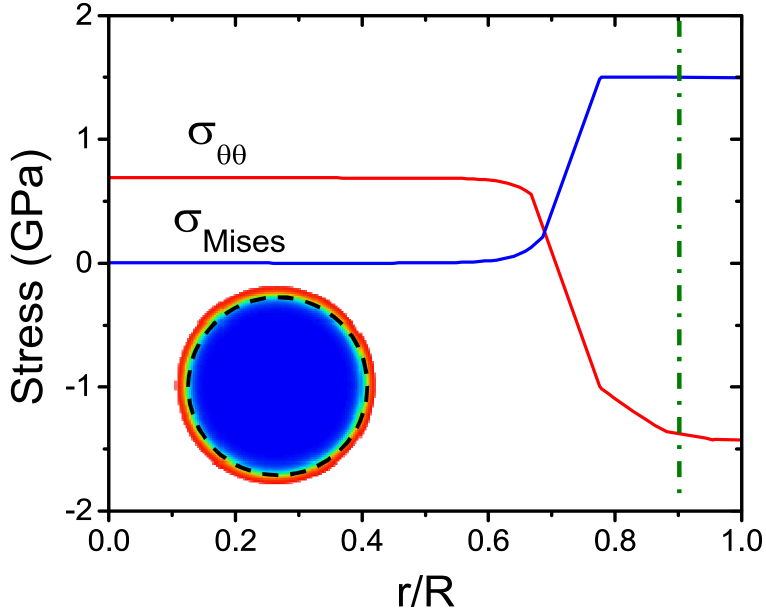
No fracture or cracking in small Si nanoparticles



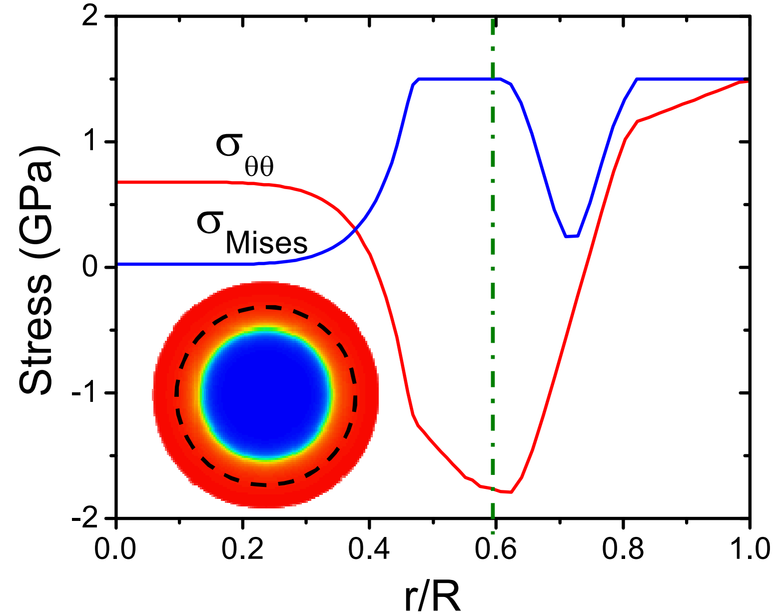
Origin of the size effect

Hoop stress reversal in the Li_xSi shell as being pushed out: compression → tension

Stress analysis of the Si nanoparticle in the different stages of lithiation:



Initial stage: compression in the lithiated shell



Later stage: hoop stress revered to tension in the lithiated surface, because the inner and newly formed *a*-Li_xSi is pushing out

Origin of the size effect

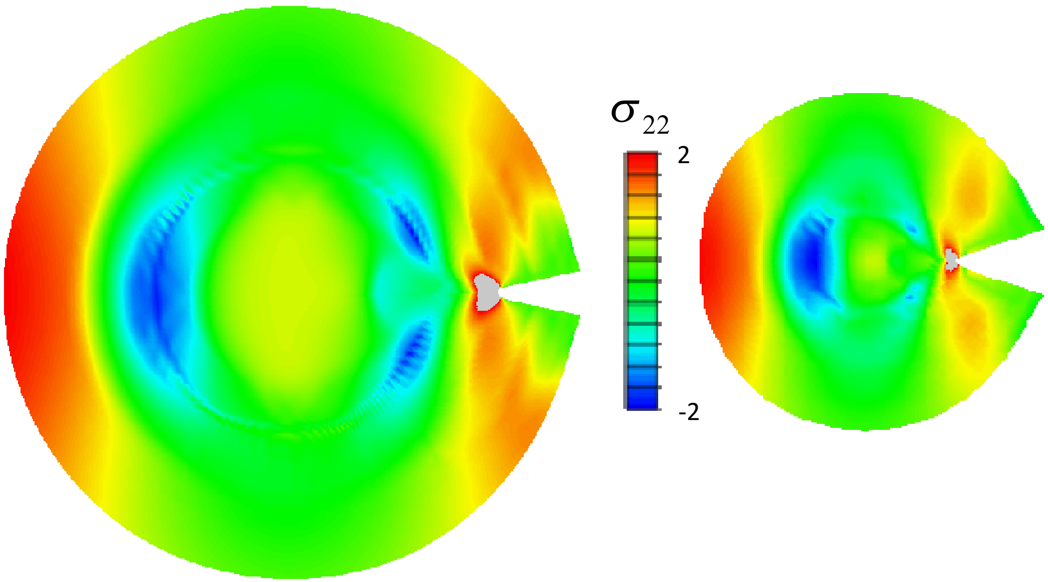
Hoop stress reversal in the Li_xSi shell as being pushed out: compression → tension

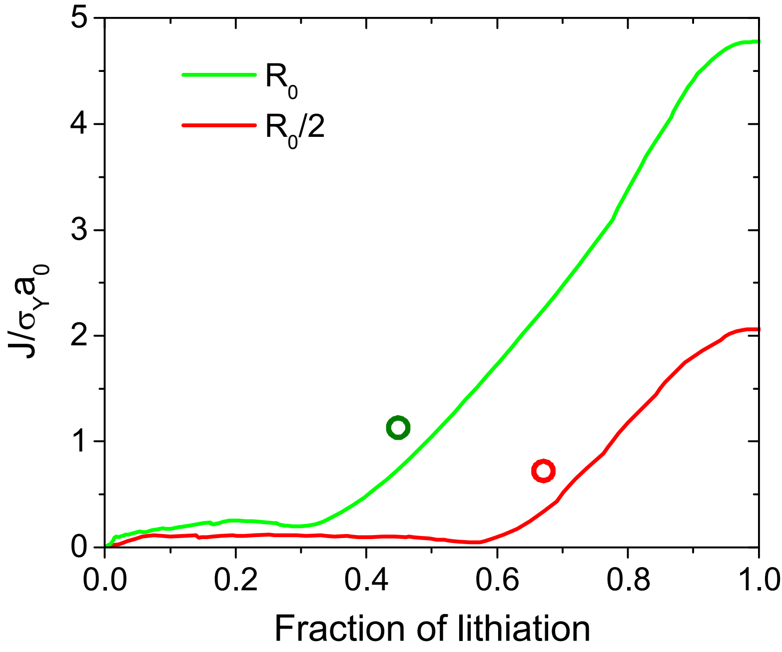
Why cracking only in large particles?

Releasing mechanical energy by crack propagation

Versus

Increasing surface energy by generating new surface





In small particles, the driving force is for crack propagation is insufficient.

A brief summary

Size-dependent fracture of Si nanoparticles

1. Larger Si nanoparticles (*D* > 150 nm) always crack and fracture upon the first lithiation process;

2. Smaller Si nanoparticles avert fracture, suggesting that nano-Si may be good for fabricating durable Si electrodes (*e.g.*, dispersing small Si particles in an elastomeric matrix to accommodate the volumetric changes);

3. Surface cracking was revealed, in contrast to the previously predicted center cracking models.

4. Conclusions on lithiation of crystalline Si

Based on the *in-situ* TEM experiments of various Si nanomaterials

1. Crystalline Si undergoes a two-step lithiation process, namely *c*-Si → *a*-Li_xSi → *c*-$Li_{15}Si_4$, accompanied by 281% volumetric change;
2. Si lithiation is the fastest along <110> and slowest along <111>;
3. Si nanoparticles smaller than 150 nm do not crack or fracture upon lithiation;
4. *In situ* TEM is a powerful tool for the study of degradation mechanism of battery materials.

Related publications:

[1] Liu, X. H., *et al.* ***Nano Letters*** 11, (6), 2251-2258 (**2011**).
[2] Liu, X. H., *et al.* ***Nano Letters*** 11, (8), 3312-3318 (**2011**).
[3] Liu, X. H., *et al.* ***Nano Letters*** 11, (9), 3991-3997 (**2011**).
[4] Liu, X. H., *et al.* ***Energy & Environmental Science*** 4, 3844-3860 (**2011**).
[5] Liu, X. H., *et al.* ***Applied Physics Letters*** 98, (18), 183107 (**2011**).
[6] Liu, X. H., *et al.* ***ACS Nano,*** 6: 1522-1531 (**2012**).
[7] Liu, X. H., et al. ***Adv. Energy Mater.***, DOI: 10.1002/aenm.201200024 (**2012**).

Thank you for your attention!

Sandia National Laboratories

Center for Integrated Nanotechnologies (CINT)