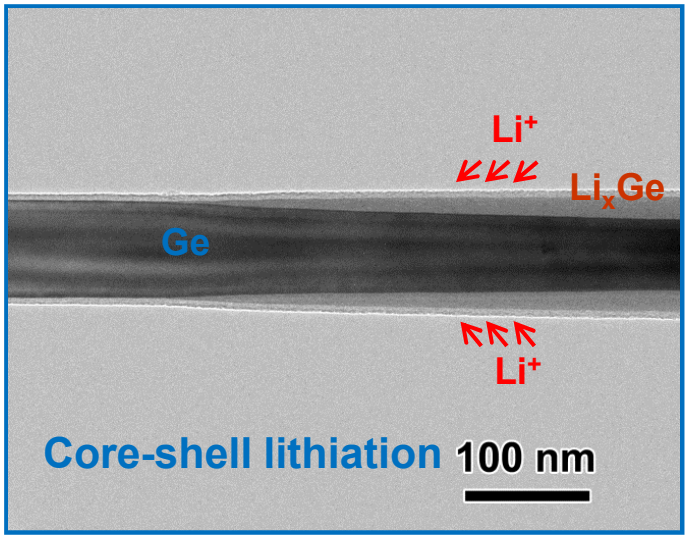
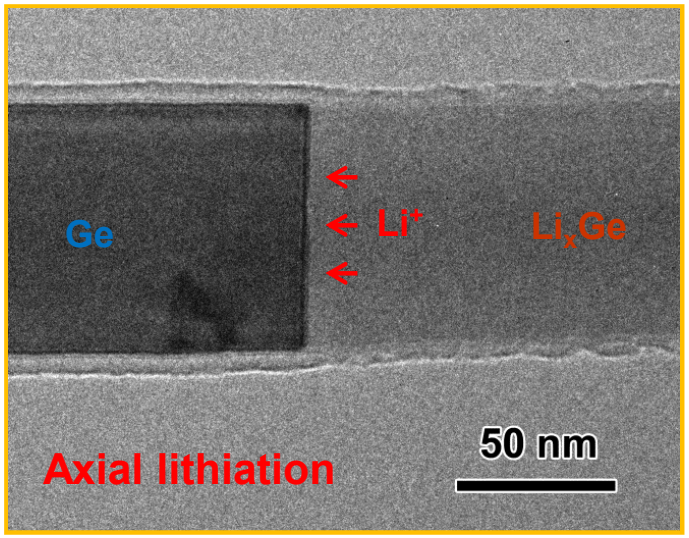
Controlling the Lithiation Behavior of Ge Nanowires via Surface Modifications: An *in-situ* Transmission Electron Microscopy Study

SAND2012-10069C





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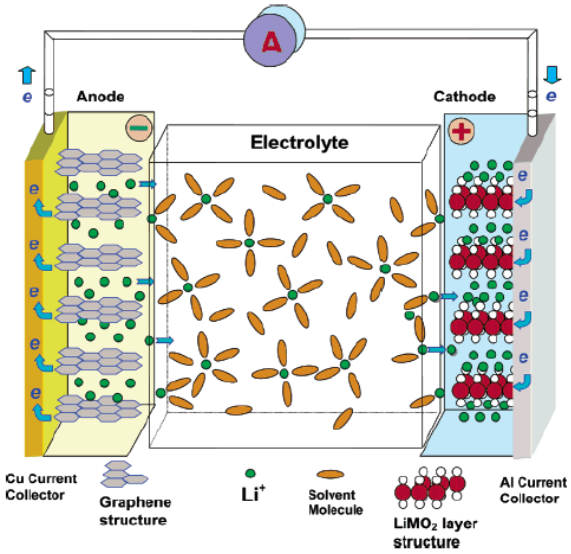
Motivation

High energy and power density
Good cyclability
Low cost



Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 2-4, 2007

- A fundamental understanding of the microstructural change of the electrodes and SEI layer during battery operation.
- Li-ion batteries (LIB) generally use liquid electrolyte, which is not compatible with the high vacuum of a transmission electron microscope (TEM).
- How to create a working nano LIB inside a TEM?
- Understanding the fundamental nano-electrochemistry.

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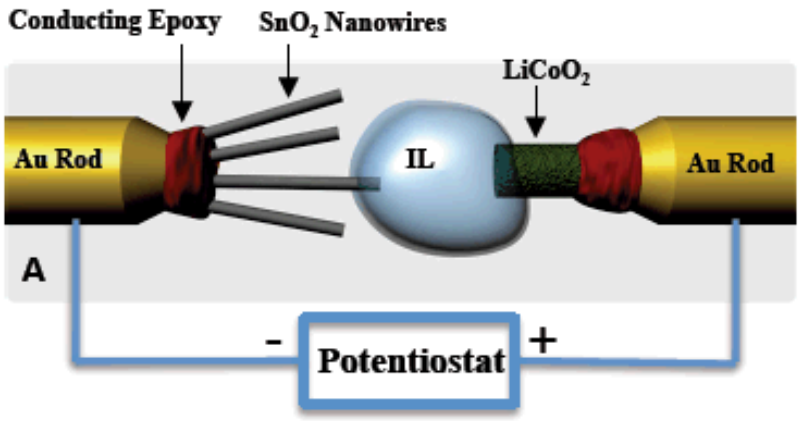
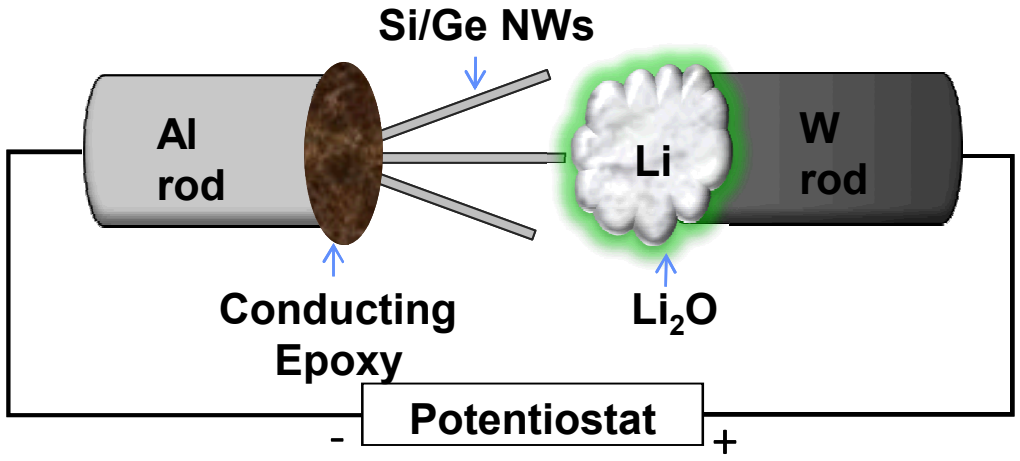
Experimental setup of *in situ* TEM battery test



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

Introduce a vacuum-compatible electrolyte.

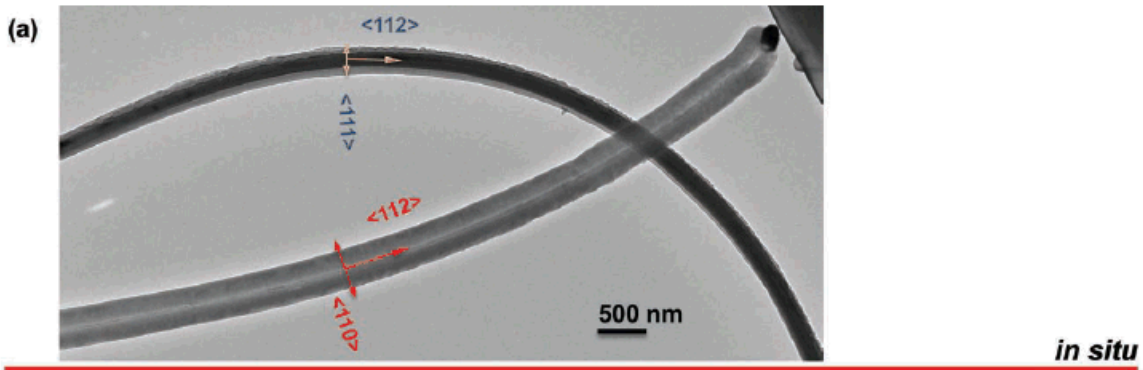


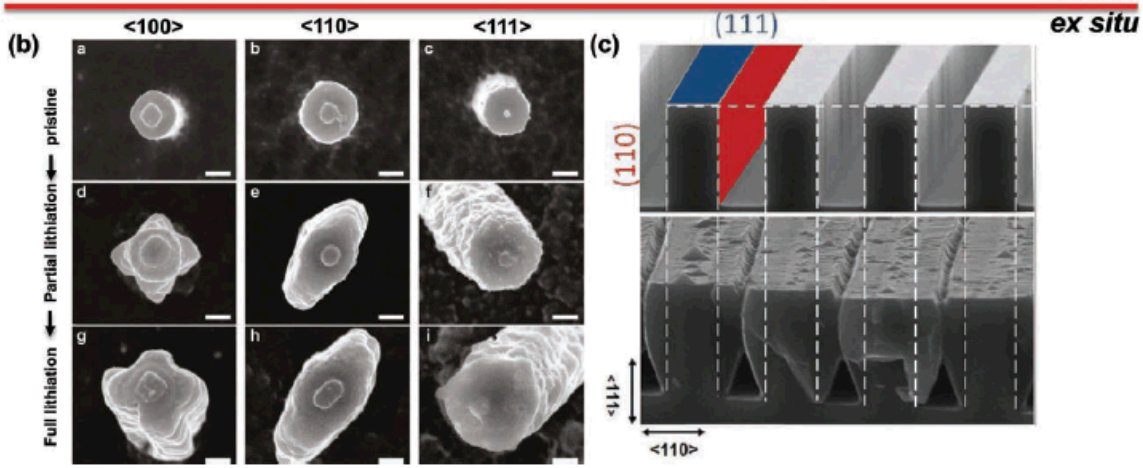
Liu *et al*., ***Adv. Energy Mater.*** 2, 722 (2012)

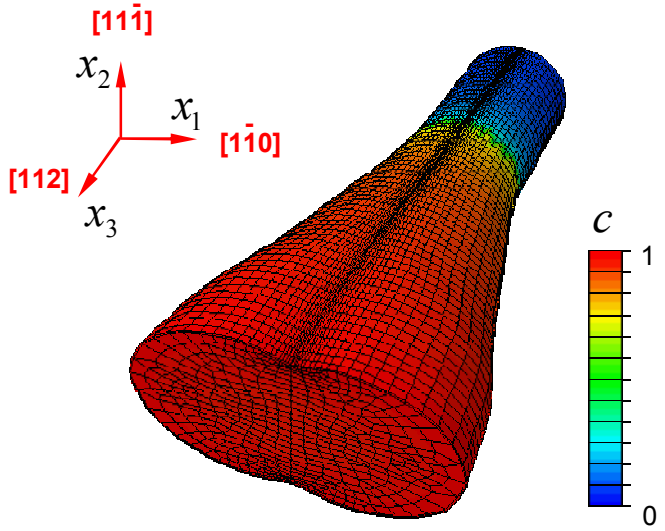
Using the naturally oxidized Li_2O layer on Li metal as the solid electrolyte.
The Li_2O here can be replaced by other kinds of solid electrolytes, such as LiPON and LiAlSiO.

Building a nano-battery in a TEM, allowing for real time and atomic scale observations of battery charging and discharging processes.

Anisotropic Lithiation of Si







Liu *et al*., ***Nano Lett.*** 11, 3312 (2011); Liu *et al*., ***Adv. Energy Mater.*** 2, 722 (2012)
Lee *et al*., ***Nano Lett.*** 11, 3034 (2011); Goldman *et al*., ***Adv. Funct. Mater.*** 21, 2412 (2011)

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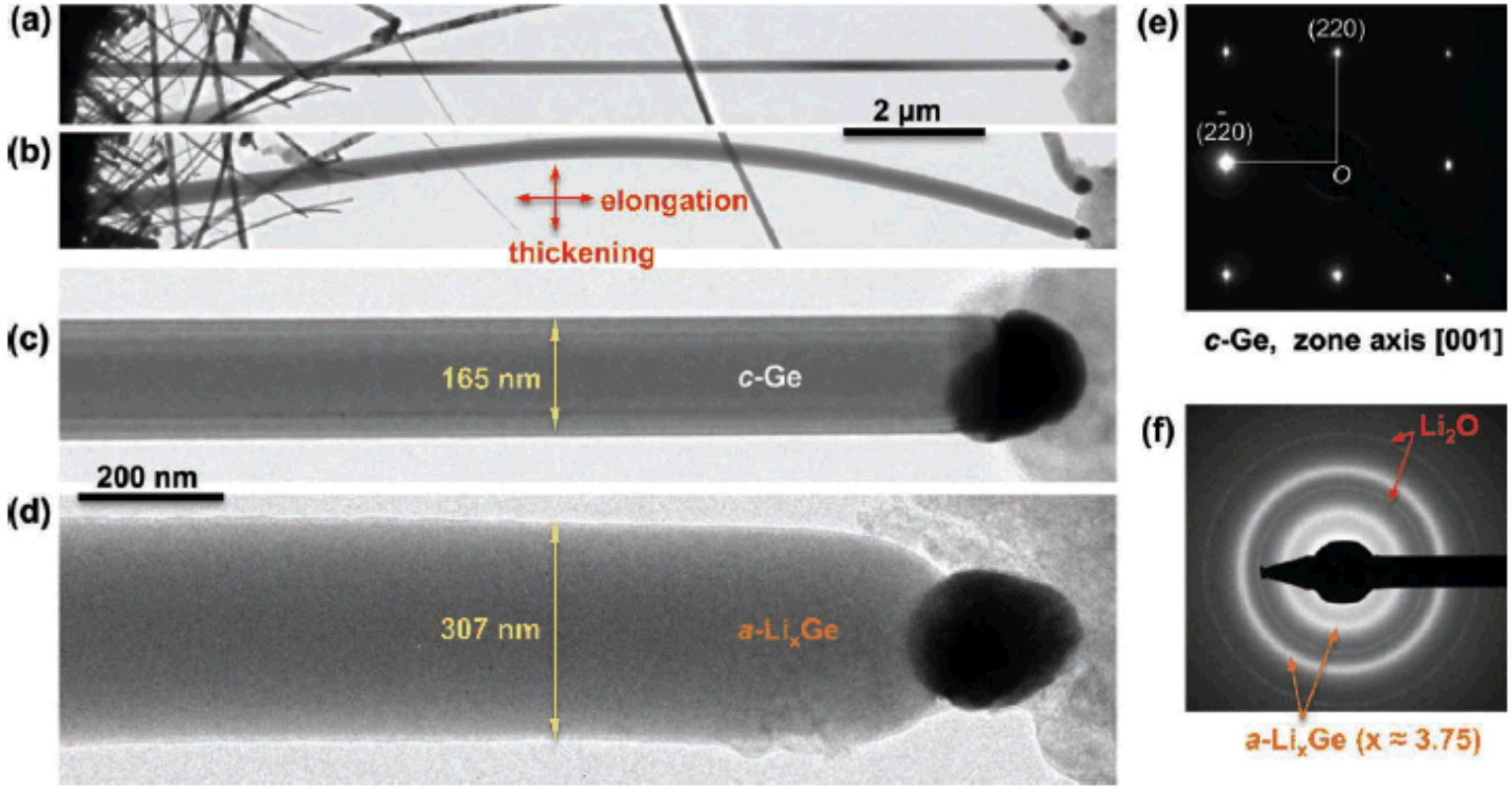
Isotropic Lithiation of Ge



Liu *et al.*, ***Adv. Energy Mater.*** 2, 722 (2012)
Liu *et al.*, ***Nano Lett.*** 11, 3991 (2011)

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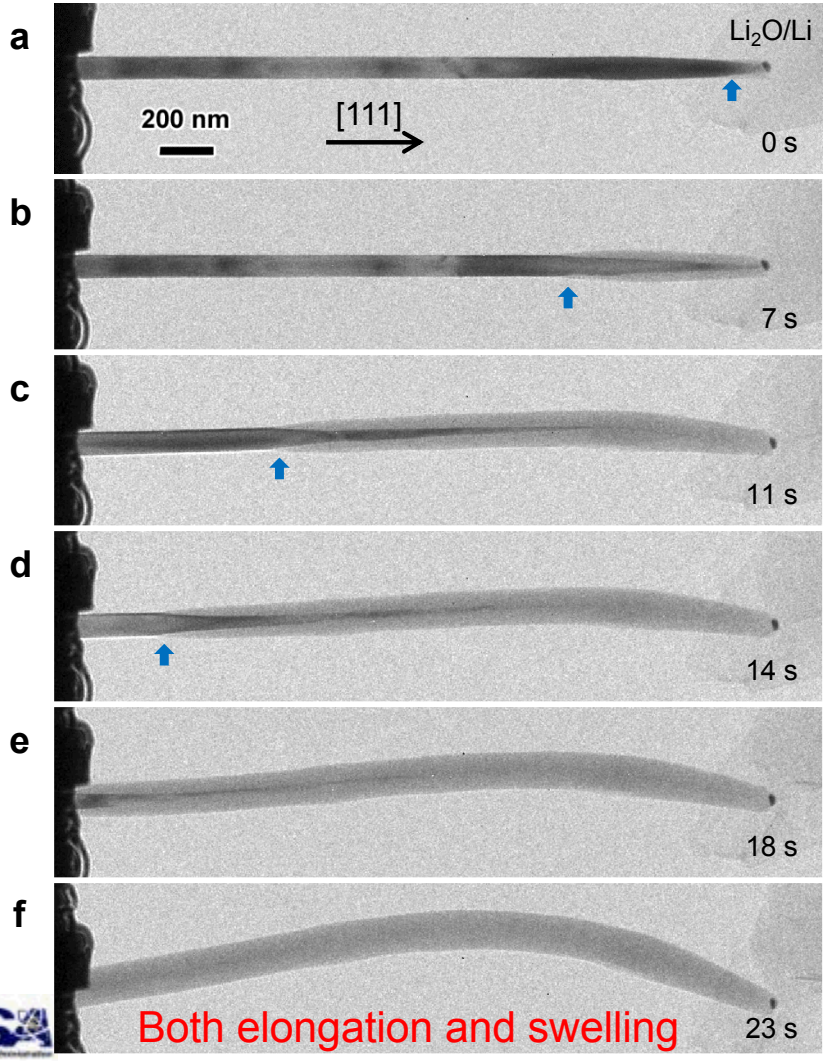
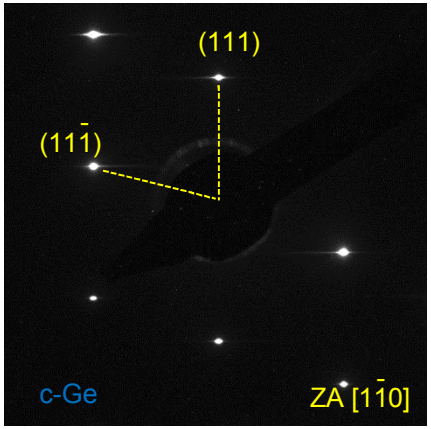
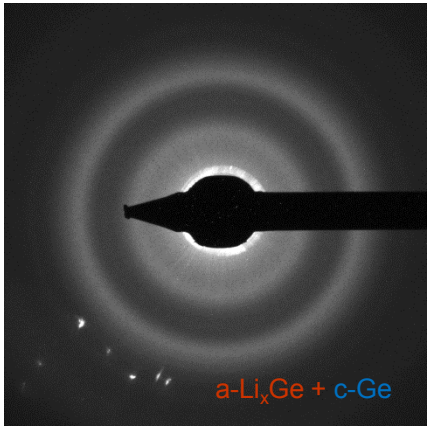
Core-shell Lithiation of Pure Ge nanowire







How about
Surface thin
Si layer coating?

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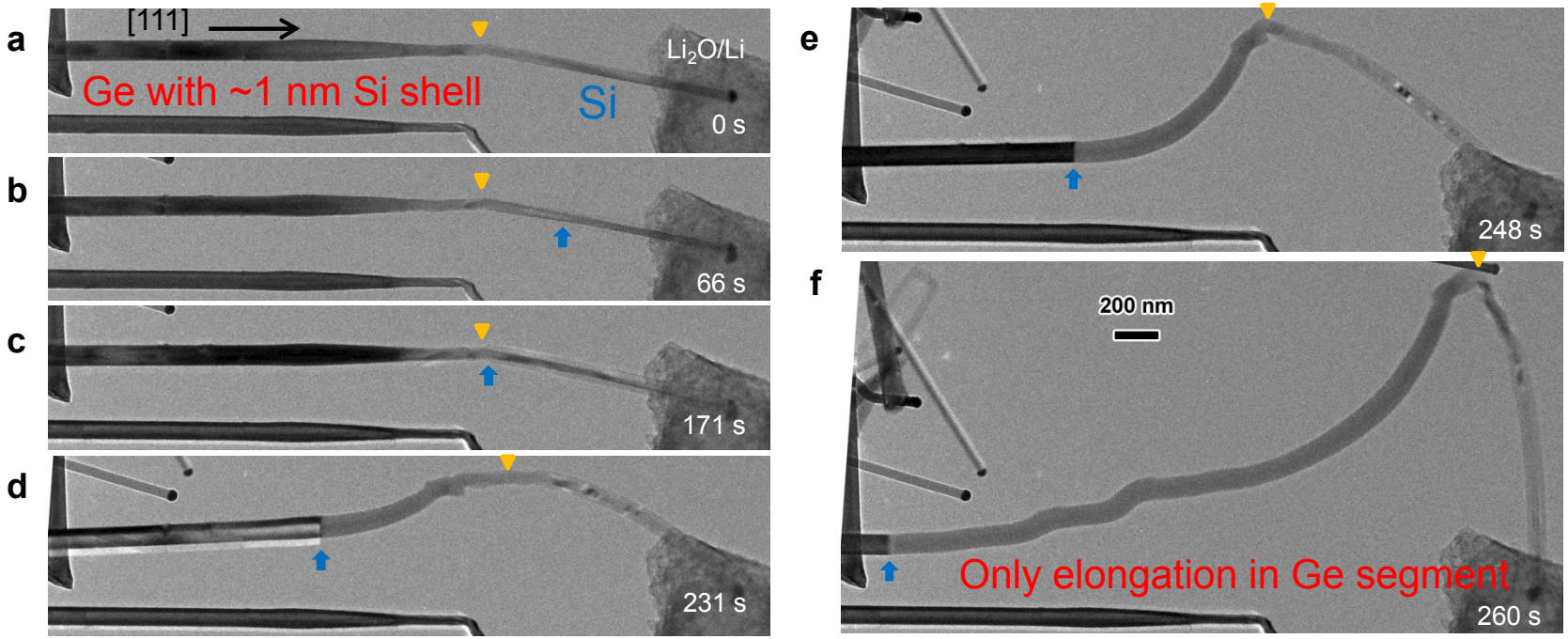
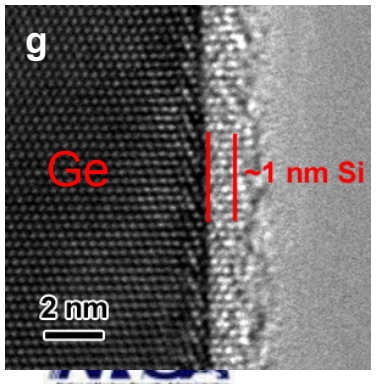
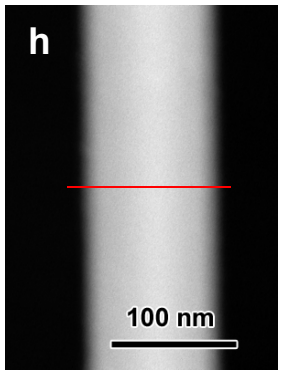
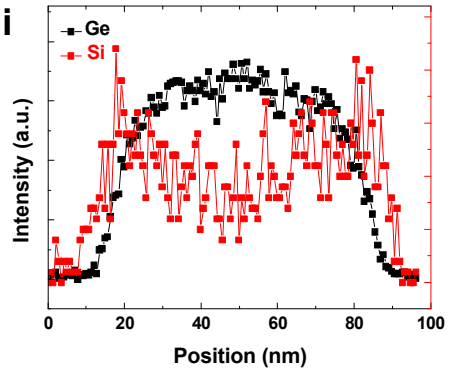
Change to axial lithiation!

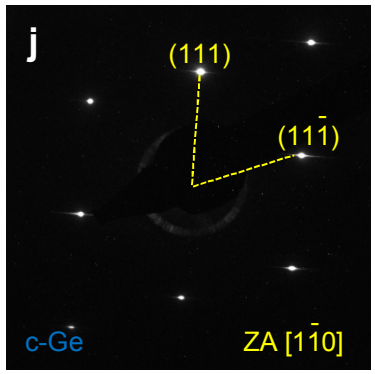
Axial Lithiation of Ge/Si core/shell nanowire

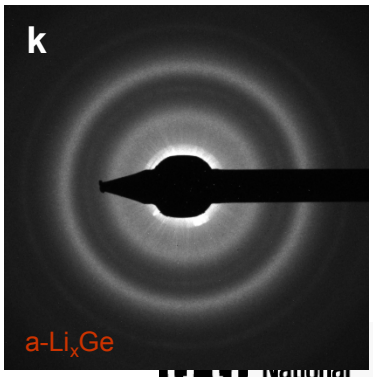




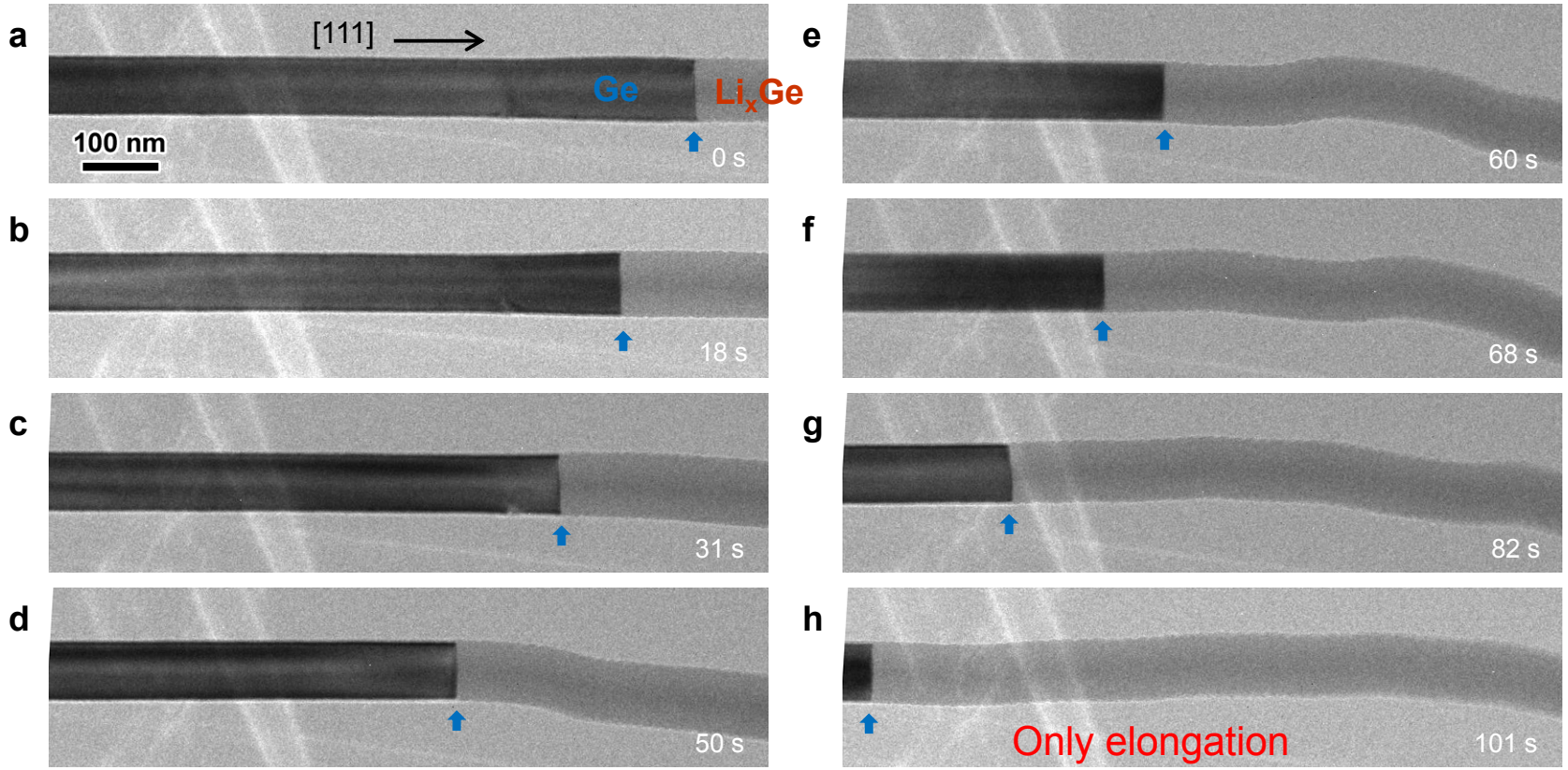








Axial Lithiation of Ge/Si core/shell nanowire

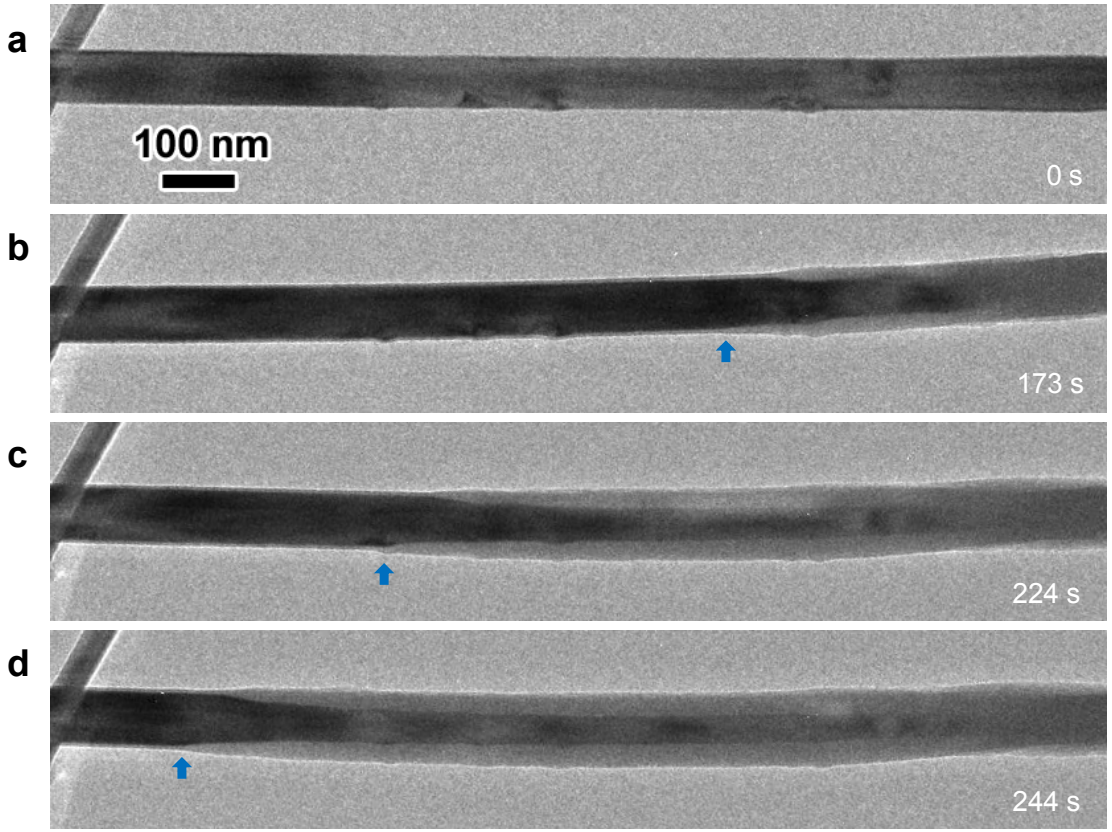


Reaction front along (111) plane

How about oxidizing the surface Si coating?

Change to core-shell lithiation!

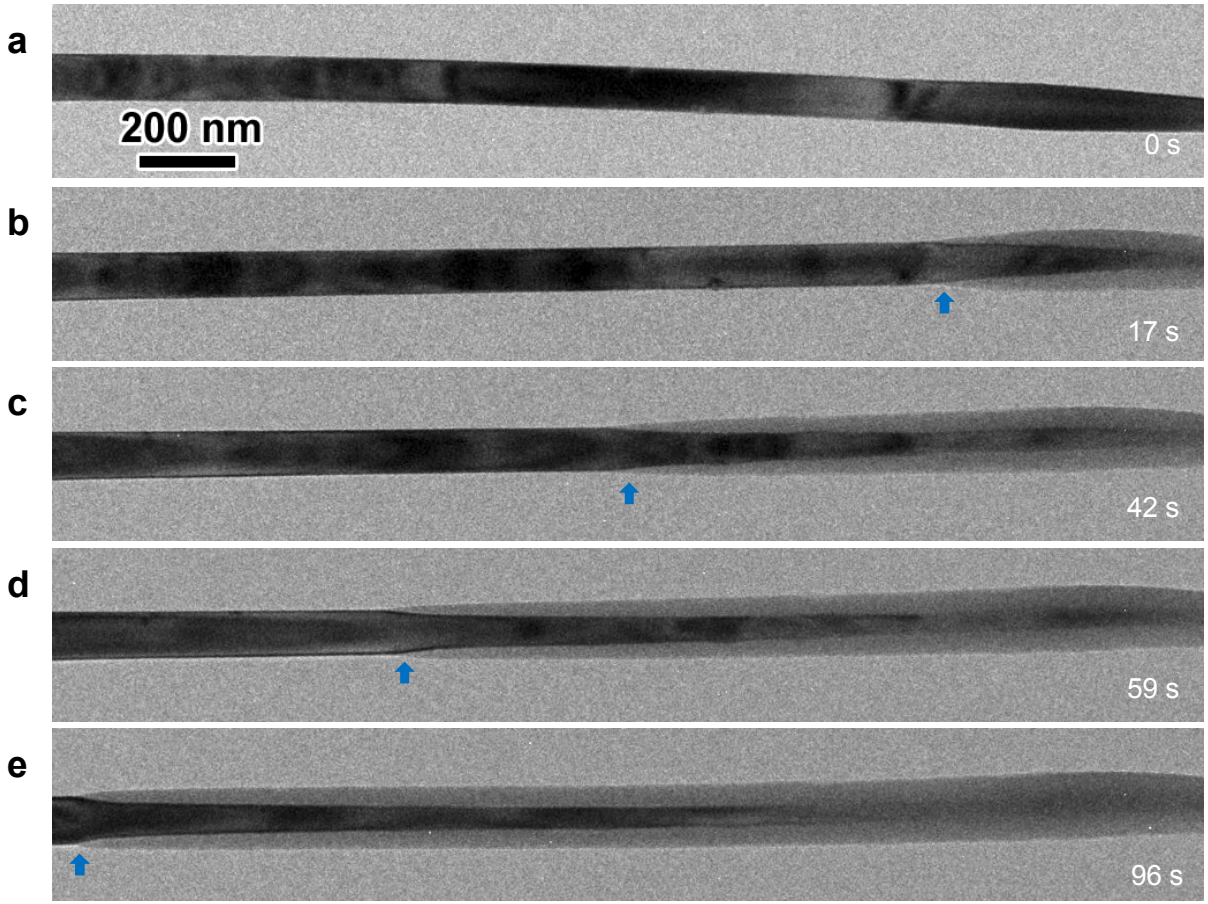
Core-shell Lithiation after surface oxidization



How about remove the surface Si layer?

Change to core-shell lithiation too!

Core-shell Lithiation after surface Si etching



Surface Si layer matters!
Why?

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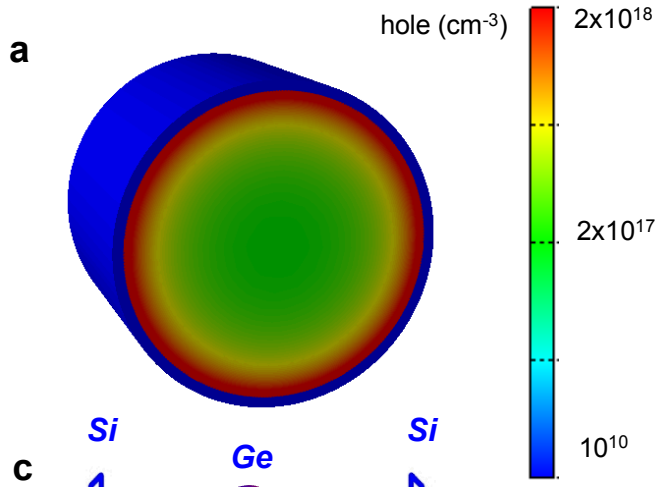
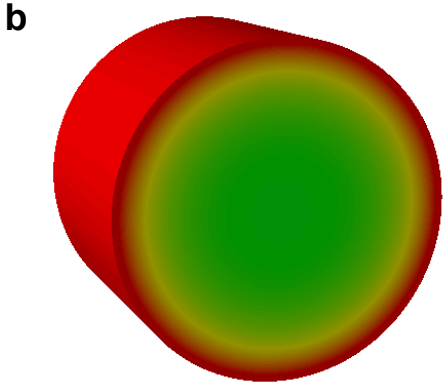
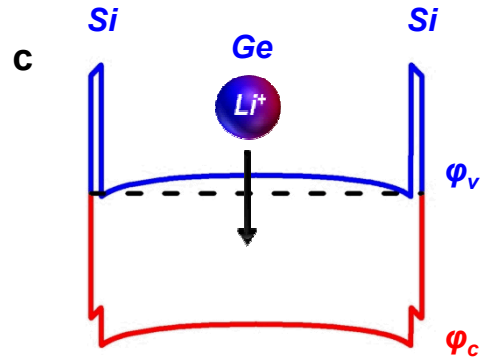
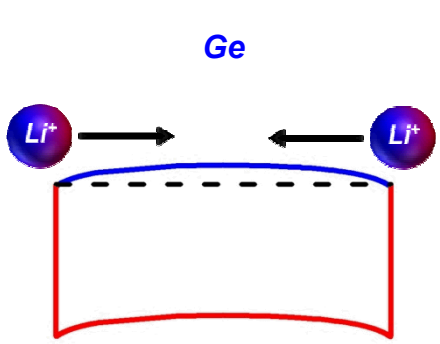
Electronic band strucures of Ge/Si core/shell nanowire and pure Ge nanowire



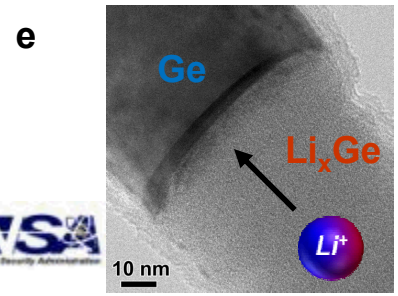


Electrons/holes are depleted at the surface Si layer, which blocks the lithiation process.

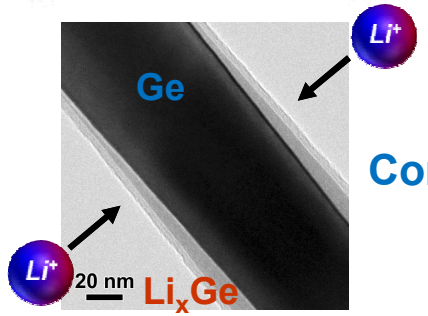




Lithiation behavior (swelling or elongation?) can be changed via band structure engineering!!!



Axial lithiation



Core-shell lithiation

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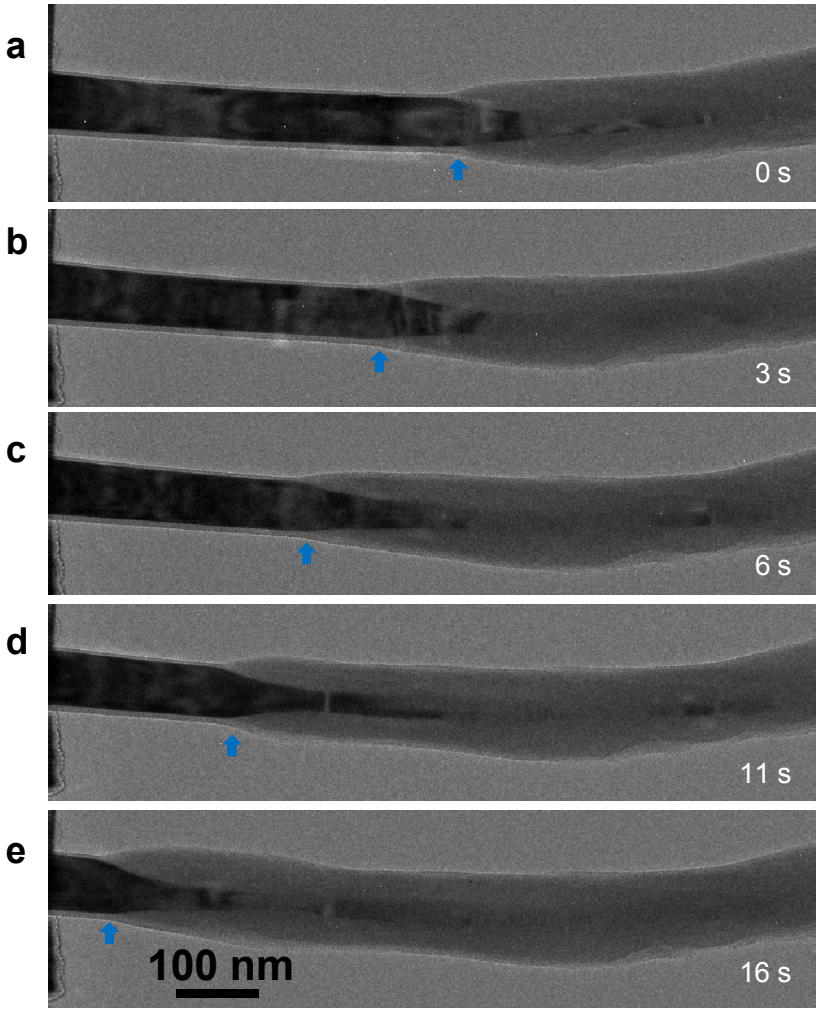
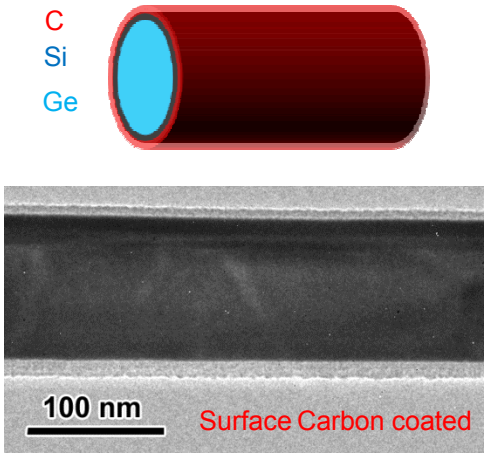
Change to core-shell lithiation too!

Core-shell Lithiation after carbon coating





Carbon layer provides a large sea of electrons to activate the lithiation at the surface.

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Conclusions

- Lithiation of individual pure Ge nanowires and Ge nanowires with various surface modifications, such as thin Si layer coating, Si layer oxidization, Si layer etching, and carbon coating, were conducted inside the TEM.
- Although the lithiation of Ge is isotropic, core-shell lithiation to axial lithiation to core-shell lithiation behaviors were observed upon surface modifications, which can be attributed to electrochemical effect and the electronic band effect.
- Lithaition behavior, volume expansion directions can be tailored via band structure engineering.
- These results can provide insights into the electrodes design in Li-ion batteries.

ACKNOWLEDGMENTS

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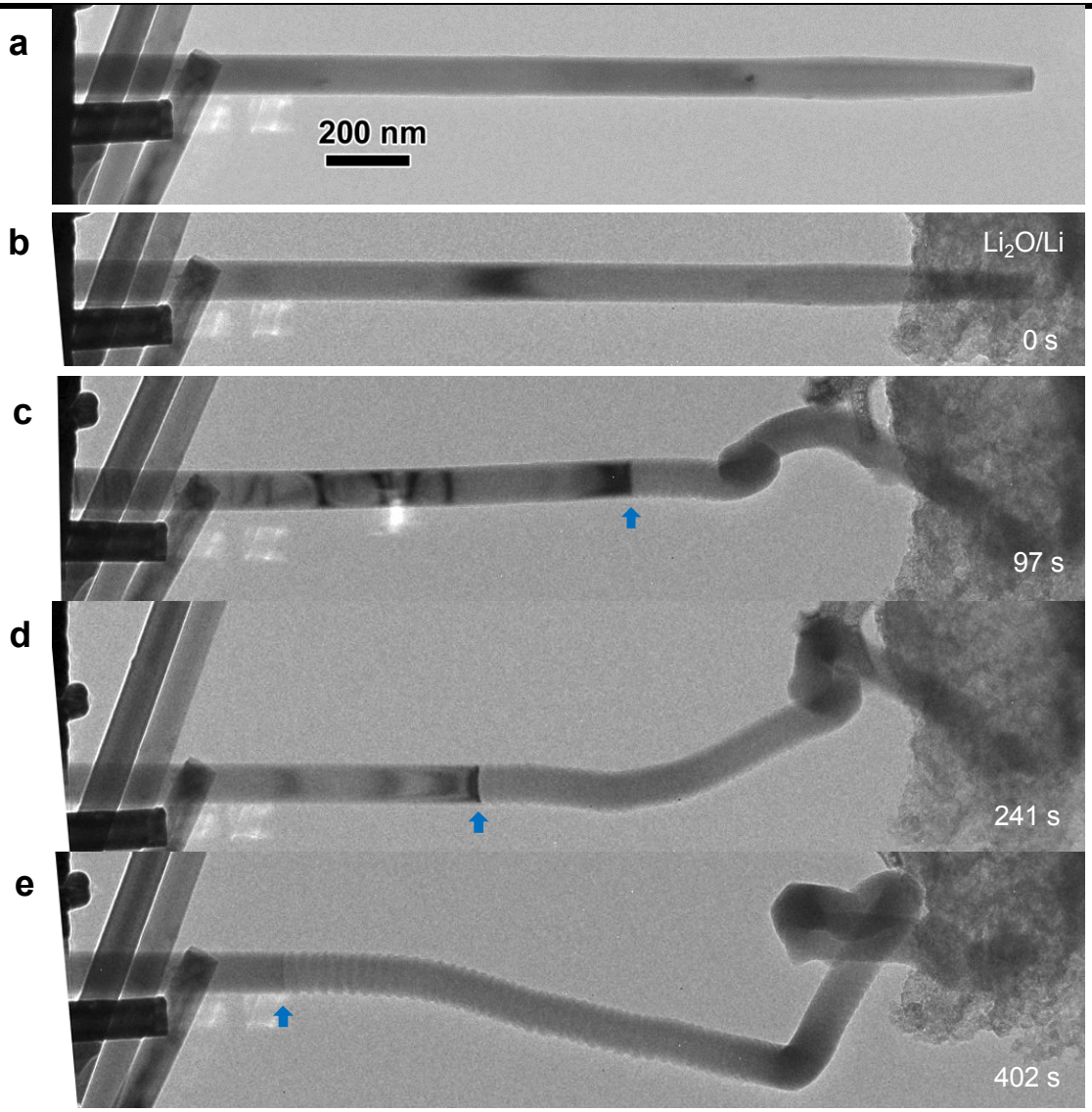
Lithiation of Ge segment only



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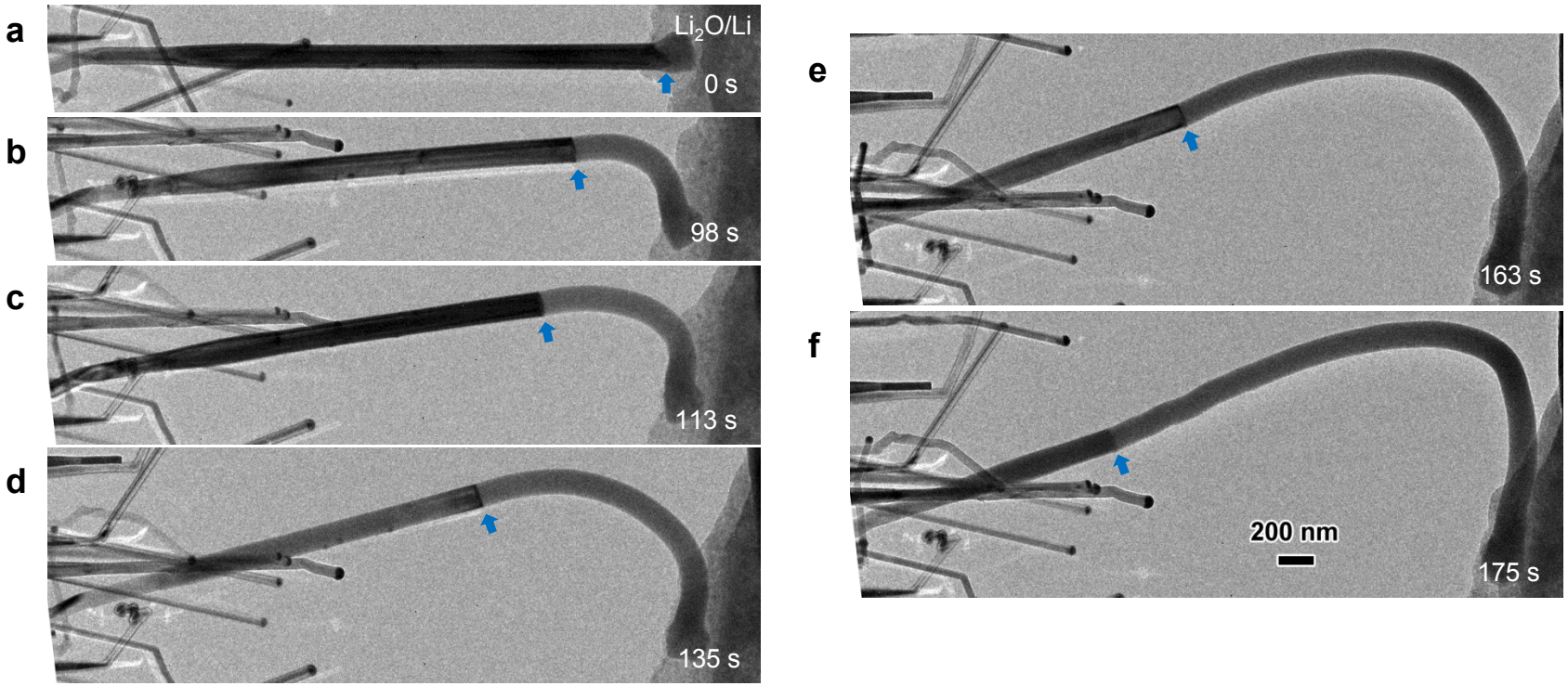
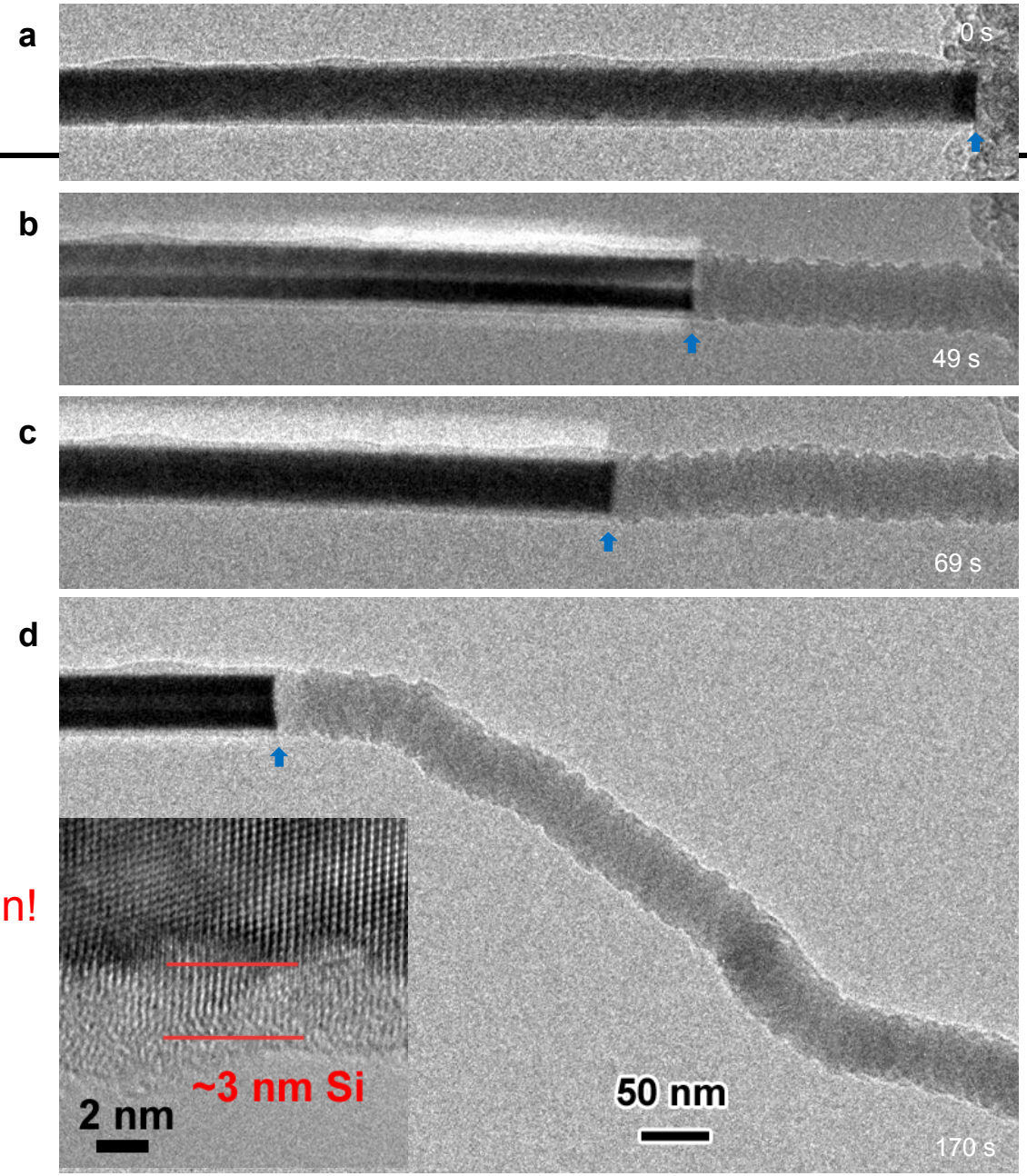
Lithiation from Ge end





Lithiation of Ge NW with ~3 nm Si shell, showing axial lithiation!

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