Solid-state Thin Film Batteries in 3D

J.R. Gaines, Jr.,
Technical Director of Education
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Kurt J. Lesker Company
Enabling Technology for a Better World
www.lesker.com
PROCESS EQUIPMENT DIVISION
THIN FILM
Deposition
Experts

Solid-state Thin Film Batteries

- How a thin film battery works
- Some examples in 2D
- Some history on the current technology
- New Processes
- New Architectures

Solid-State Thin Film Battery (Dudney, ORNL)

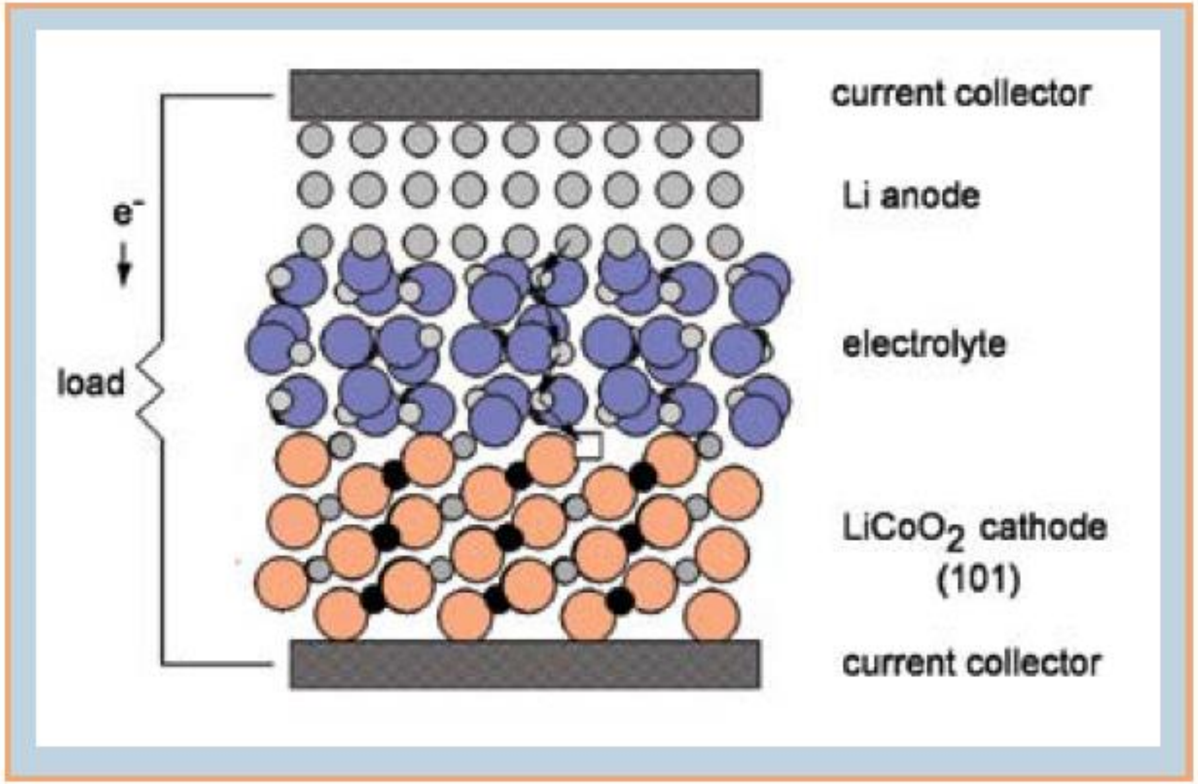
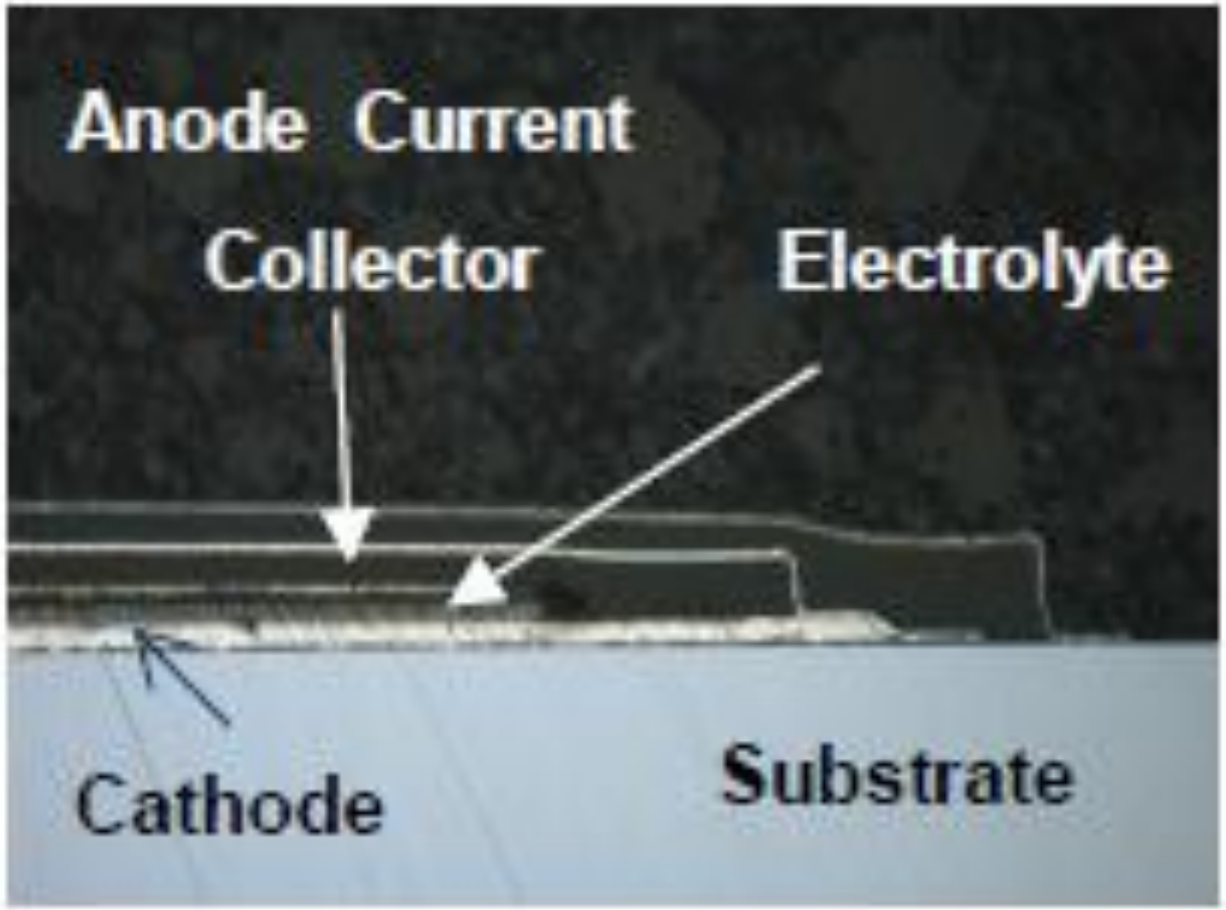


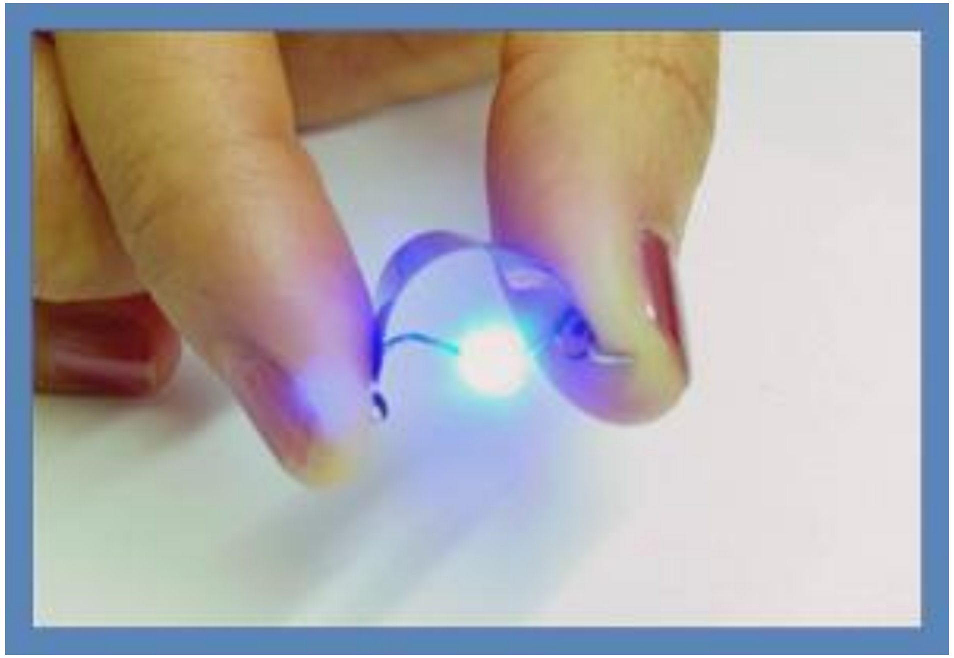
FIG. 2. *Schematic illustration of a thin film battery. The arrows indicate the discharge reaction where a Li ion diffuses from the lithium metal anode to fill a vacancy in an intercalation compound that serves as the cathode. The compensating electron is conducted through the device.*

“Thin” means battery @ 20 microns but the substrate is 170 microns!!



- Unique Technical Features
  - ‘Perpetually’ rechargeable +75,000 cycles demonstrated by ORNL and Manufacturers
  - Operating temp range -40 to +200 C
  - Nominal 4 volts (next gen 5 volts?)
  - Self discharge <1% per year (studied over 6 years – rates nearly unmeasurable)
  - Fast recharge to 90% in less than 10 min
  - Highly embeddable and safe

- Thin AND flexible (Kapton, SS, thin silicon)

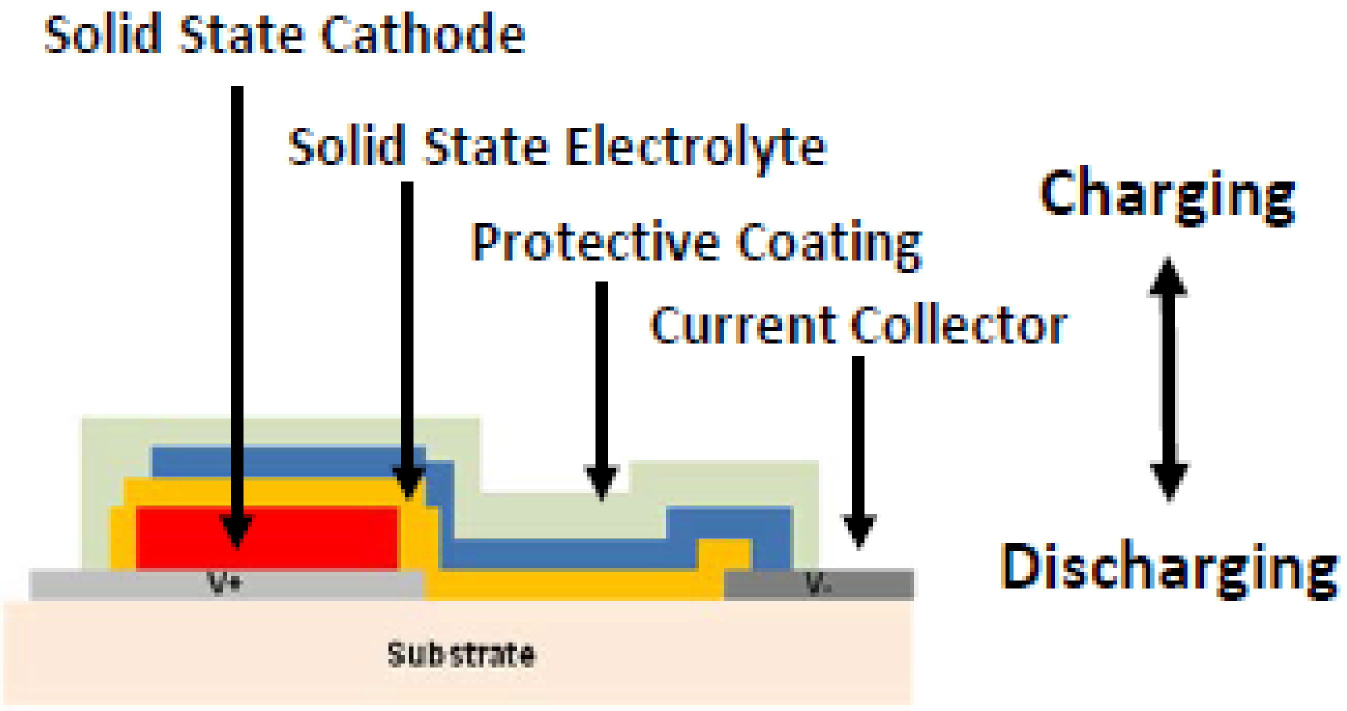


Front Edge Technology's Flexible TFB in action

Lithium ion Vs Electrons

- Size of a Lithium Ion = 182 pico meters
- Size of an electron = 0.00281 pico meters
- A Lithium Ion is nominally 65,000 x larger than an electron – so the anode doubles!!

Battery doubles or triples in thickness on charging



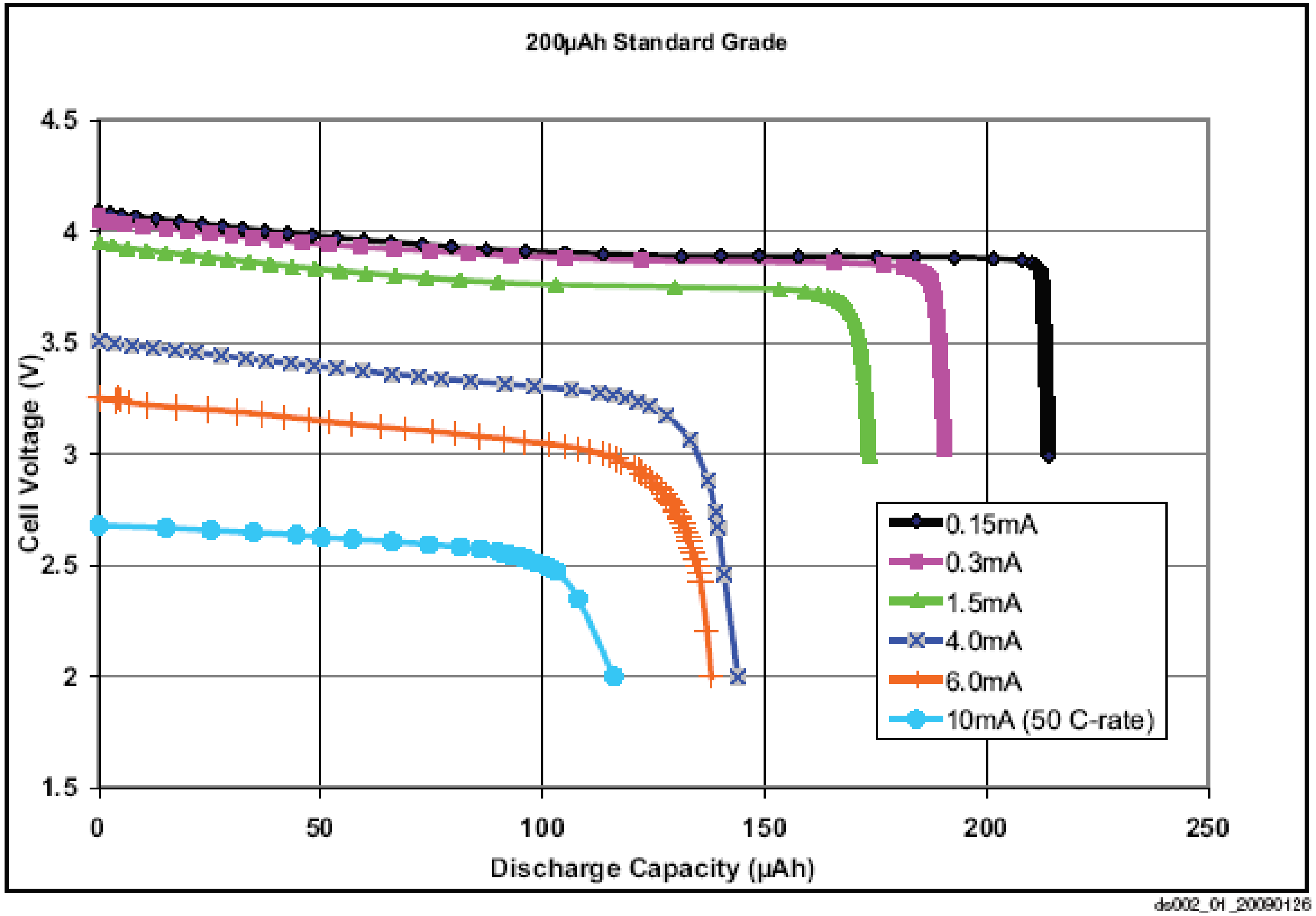
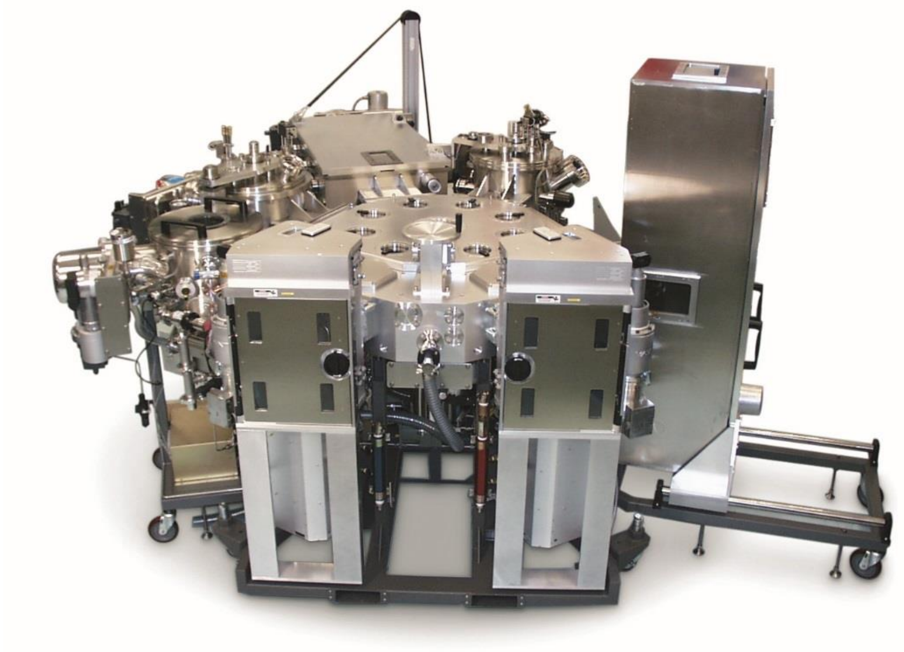


Figure 1: **Typical Discharge Curves @25°C (200 µAh Standard Grade Cell)**

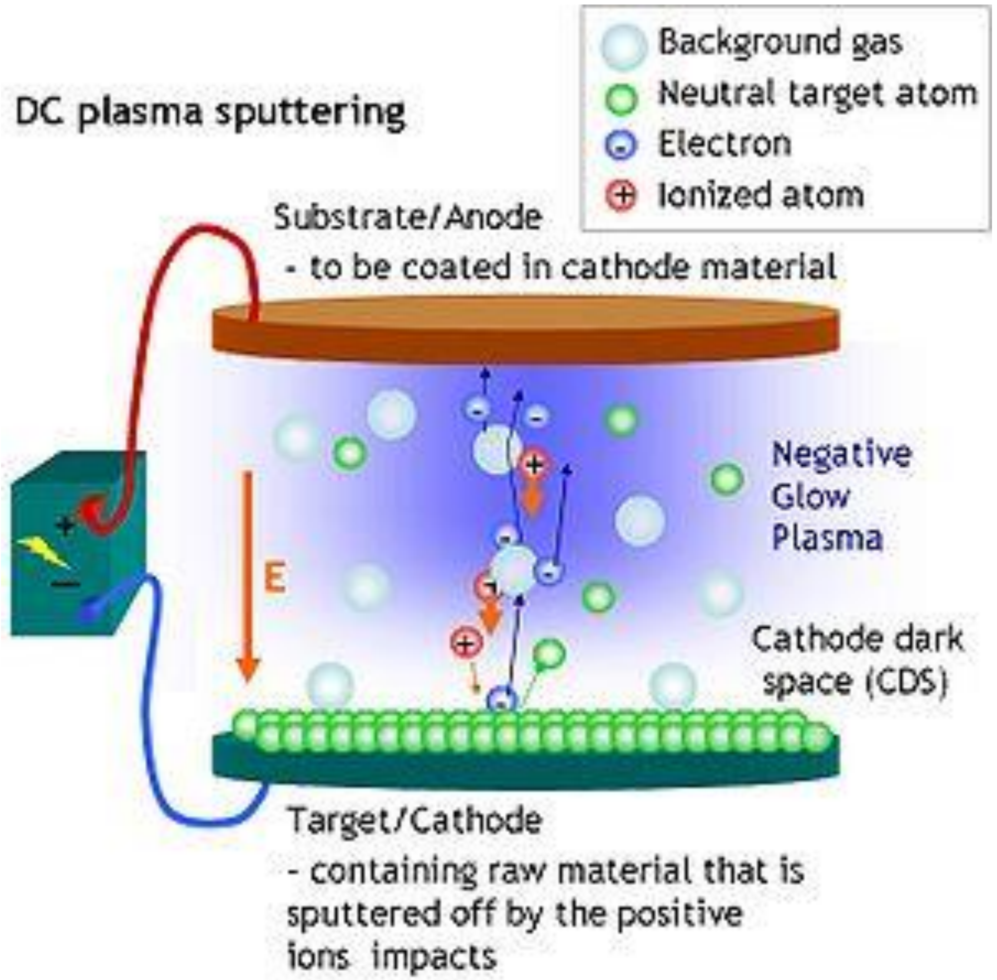
- Development and Commercialization of Thin Film Batteries
  - ORNL developed the technology and nucleated the commercialization process
  - Companies formed specifically to manufacture and commercialize TFB
  - Existing companies have added TFB manufacturing and commercialization to their product line

TFB Manufacturing Process

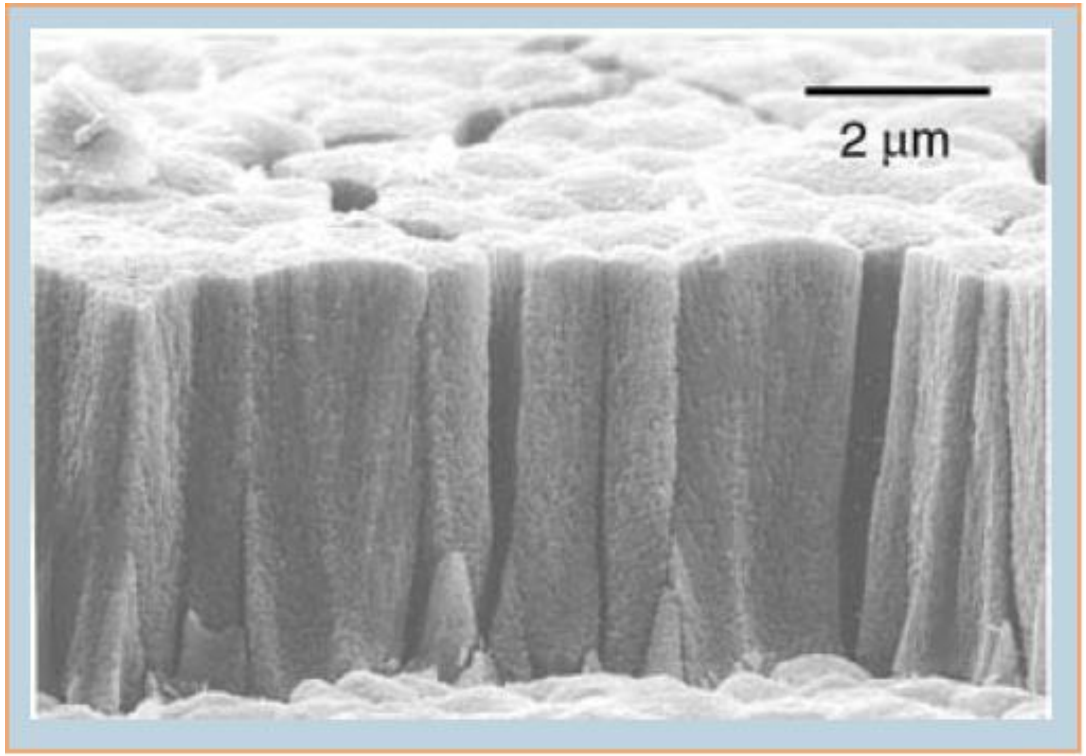


- Deposit metal electrode on substrate (DC sputter)
- Deposit cathode, $LiCoO_2$ (DC sputter)
- ***Break vacuum and anneal***
- Deposit electrolyte, Li_3PO_4 (Rf sputter)
- Deposit anode layer, Li or other, (evaporation)
- Deposit top metal electrode (DC sputter)
- Encapsulate the battery
- Dice the substrate

Creating Ions to Ablate the Target



- Thin Film cathode of $LiCoO_2$ has microstructure that is oriented and dense

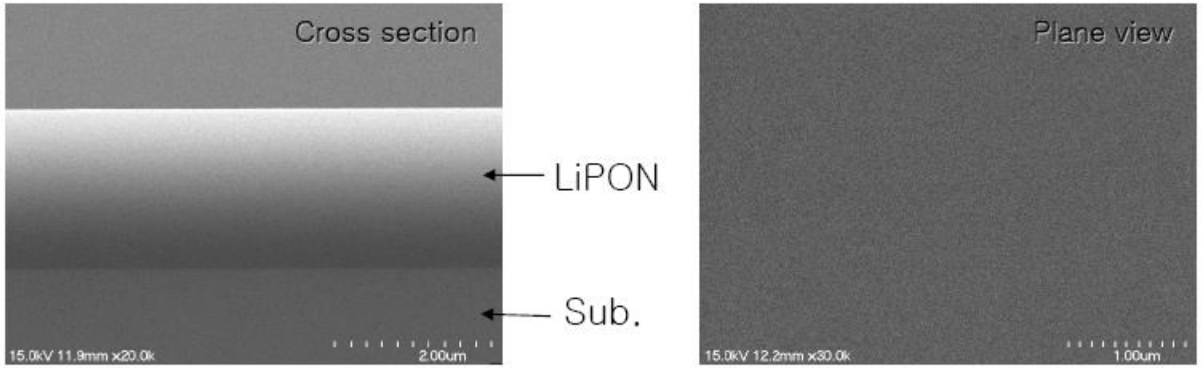


Lithium cobalt oxide after high temp anneal

Unique Electrolyte that is VERY THIN and pore-free to promote ion transport

SEM images : LiPON Thin Film by Nitrogen Reactive Sputtering

World No.1 in Thin Film Battery



Glass-like morphology with smooth surface.

Why is there a market
for ***Solid-State*** Thin Film Batteries?

- The perpetually shrinking wireless gizmo
- Limits on the ‘shrink-ability’ of conventional energy storage technologies
- Safety concerns with flammable (liquid) electrolytes
- ‘Green Battery’ where device life < battery life

Range of Mobile Devices

- “Big Energy Users ” = Mobile Cellular phones
- “Small Energy Users” = Active RFID tags, or IoT, Real time clocks

ST Micro's 'EnFilm' – available for sale now

EFL700A39

EnFilm™ - rechargeable solid state lithium thin film battery

Datasheet — preliminary data

Features

- All solid-state
- Ultra thin
- Fast recharge
- Long cycle life
- RoHS compliant
- UL file number: MH47669

Table 1. Device summary

Symbol	Value
Capacity	0.7 mAh
$V_{nominal}$	3.9 V
V_{op}	3.6 to 4.2 V
R_{int}	100 ohm
I_p	10 mA
Dimension	25.4 x 25.4 mm
Thickness	200 µm

Applications

Device is intended to be used in following applications:

- Sensors and sensor networks
- Smart card
- RF ID tags
- Energy storage for energy harvesting devices
- Non implantable medical applications
- Backup power

Description

The EFL700A39 is a thin film rechargeable lithium battery. The battery has a $LiCoO_2$ cathode, LiPON ceramic electrolyte and a lithium anode. This device has a footprint of 25.4 x 25.4 mm.

iPhone 7 Battery Specs

1960 mAh capacity

- Operating draw of 200 mAh
- About 8 hours of talk time

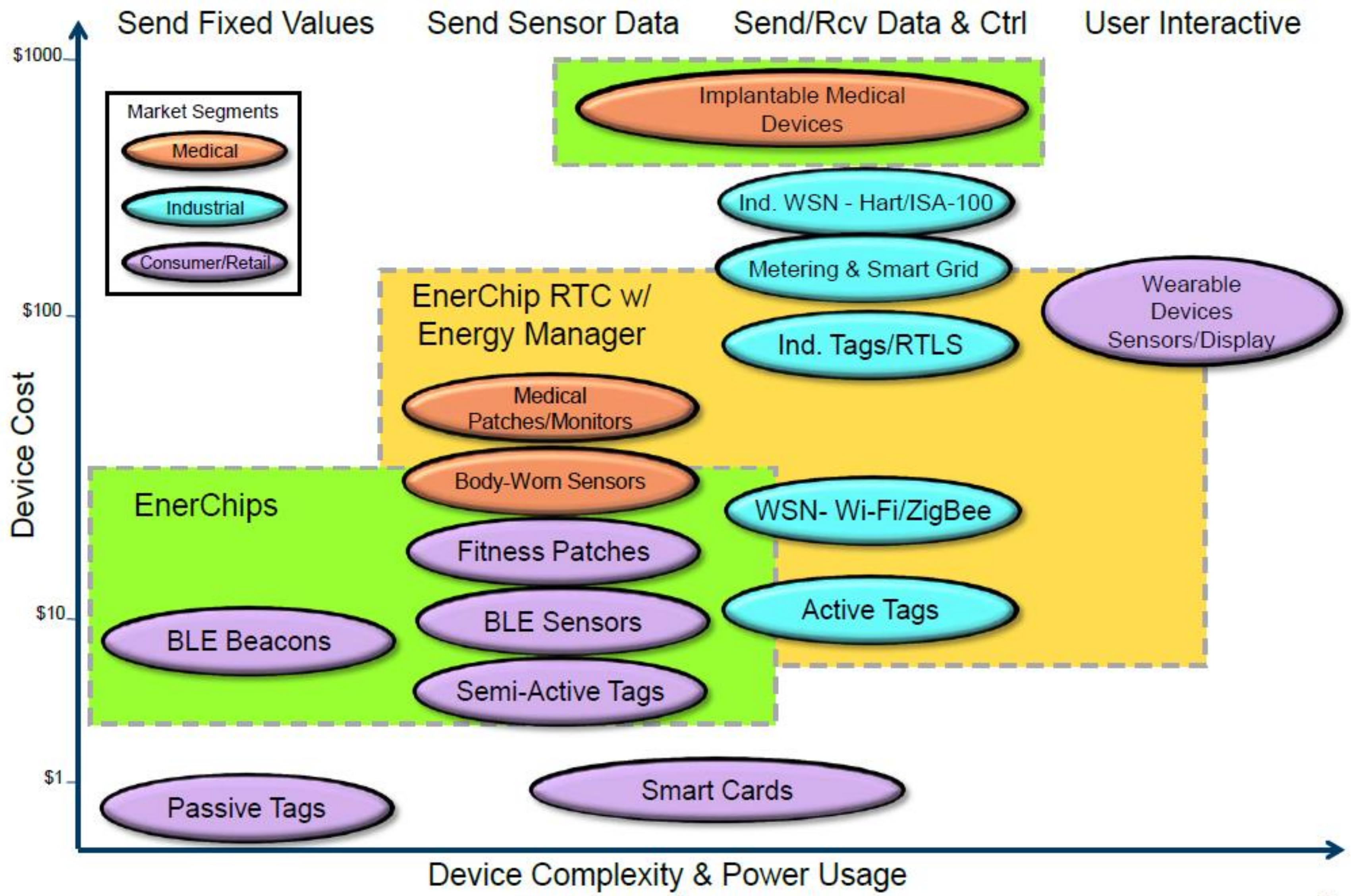
Planar TFB for Smart Phones?

- ST Micro’s battery at 1 x 1” = 700 microAh
- Will need about 2,800 sqin of TFB to replace existing technology (53 x 53”)
- Tough to fit into a 5 x 2.5” package !

MEM’s based generator for re-charge

MicroGen Systems uses vibration, coupled with Cymbet EnerChip Thin Film Battery

IOT & Wearable Device Positioning & Cymbet Solutions



www.cymbet.com Ph: +1 763-633-1780

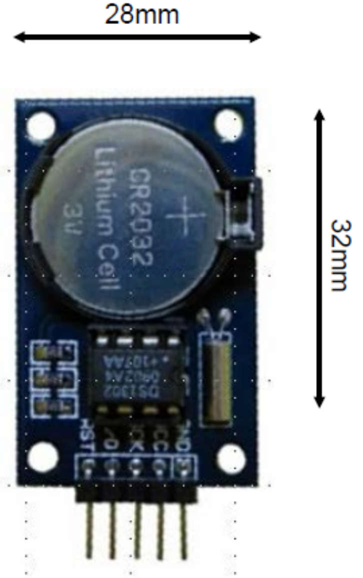
- Near term applications include
  - Real-Time Clocks for PC's, Tablets, Laptops
  - Wireless sensors
  - CMOS back-up
  - SRAM back-up
  - 'Energy Harvesting' systems
  - Smart Card
  - Active RFID tags
  - Therapy delivery systems
  - Internet of Things, smart clothing, wearables

SIZE of Real-Time Clocks

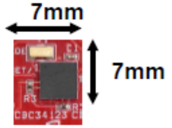
EnerChip RTC is Superior to Legacy Coin Cell

CYMBET CORPORATION

Traditional RTC with Battery Design Approach



EnerChip RTC with Optimized Crystal



95% Smaller Surface Area!

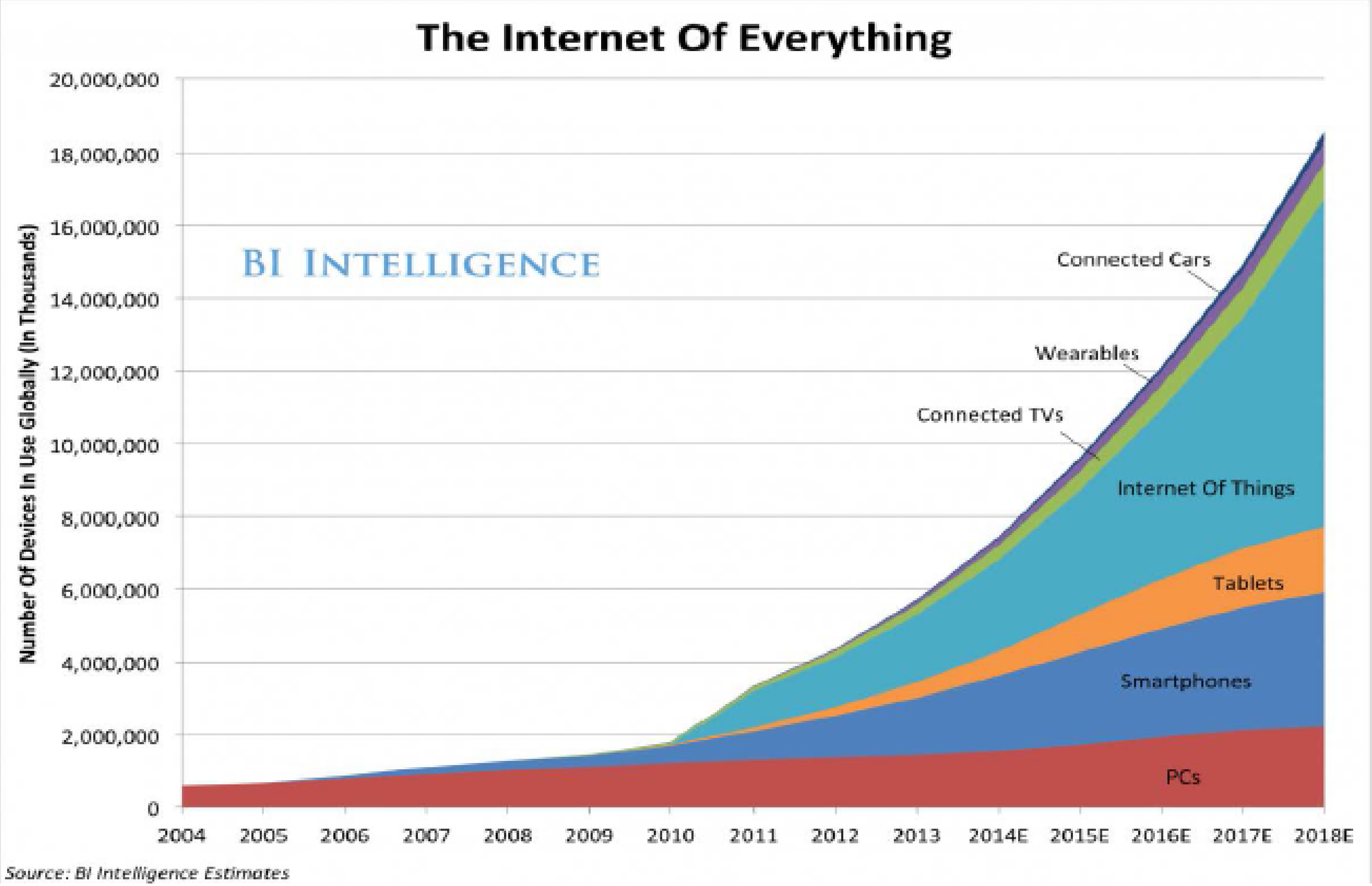
80% Lower Profile!

Type	Length	Width	Square mm Area
RTC with CR2032	32.0	28.0	896
EnerChip RTC	7.0	7.0	49
			95%

Type	Height (mm)
RTC with CR2032	7.0
EnerChip RTC	1.4
	80%

An Industry develops to make Thin Film Batteries

- For the original ‘Bates’ battery:
  - ST Micro (France) enters
  - AMAT builds tools to manufacture TFB’s
  - Apple may have eaten IPS
  - Cymbet on life support
  - ITN Energy Systems on hiatus
  - Schmidt slows
  - GS Nanotech slows
  - Johnson Research, Front Edge


The Internet Of Everything
BI INTELLIGENCE
20,000,000
18,000,000
16,000,000
14,000,000
12,000,000
10,000,000
8,000,000
6,000,000
4,000,000
2,000,000
0
Number Of Devices In Use Globally (In Thousands)
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014E
2015E
2016E
2017E
2018E
Connected Cars
Wearables
Connected TVs
Internet Of Things
Tablets
Smartphones
PCs
Source: BI Intelligence Estimates

What's Next for Thin Film Batteries?

- Commercialization of the 'Bates' battery has shown that a battery can be
  - Perfect
  - Permanent

These attributes must be scaled for more capacity

- The Bad News:

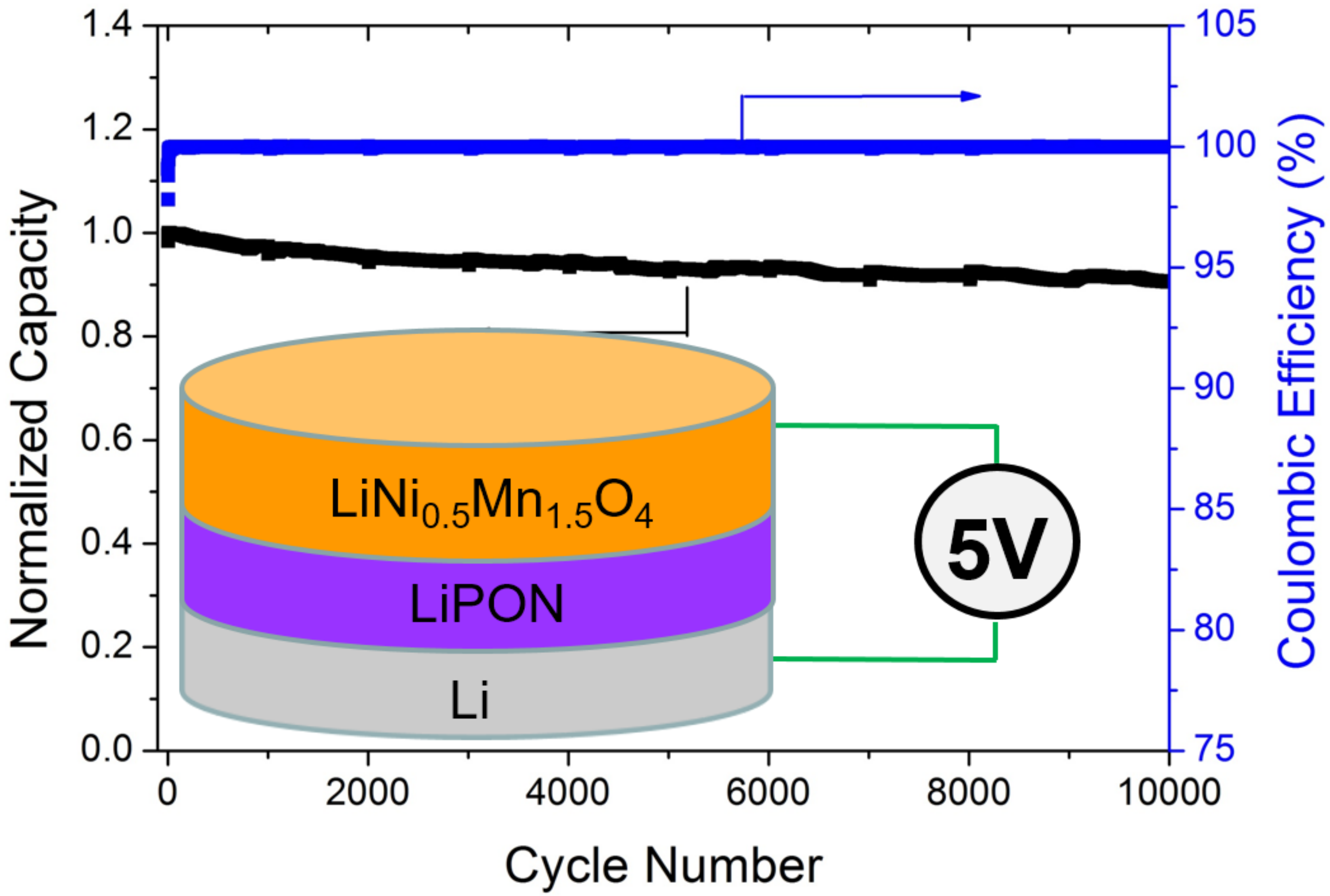
No Moore’s Law For Batteries

(electrons are tiny, Li – ions are 16,000 time larger!)

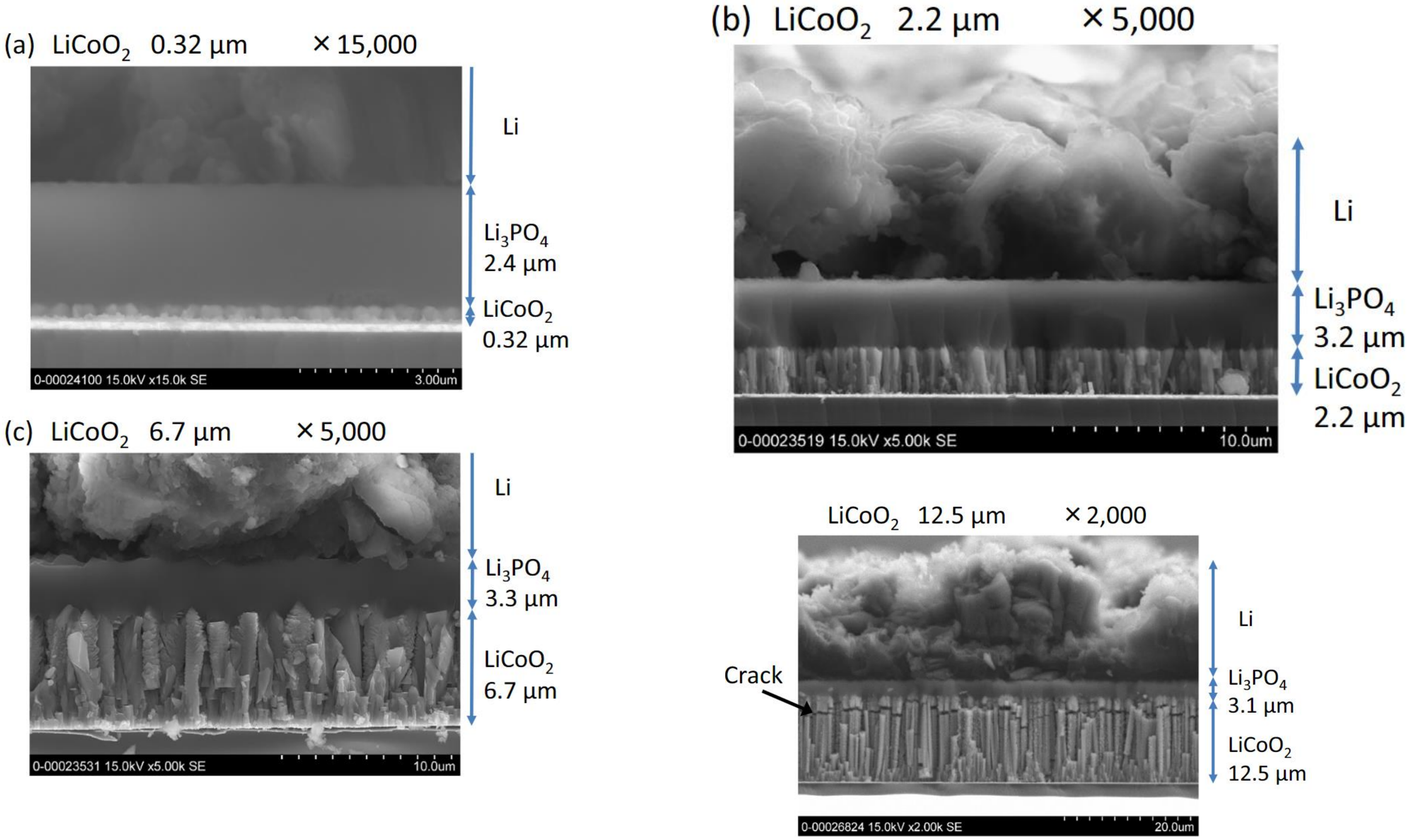
Next Generation Strategies

- Alternative materials coupling
  - Some examples
  - Ongoing search
- New architectures and substrates
- Ongoing exploration of novel deposition techniques

Alternative Cathode Materials



Morphology and Thickness

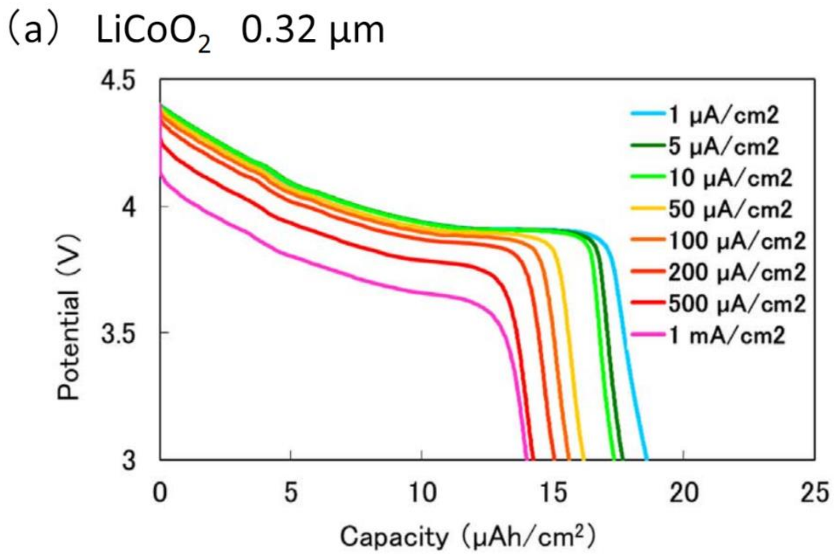


Diffusion Lengths for Lithium Ions

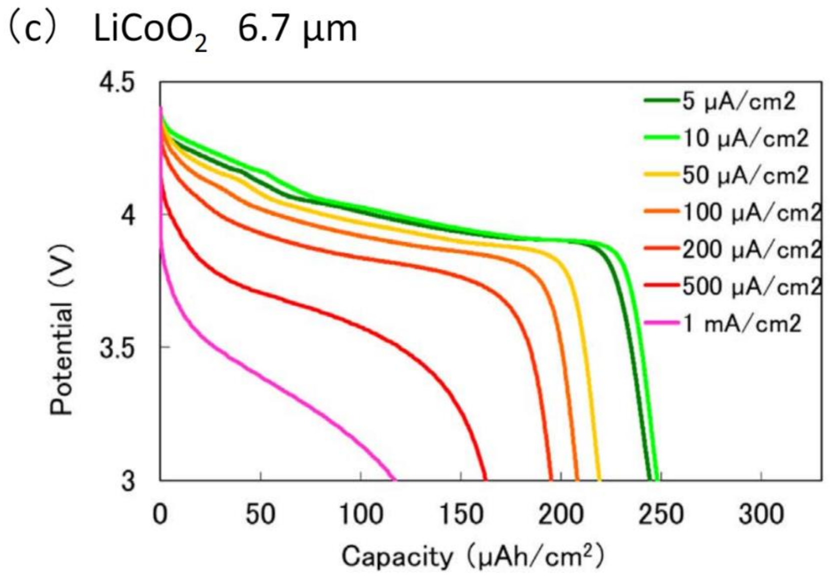
- Limits of a few microns, at low discharge rates?
- Arbitrarily thick cathodes subject to extreme stresses, defects, miss-orientation, etc.
- Much of the Cathode is Along for the Ride

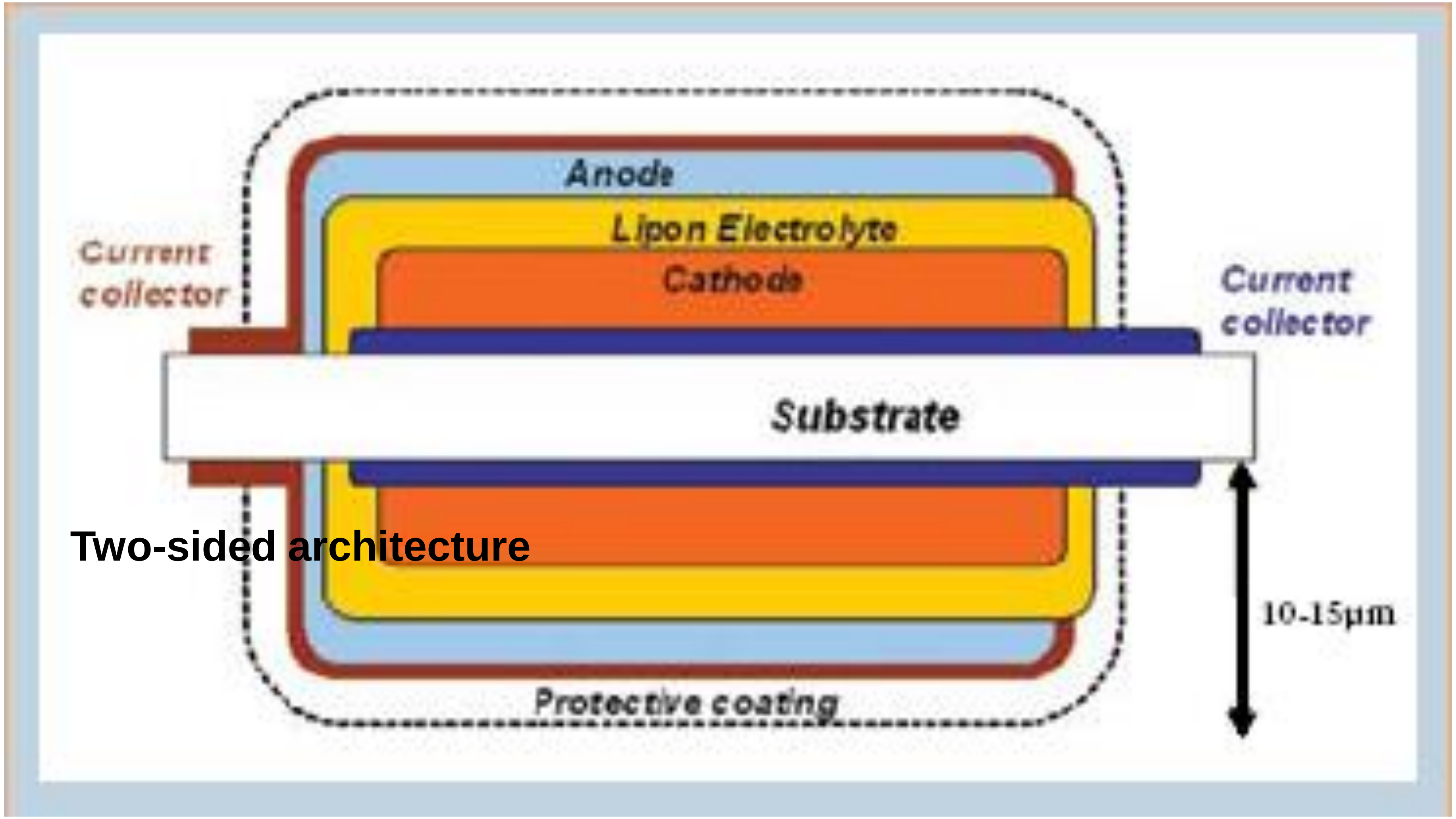
‘Thick Cathode’ Capacity Far from Theoretical

About 81% of theoretical



About 52% of theoretical

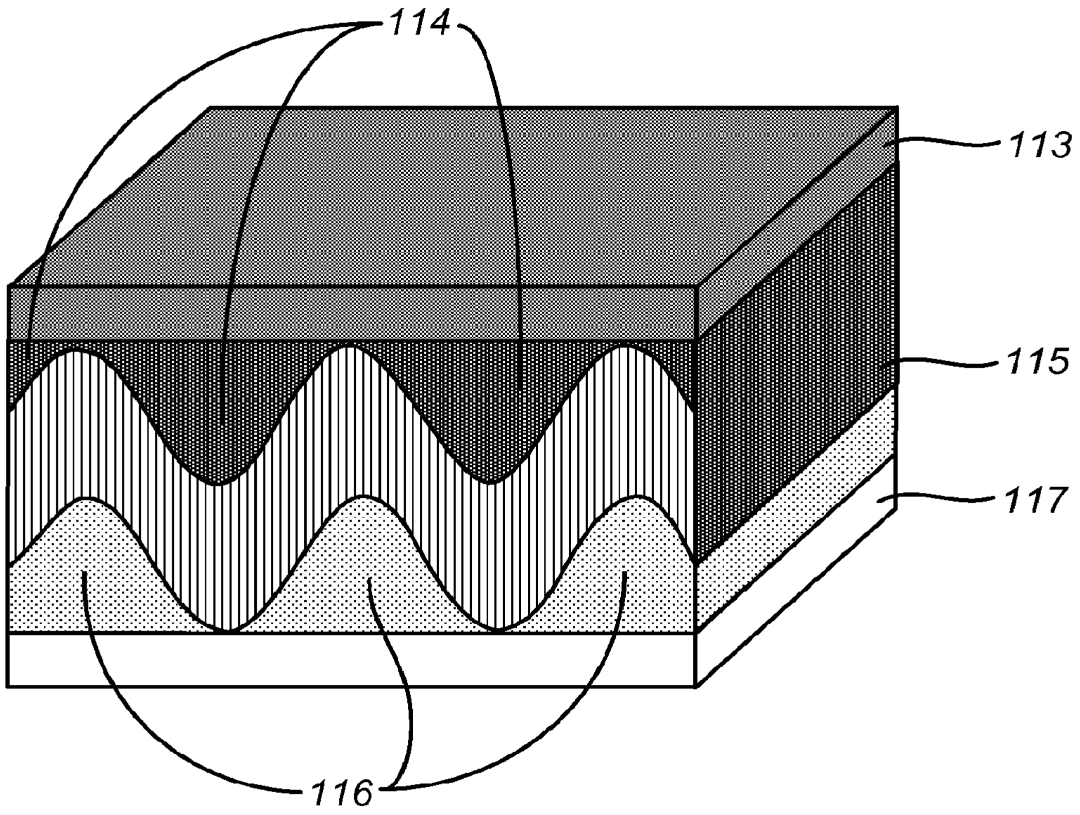




Two-sided architecture

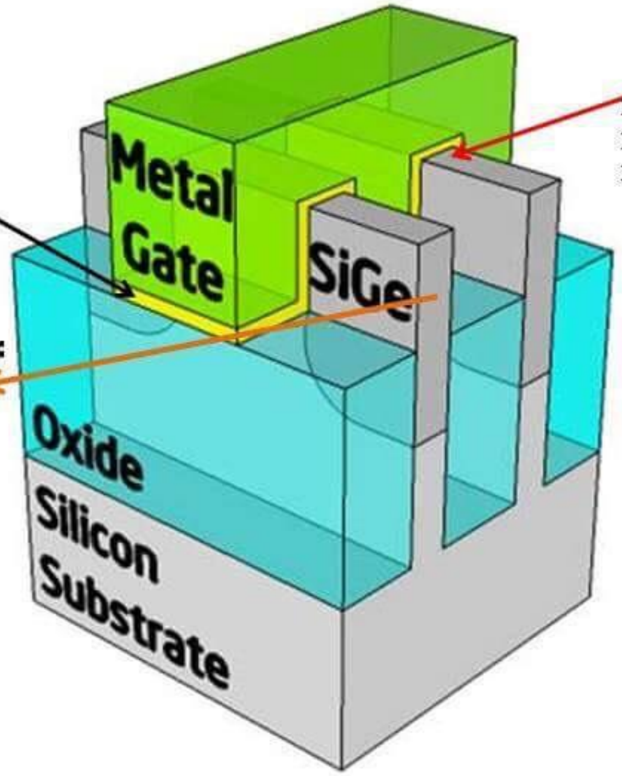
Extended architecture

Increase surface area for interfaces (Sakti3)



Advanced Gate Structure

ALD Gate Metal Barrier
Metal Source :
1. TiCl4
2. TDMAT



ALD Gate Oxide
HfO2 Source :

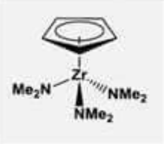
1.	TEMAHf	$Hf[(C_2H_5)(CH_3)N]_4$
2.	$HfCl_4$	$HfCl_4$

3. La (FAMD)3

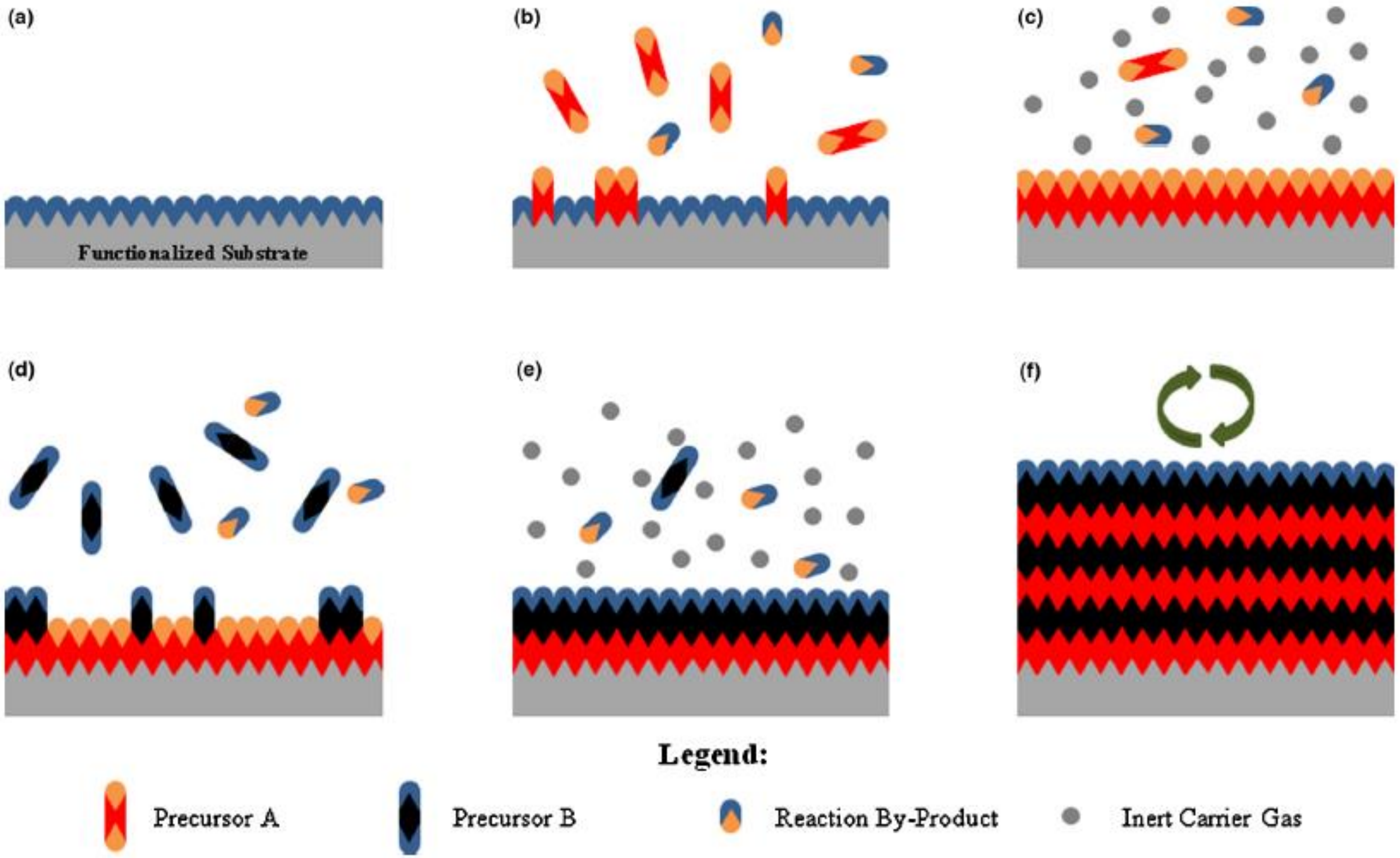
元件外接電容(Capacitor)
ALD ZrO2 或 Al2O3 Source :

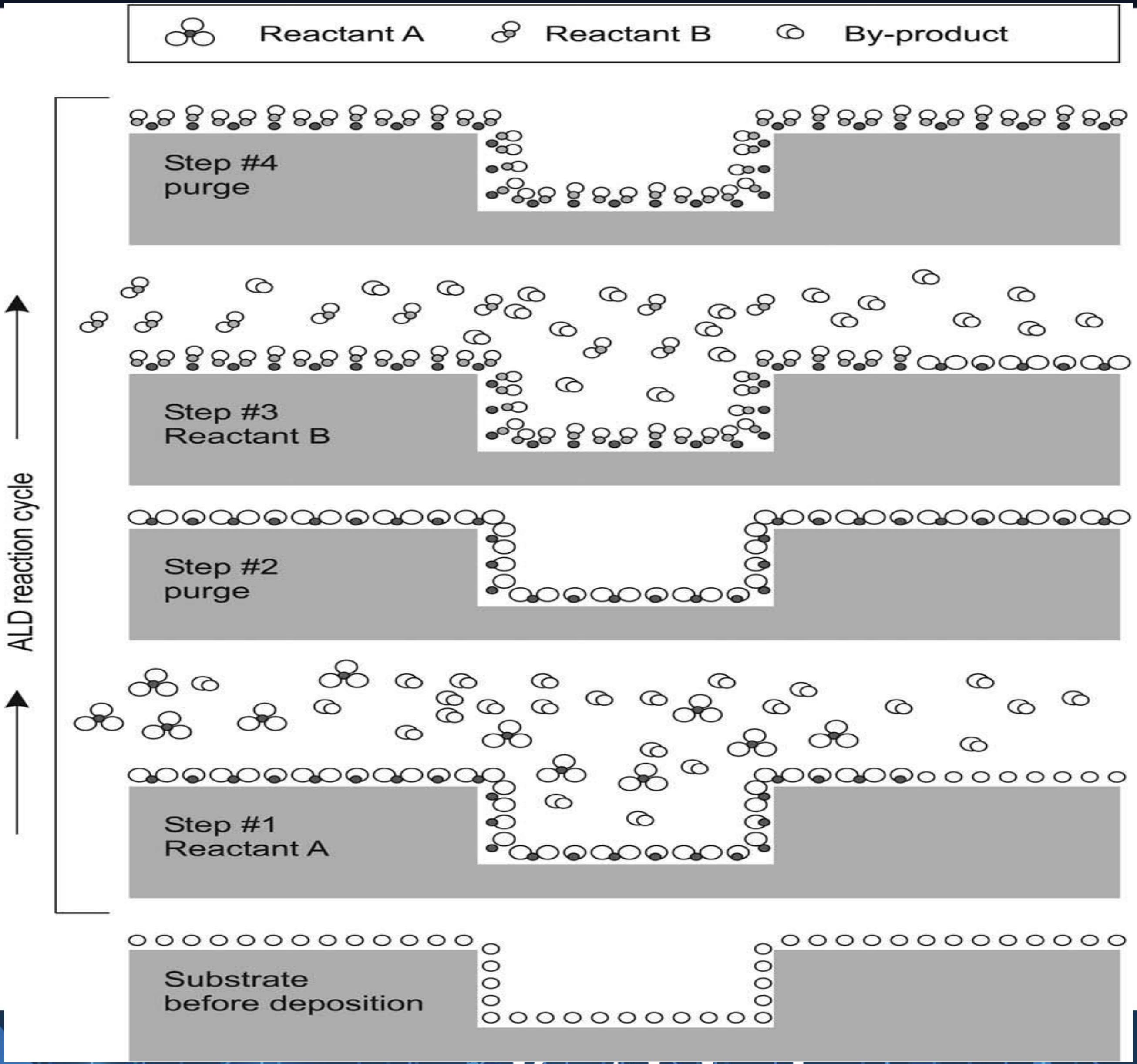
1.	TEMAHZr	$Zr[(C_2H_5)(CH_3)N]_4$
2.	$ZrCl_4$	$ZrCl_4$
3.	TMA	$Al(CH_3)_3$

4. $C_{11}H_{22}N_3Zr$



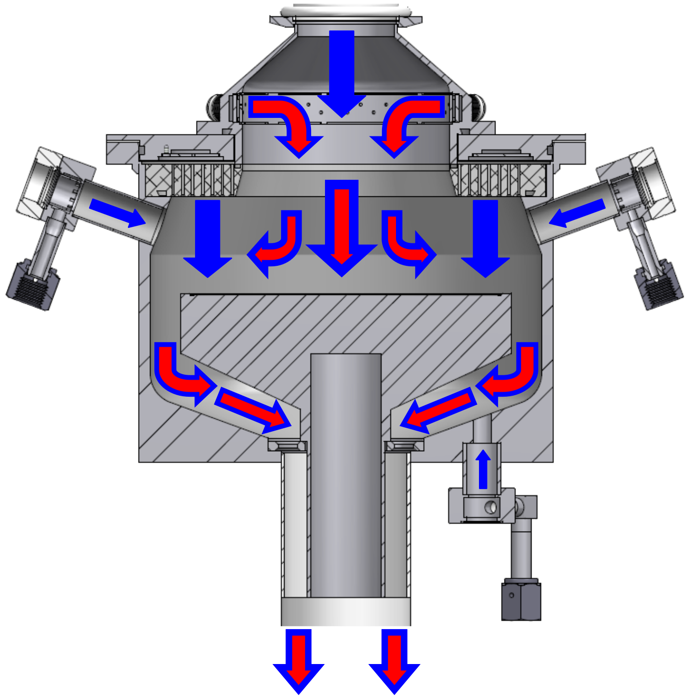
ALD - Sequential, Self-Saturating, Process




Reactant A
Reactant B
By-product
ALD reaction cycle
Step #4
purge
Step #3
Reactant B
Step #2
purge
Step #1
Reactant A
Substrate
before deposition

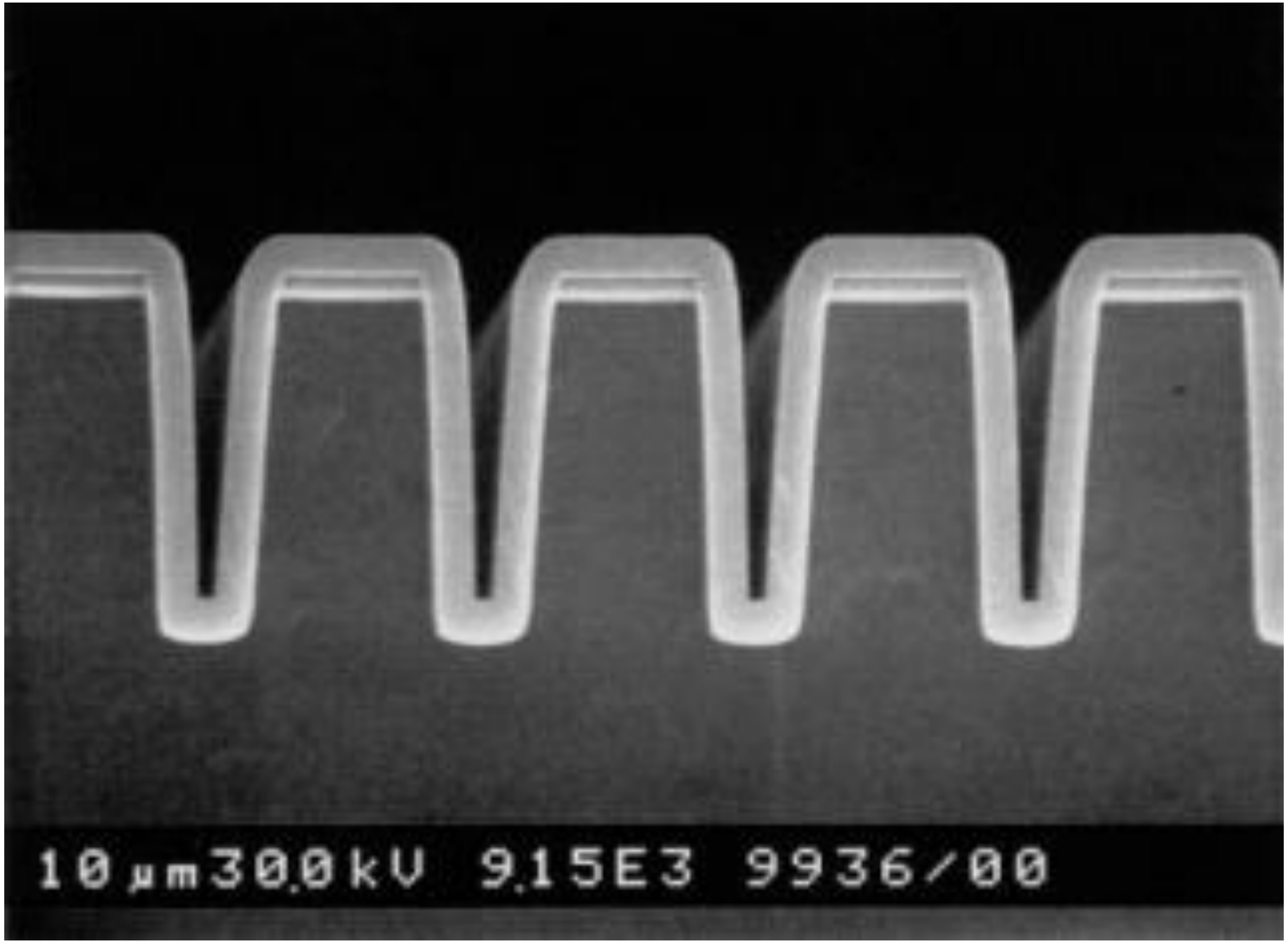
Engineered Gas Flows

- Inactive Gas Flow Distribution Focuses Precursor Onto Substrate Surface During Precursor Pulse Steps*
- Helps Protect Ports and Chamber Walls From Unwanted Precursor Exposure
- **PFT™** Enables Efficient Precursor Utilization, Purging, & Eliminates Need for Particulate-Generating Gate Valves



***KJLC Precursor Focusing Technology™ (PFT™) – Patent Pending**

Highly Conformal, Deep trench, AR = 30:1



Atomic Layer Deposition of Electrolytes (two stage process)

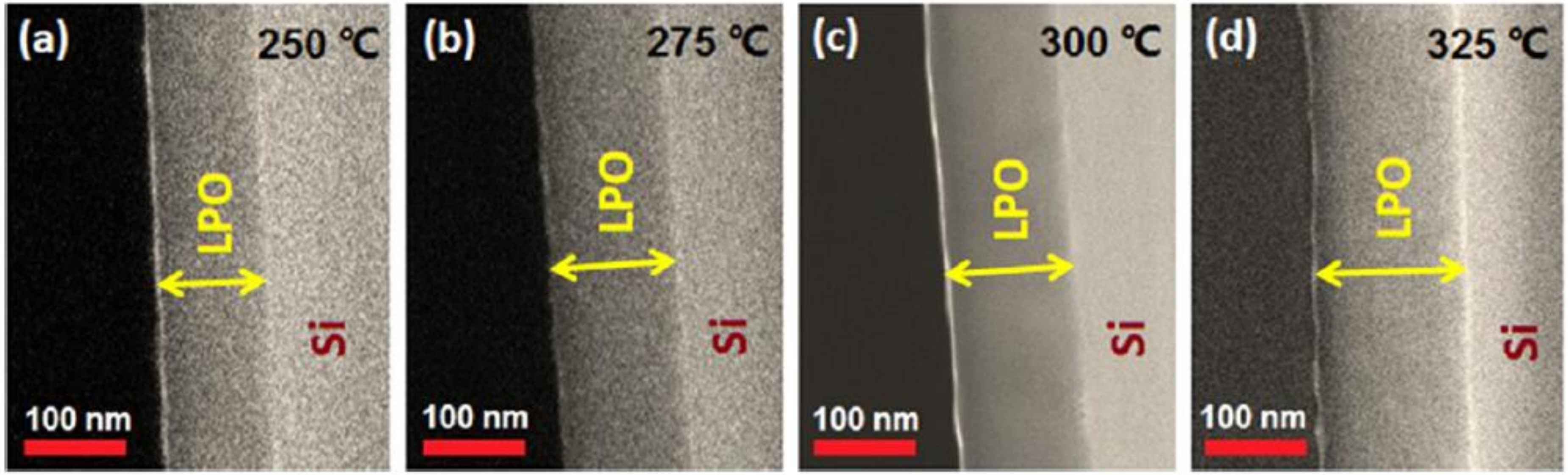
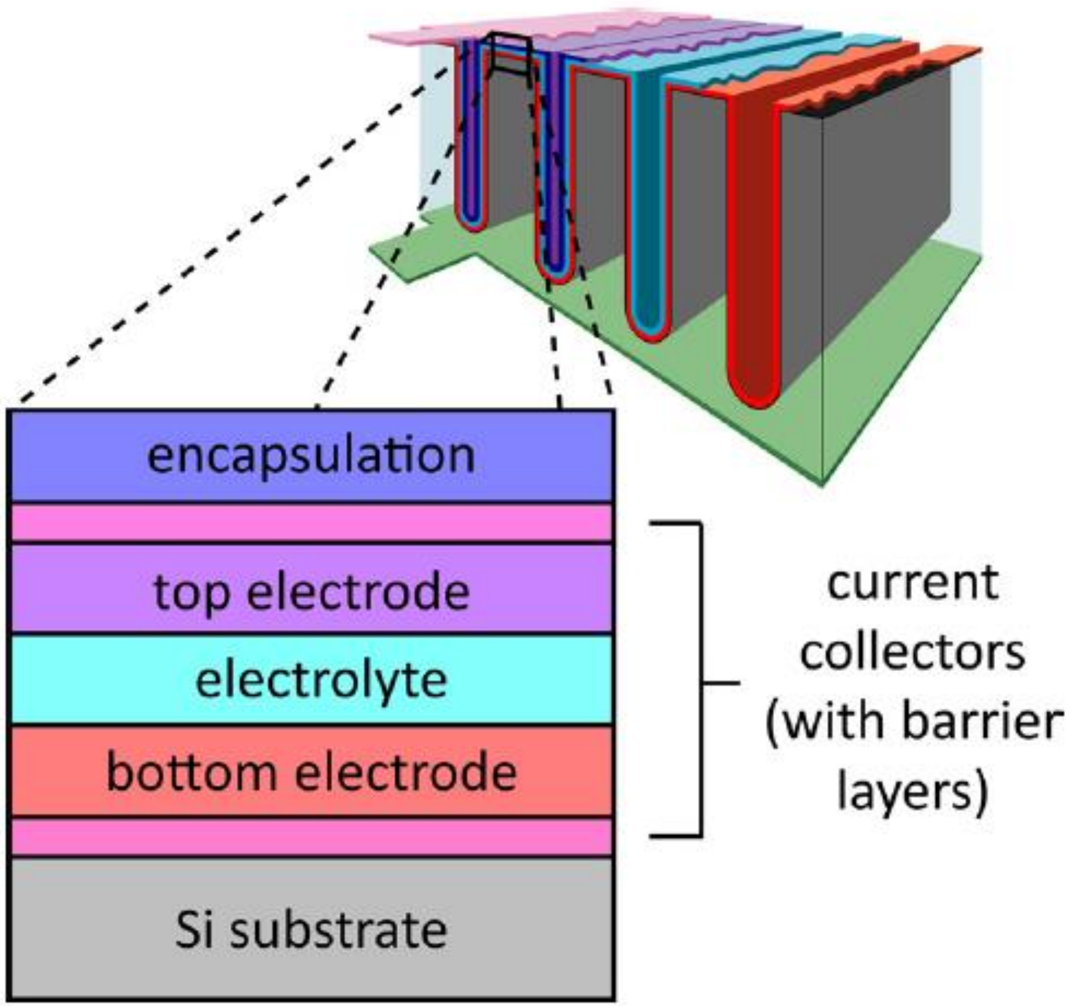
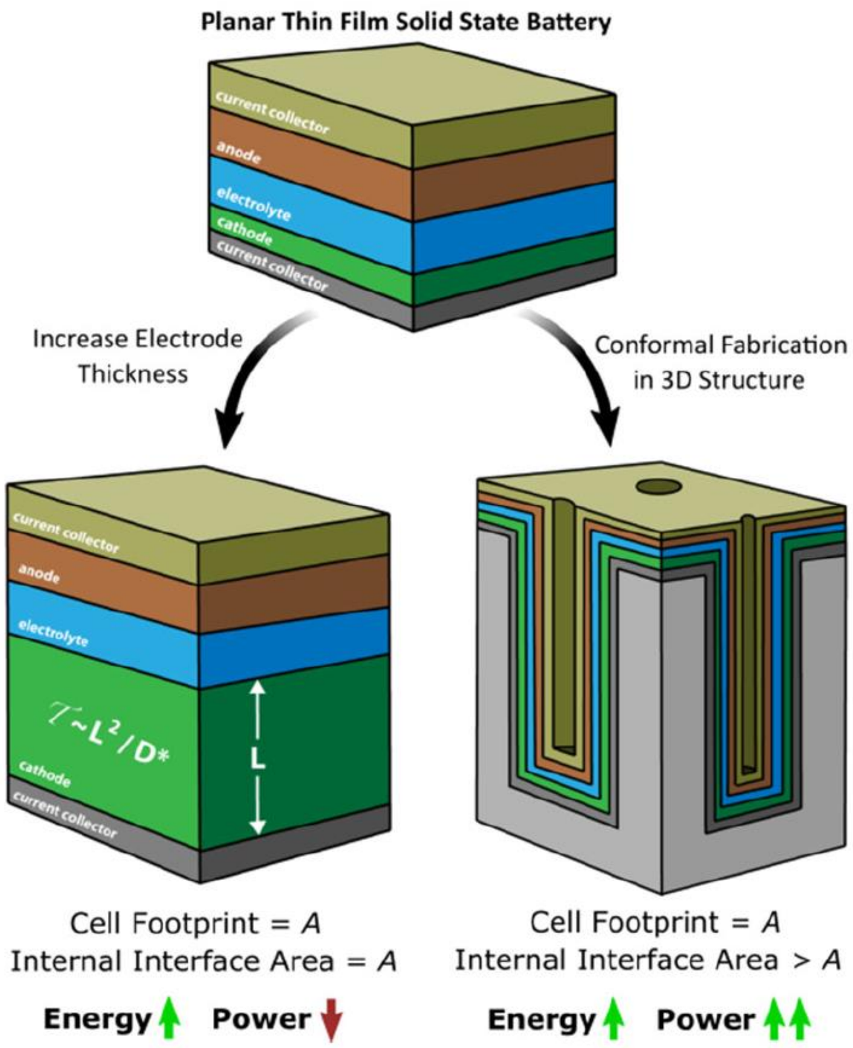


Figure 1. Cross-section SEM pictures of the ALD deposited lithium phosphate thin films on Si(100) substrates at (a) 250 °C (LPO250), (b) 275 °C (LPO275), (c) 300 °C (LPO300), and (d) 325 °C (LPO325), after 2000 ALD cycles.

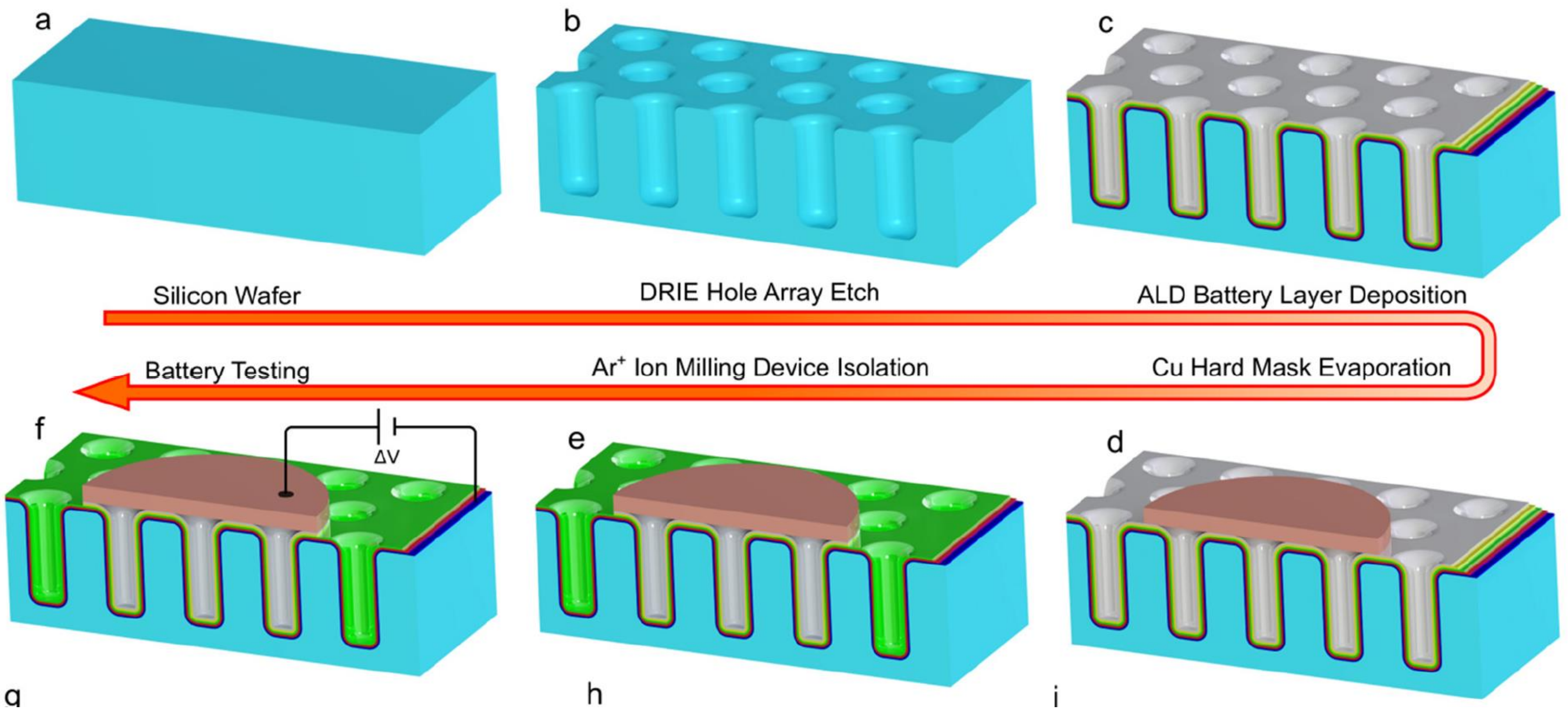
Batteries "More-than-Moore"



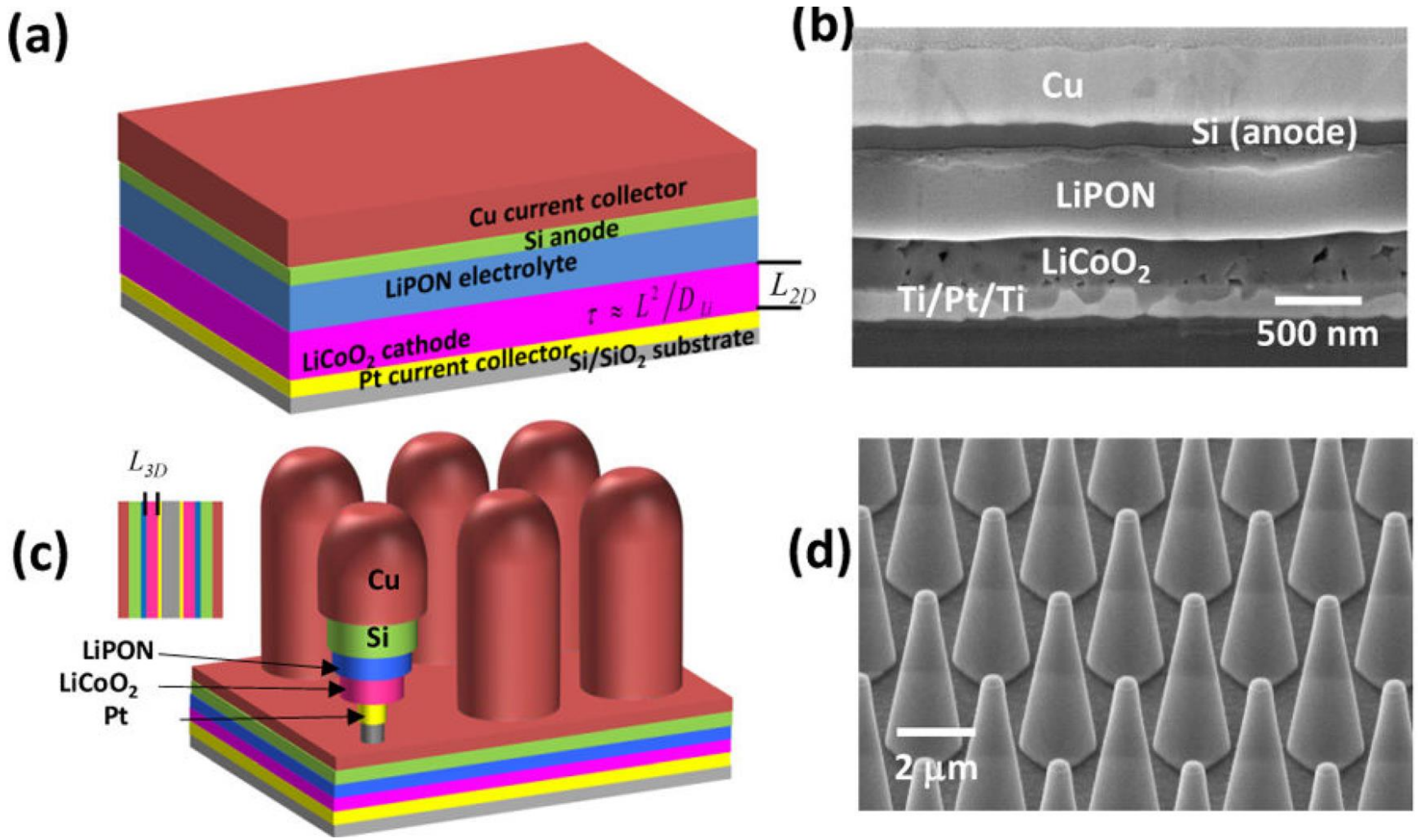
Planar Vs 3D Architecture Structures



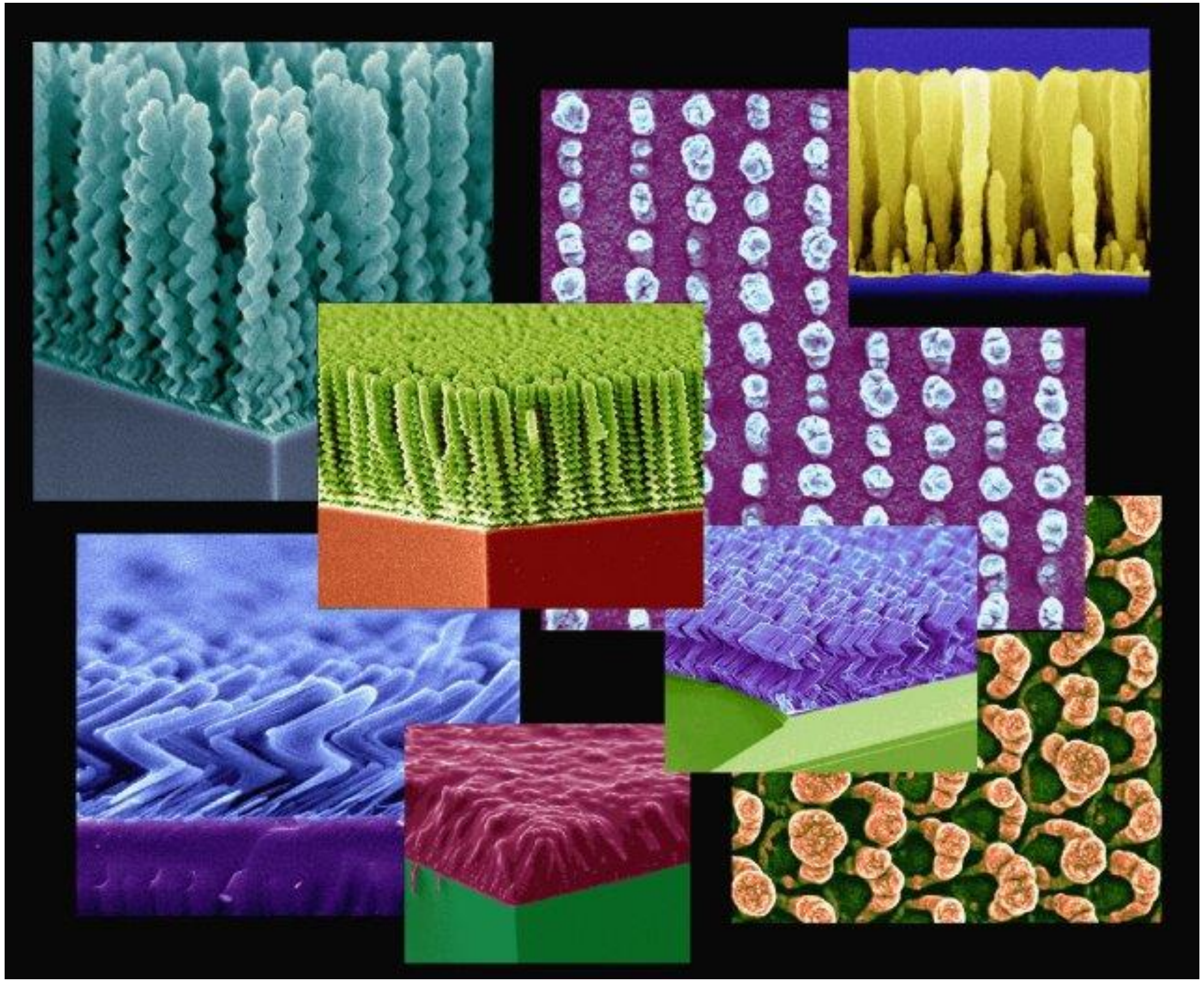
Ion Milling for Substrate Prep



Pillars Vs Pores – AEF Advantage?



Glancing angle deposition of oriented structures



Lithium anode volume expansion

Materials	Li	C	$Li_4Ti_5O_{12}$	Si
Density (g/cm^3)	0.53	2.25	3.5	2.3
Lithiated phase	Li	LiC_6	$Li_7Ti_5O_{12}$	$Li_{4.4}Si$
Theoretical specific capacity (mAh/g)	3862	372	175	4200
Volume change (%)	100	12	1	420
Potential versus Li (V)	0	0.05	1.6	0.4

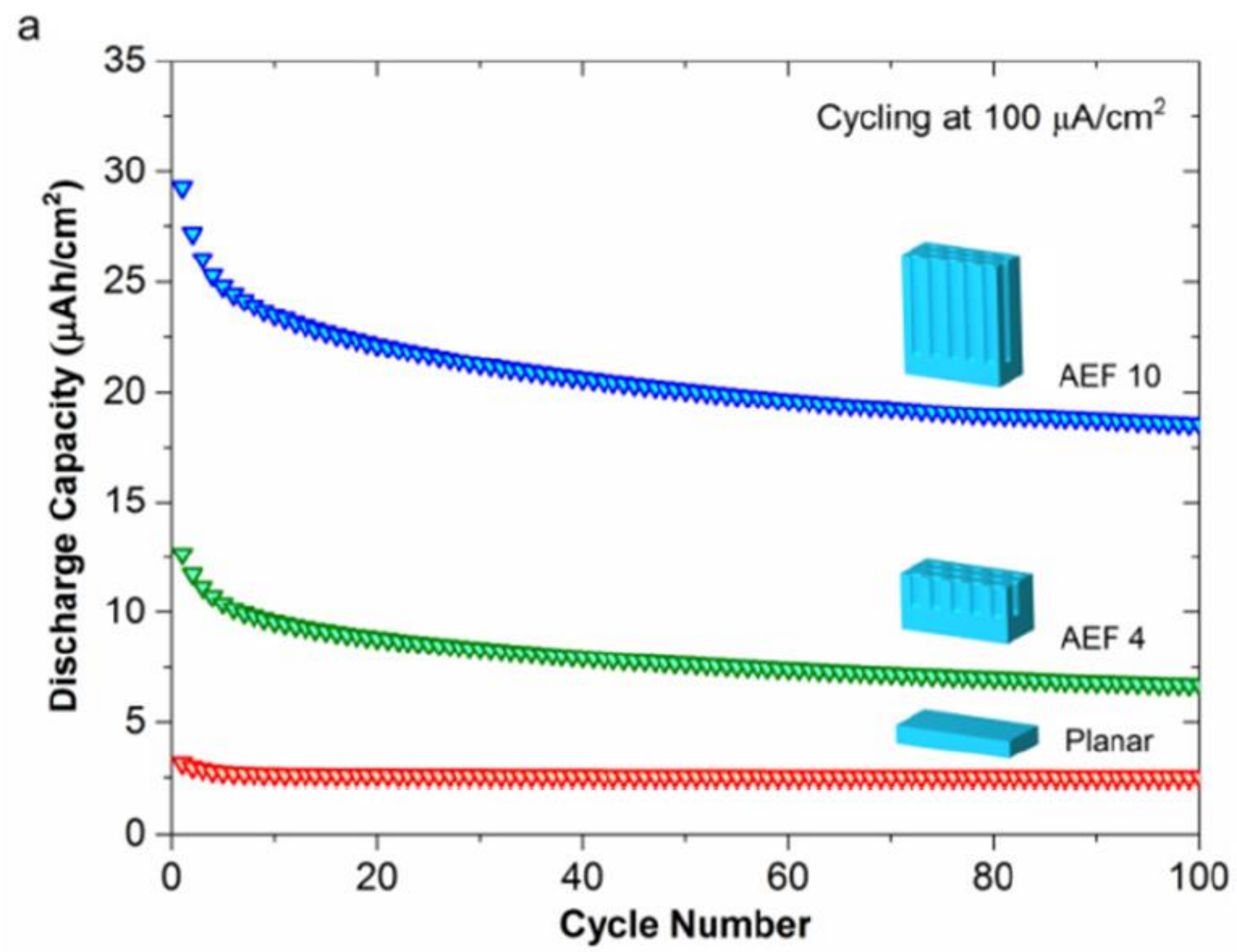
Area Enhancement Factor (AEF)

- Pillars Vs Pores – still need about 30x to break even with Planar architecture

- Smartphone requires AEF of 400!

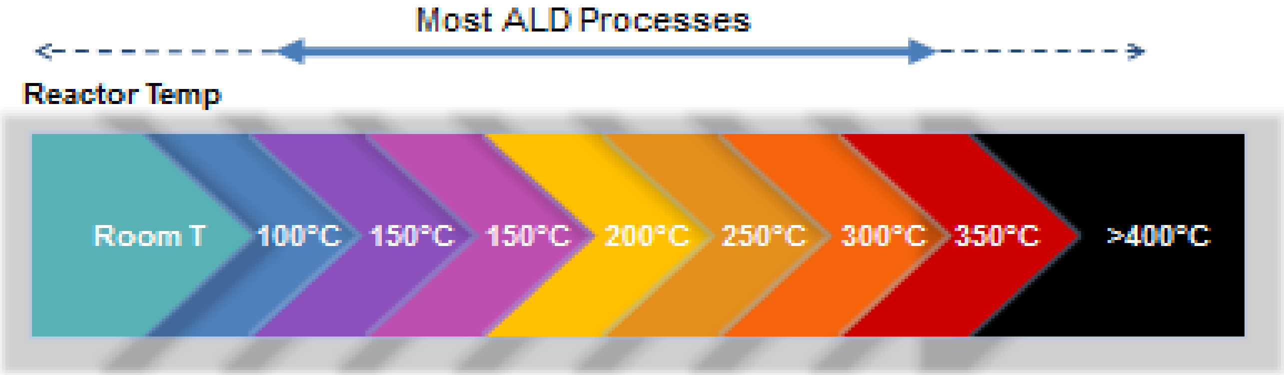
- Current demonstrations at AEF = 50

Demonstrated Capacity Scales with AEF



ALD Reaction Temperatures

- ALD is a chemistry driven process
- Based on precursor volatility/reactivity

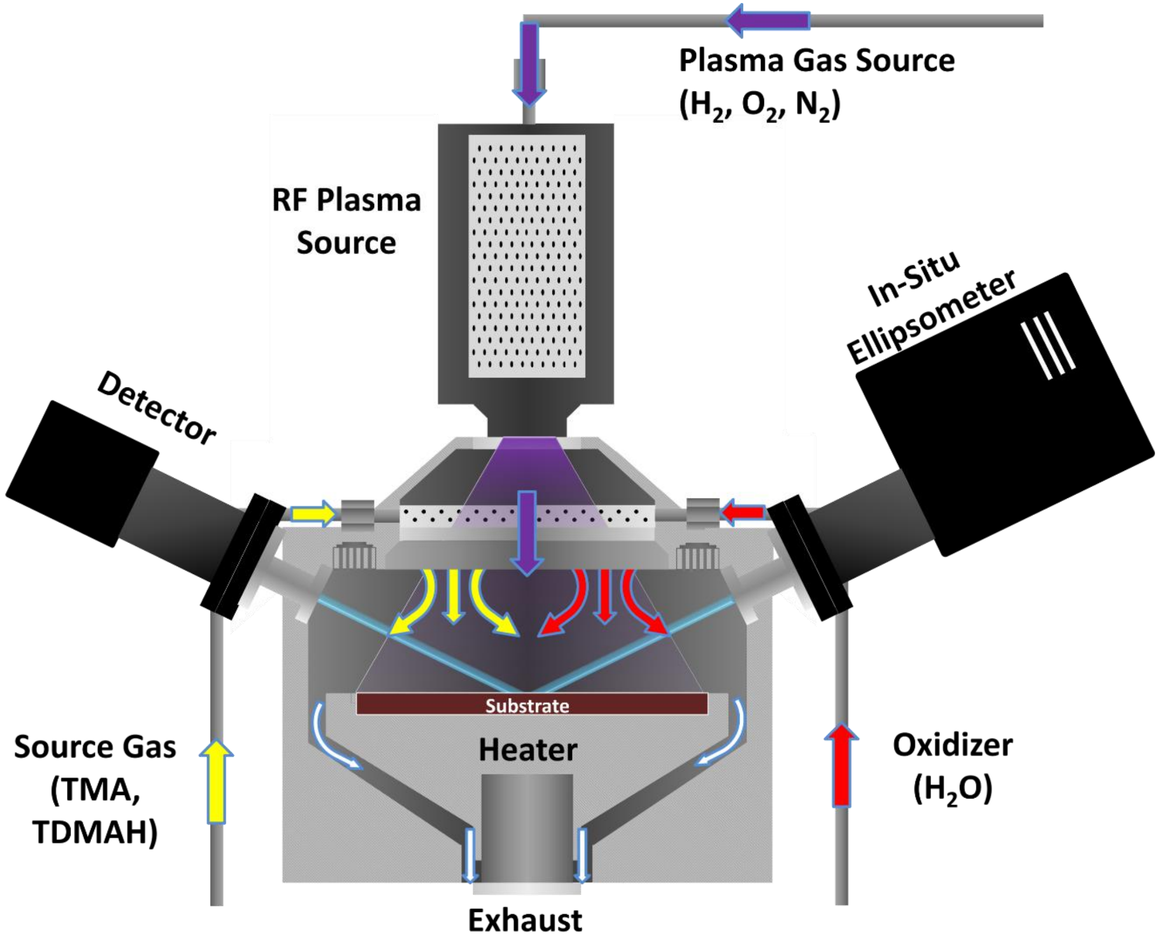


Lower precursor volatility,
Slow desorption of precursors

High precursor volatility,
lower thermal stability of precursors

Remote Inductively Coupled Plasma (ICP)

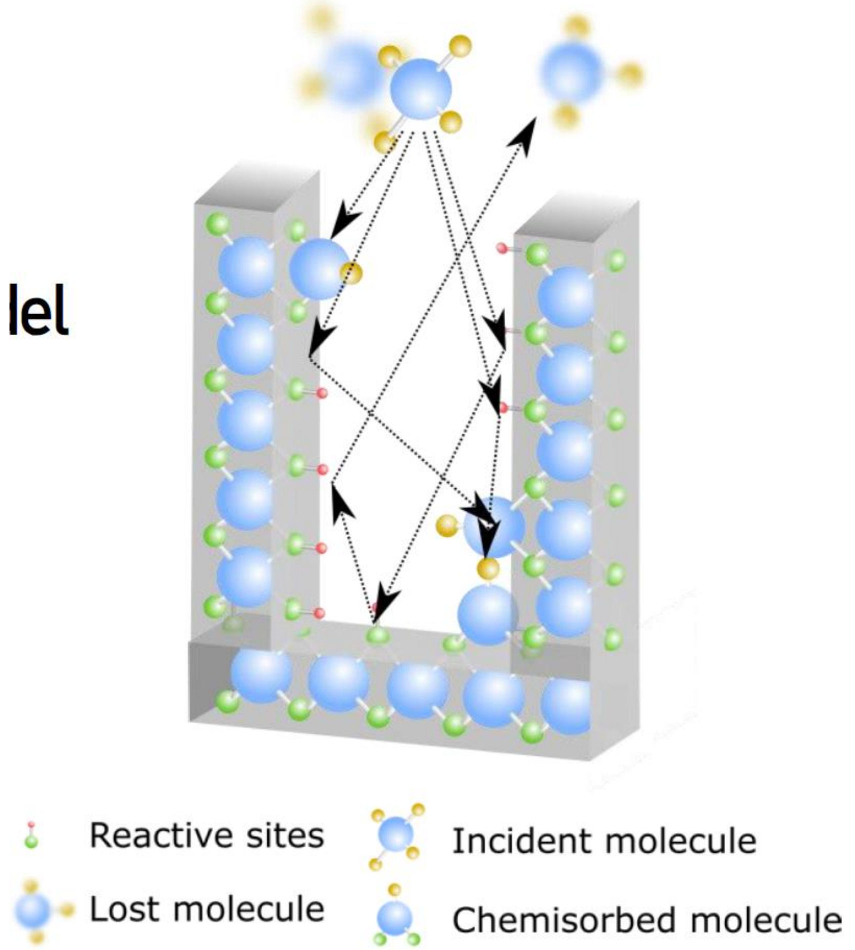
- ✓ 500 W Ar/O_2 plasma
- ✓ Cylindrical quartz plasma tube w/ helical inductive coil geometry
- ✓ 13.56 MHz frequency



PEALD chamber

Gas/Solid Interactions are Classic

- Physiosorption
- Desorption
- Chemisorption
- Effected by –
  - Incident angle
  - Precursor density
  - ‘energy’ (temp, plasma)



Recombination of Hydrogen

- Plasma cracks about 50% of H2 into H

- (Atomic) H quickly recombines, over a few cm’s, to become H2 again

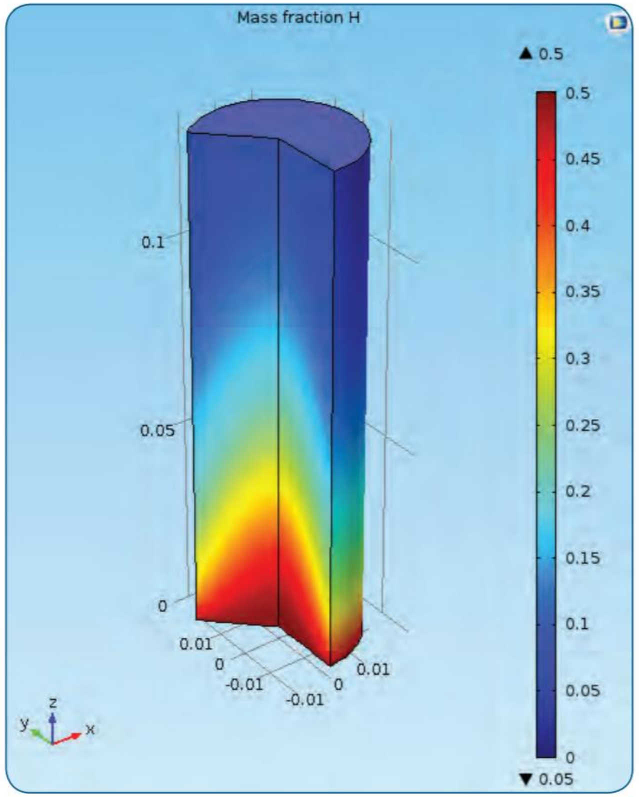
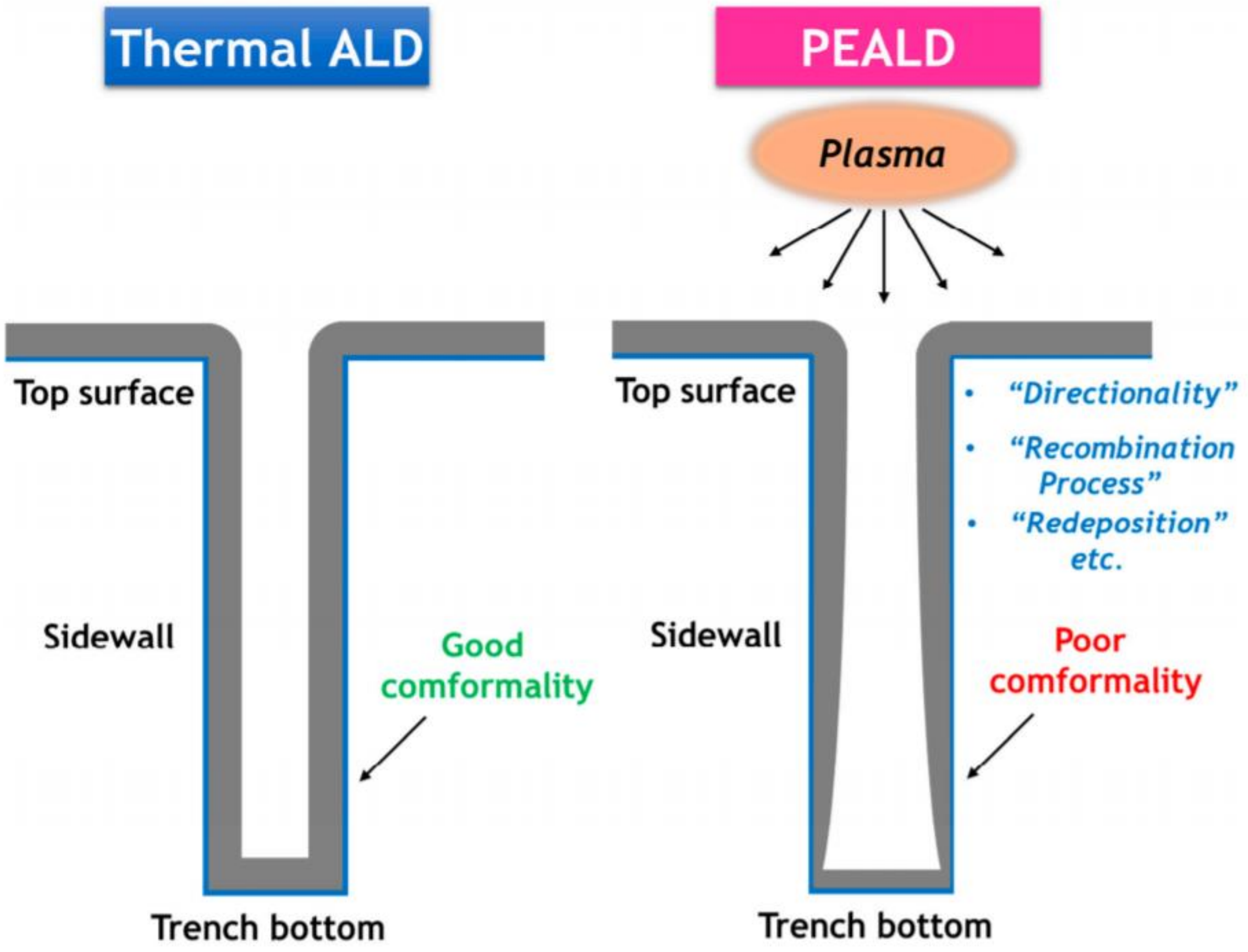
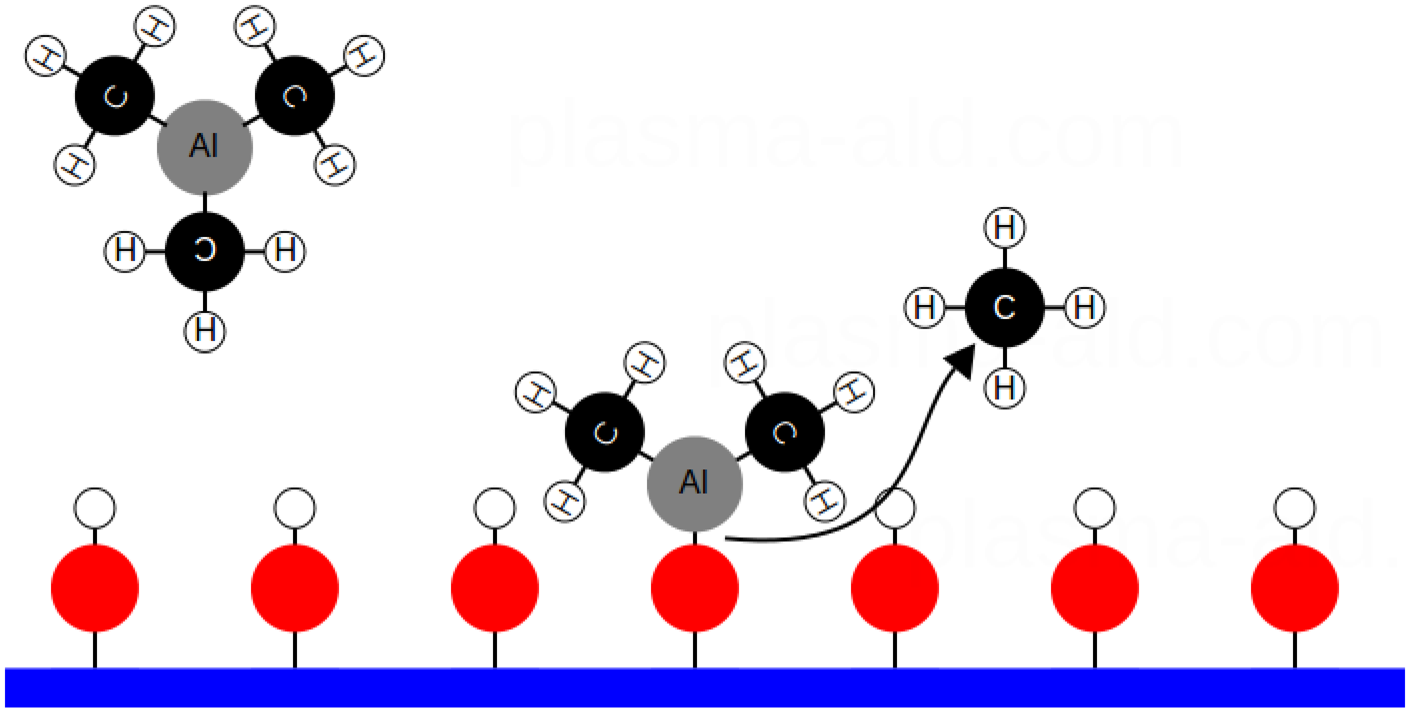


Figure 1. Hydrogen recombination simulation geometry (40mmϕ x 130mm). Color is mass fraction of H. Input H_2 flow=2.0 slm, P=1.0 Torr, γ =0.01.

Recombination of Ions in Trenches



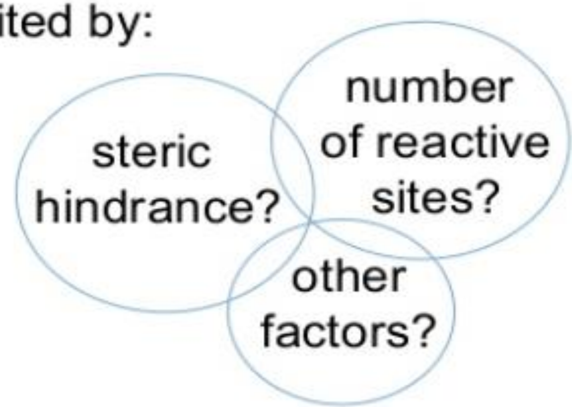
Example of Steric Hindrance



Growth per cycle Less than 1 mono layer

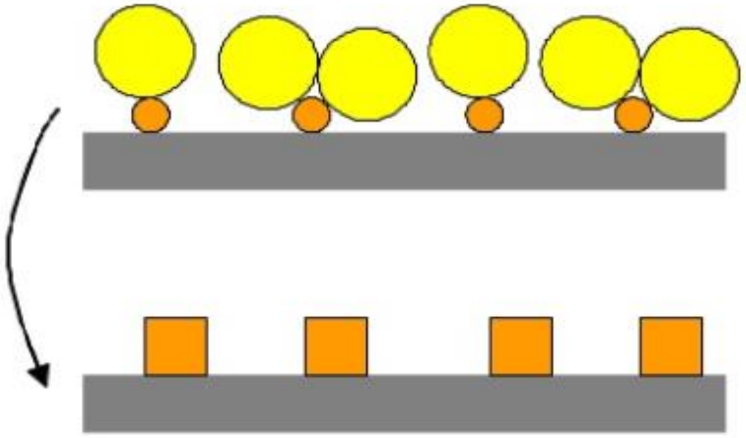
Growth per cycle

- typically ~5-50% of ML
- limited by:



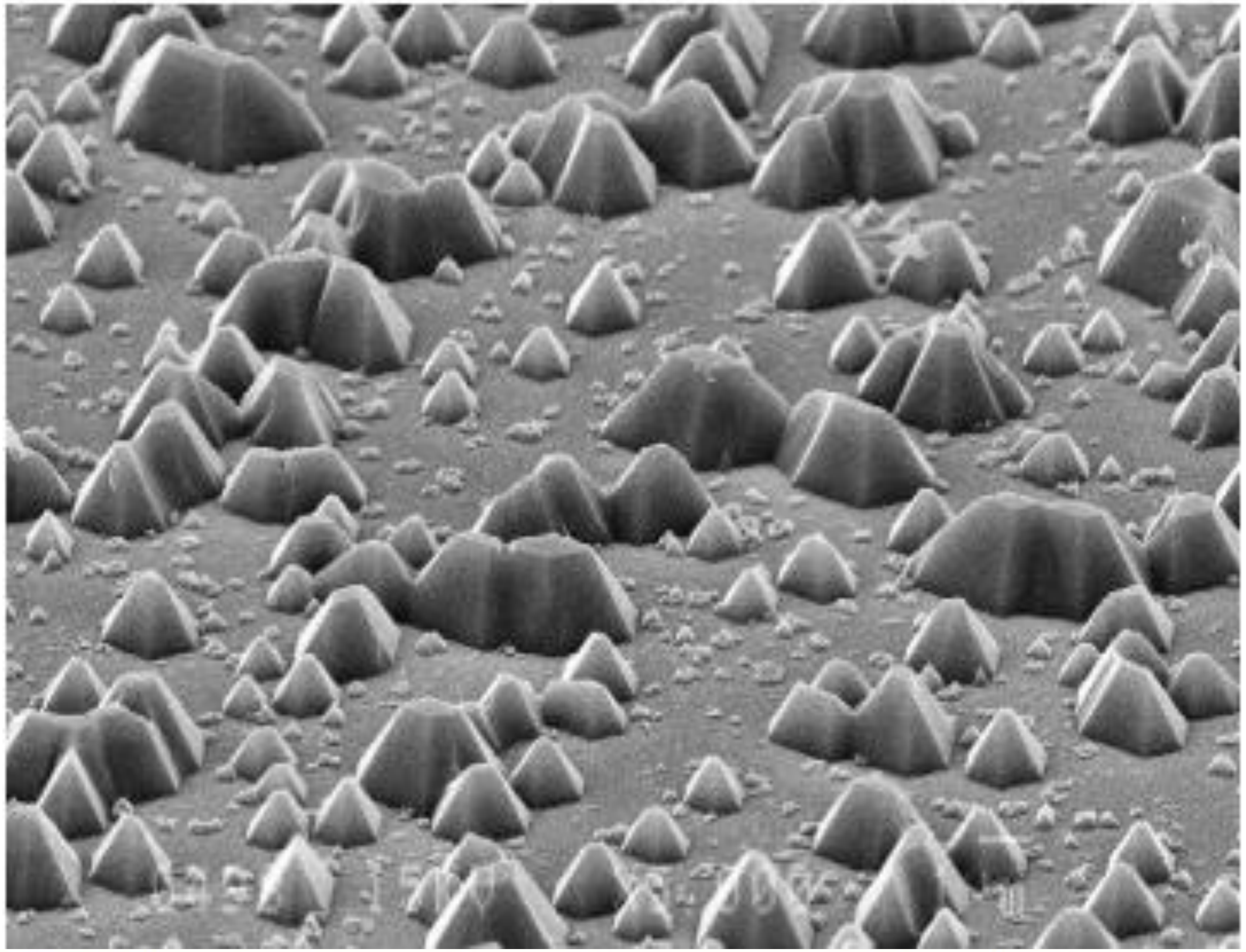
- Less than ML growth has consequences to growth mode and layer characteristics

Reactant A, chemisorbed monolayer



ALD-grown material

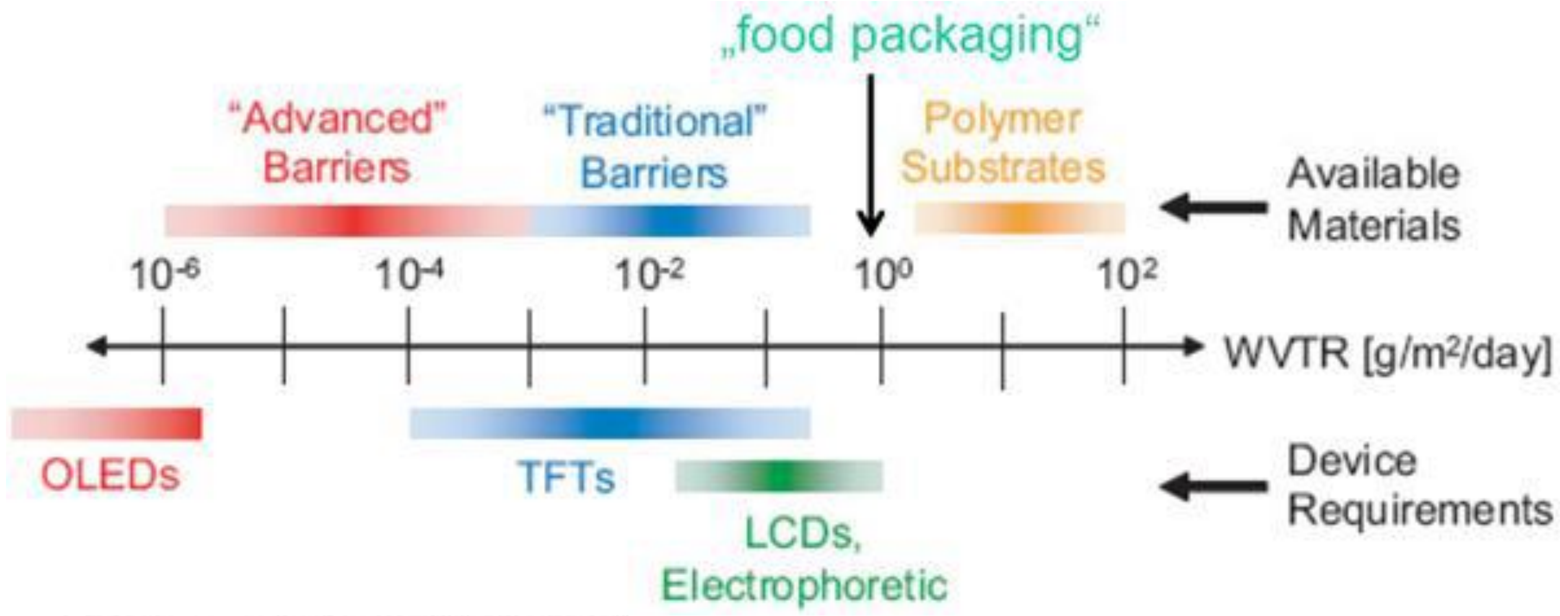
Random Growth Mode

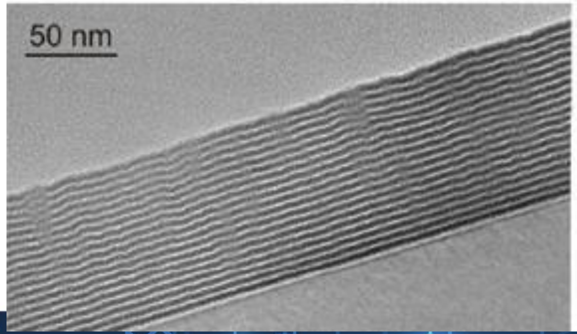


Modeling of ALD Film Growth

- Add Univ of Alberta data on ALD in deep vias.
- Modification of pulse times to fully occupy all available functionalized sites
- Alternative pulsing patterns to optimize growth-per-cycle

ALD Capping Layers for TFB's

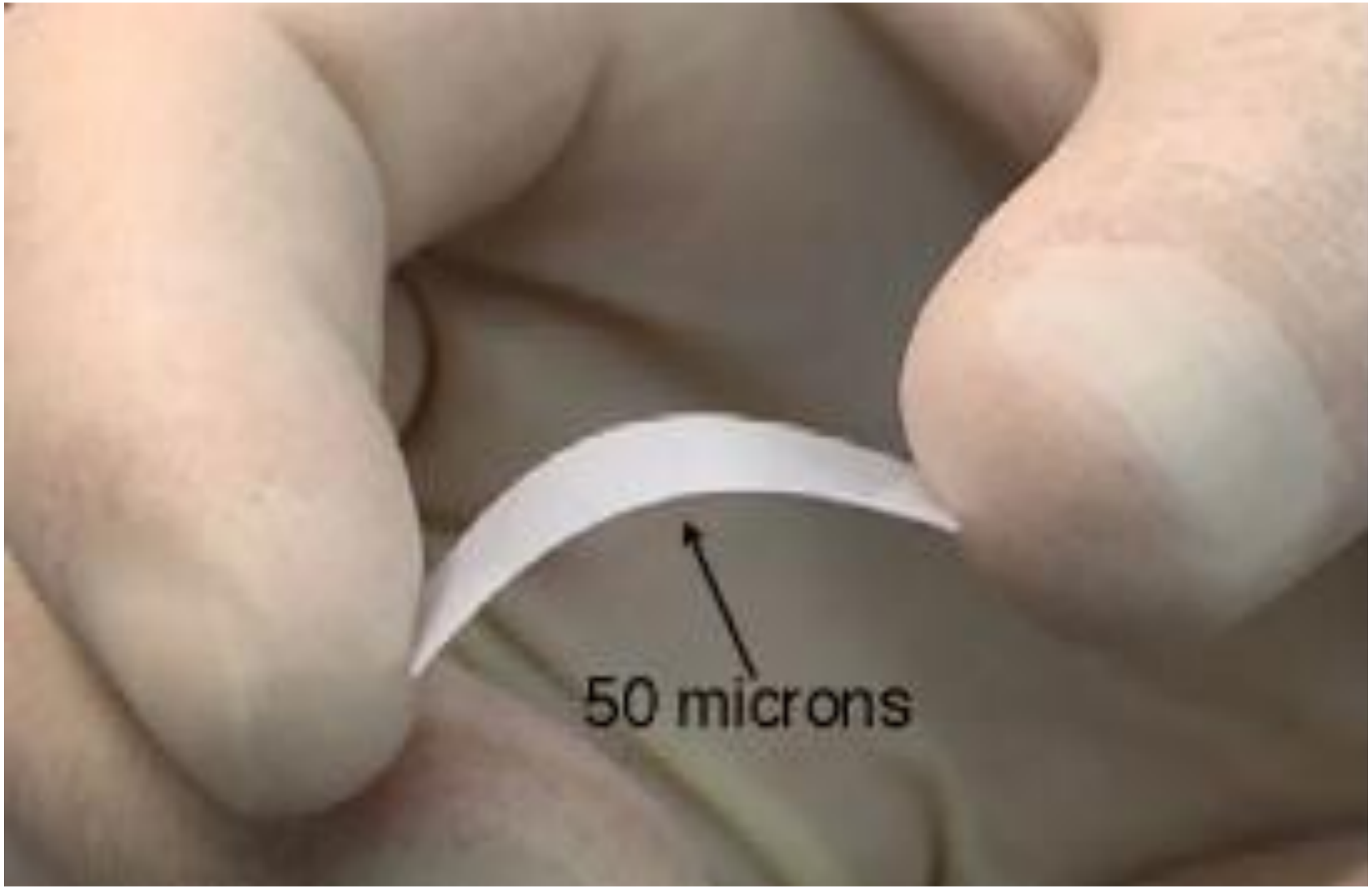




Water Vapor Transmission Rate (WVTR) <10−6 g/m2 day demonstrated

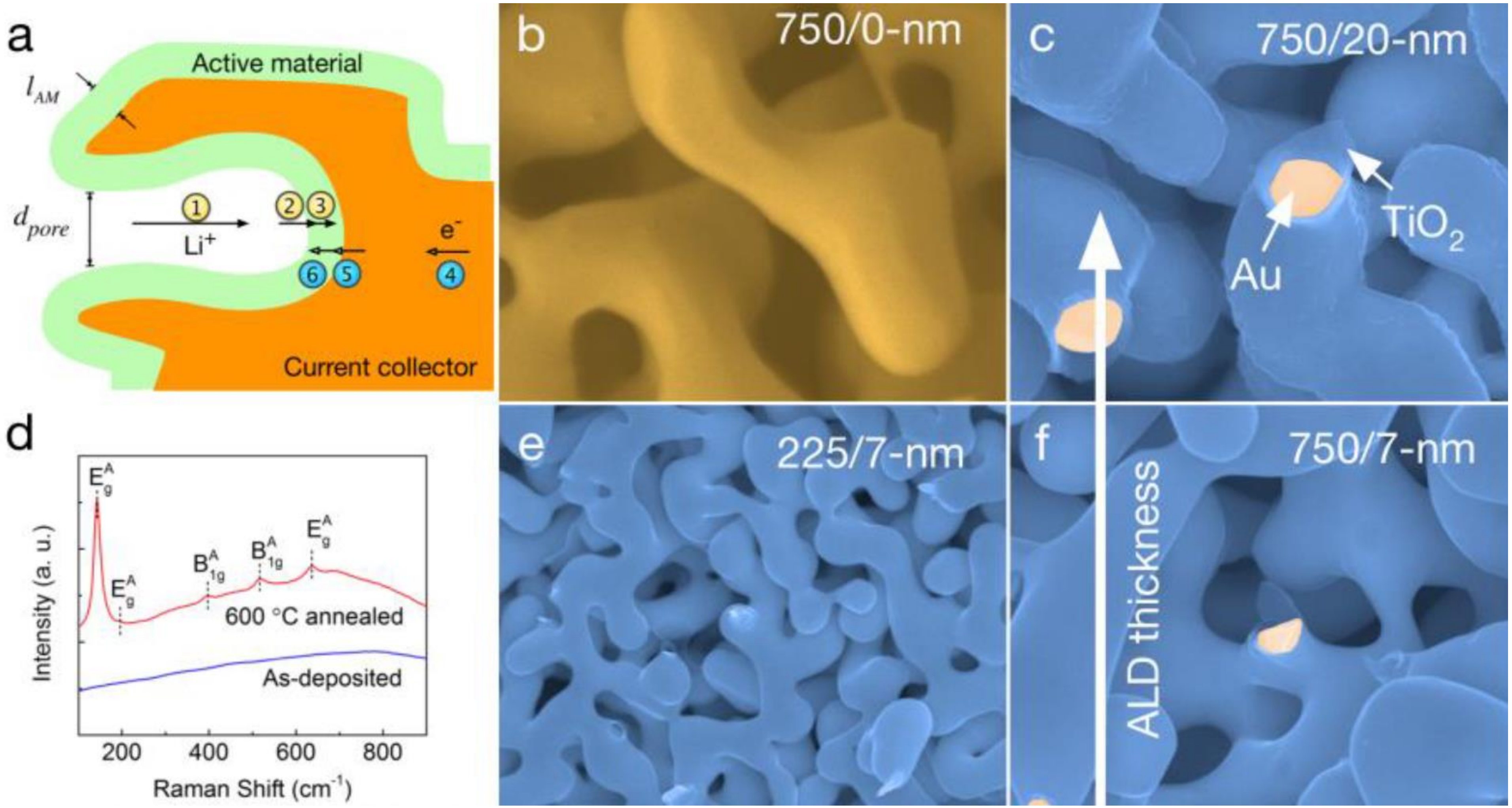
- Other substrates and architectures

Micro-thin substrates Lithium ion conductor - Ohara



Ultra thin glass – 25 microns - Schott Optical

Foam and Aerogel Electrodes



- Summary
  - More than 20 years in the making
  - Showed the way toward a perfect, permanent battery and re-energized battery research
  - ***Convergence of electronic device design (smaller, more energy efficient) & solid-state secondary microbatteries = commercialization***

KURT J. LESKER COMPANY

J.R. Gaines, Technical Director of Education

JRG@Lesker.com

614-446-2202