Chalcogenide Active Materials for Photonics and Photovoltaics

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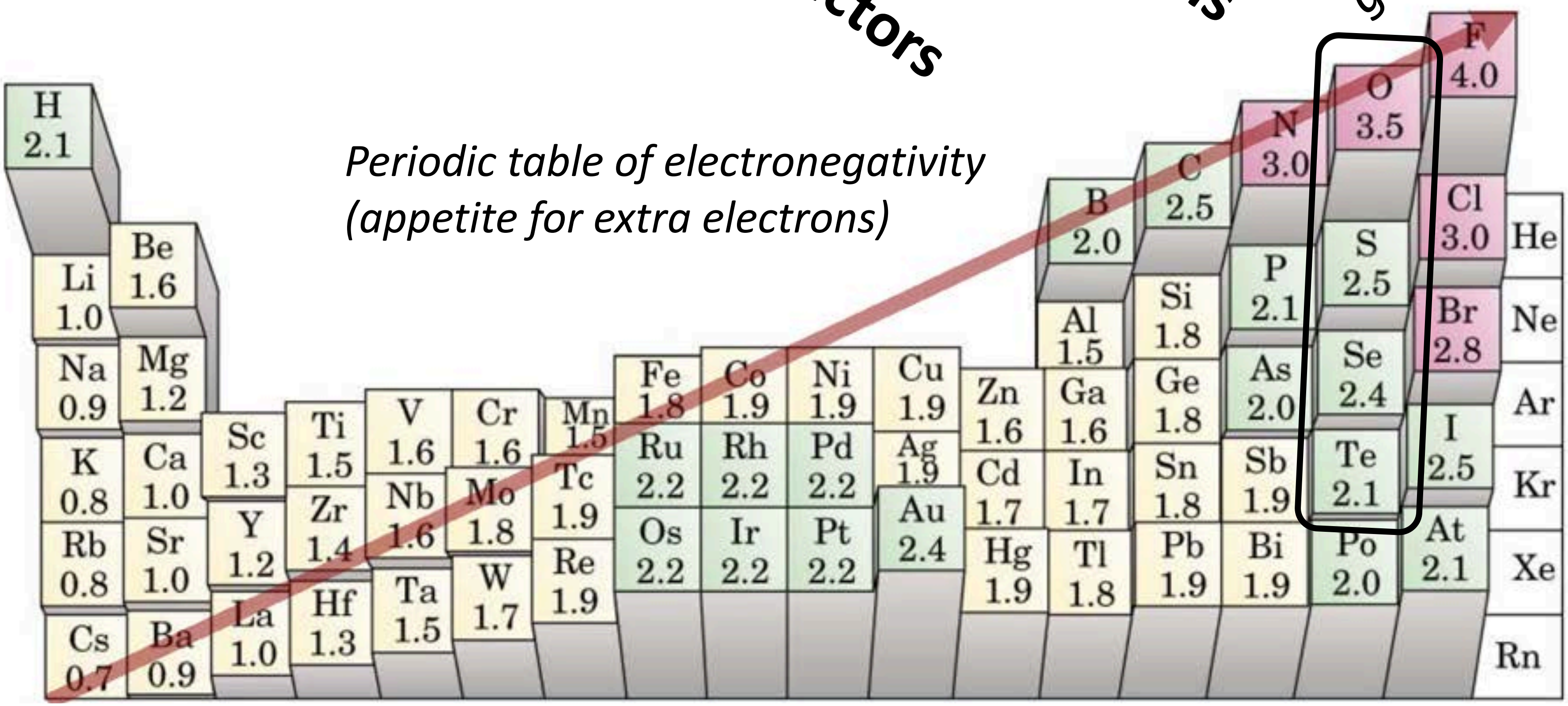
Chalcogenides & electronegativity

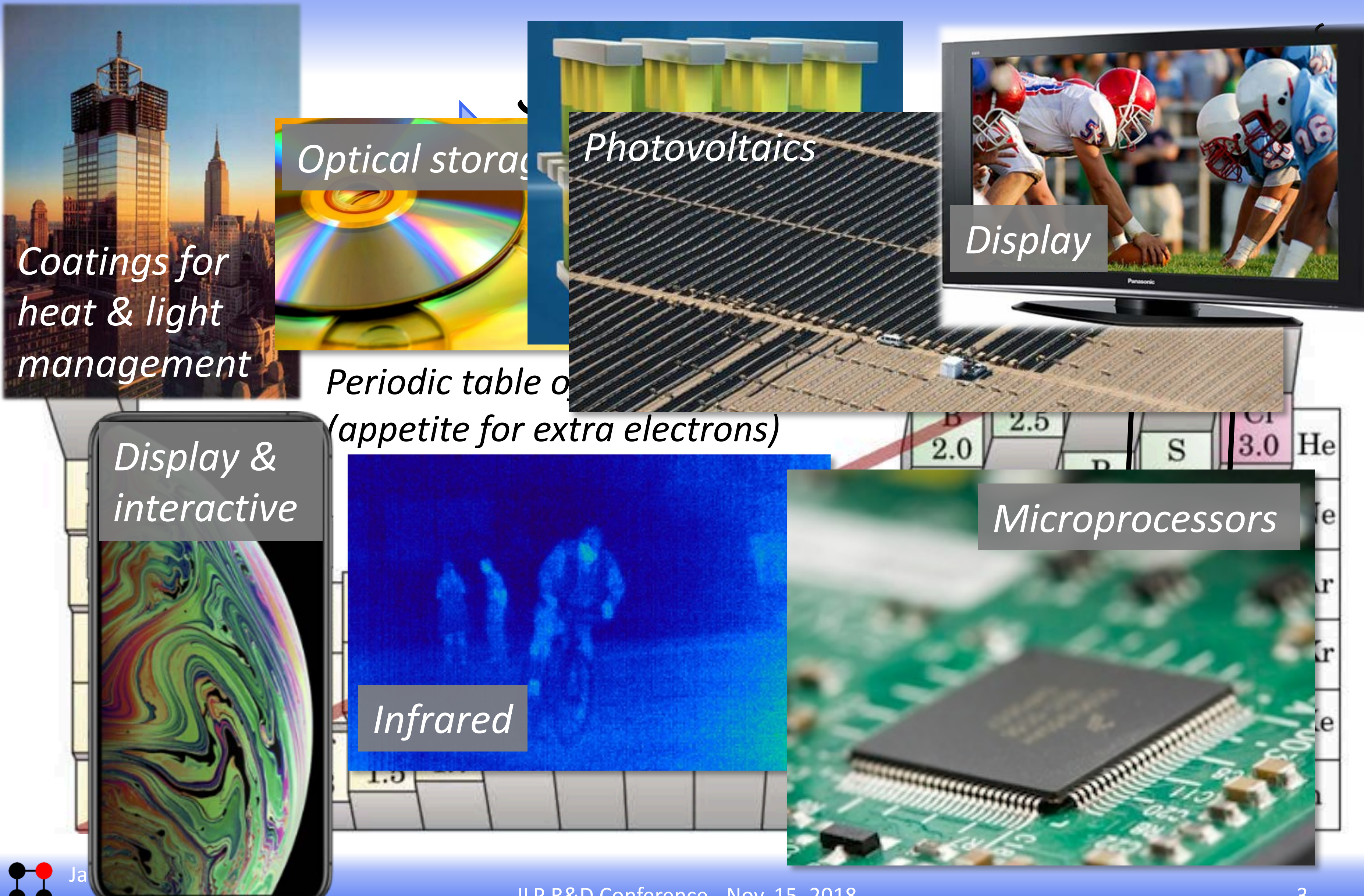
Dielectrics → **Semiconductors** → **Semi-metals**

chalcogenides
group 6A

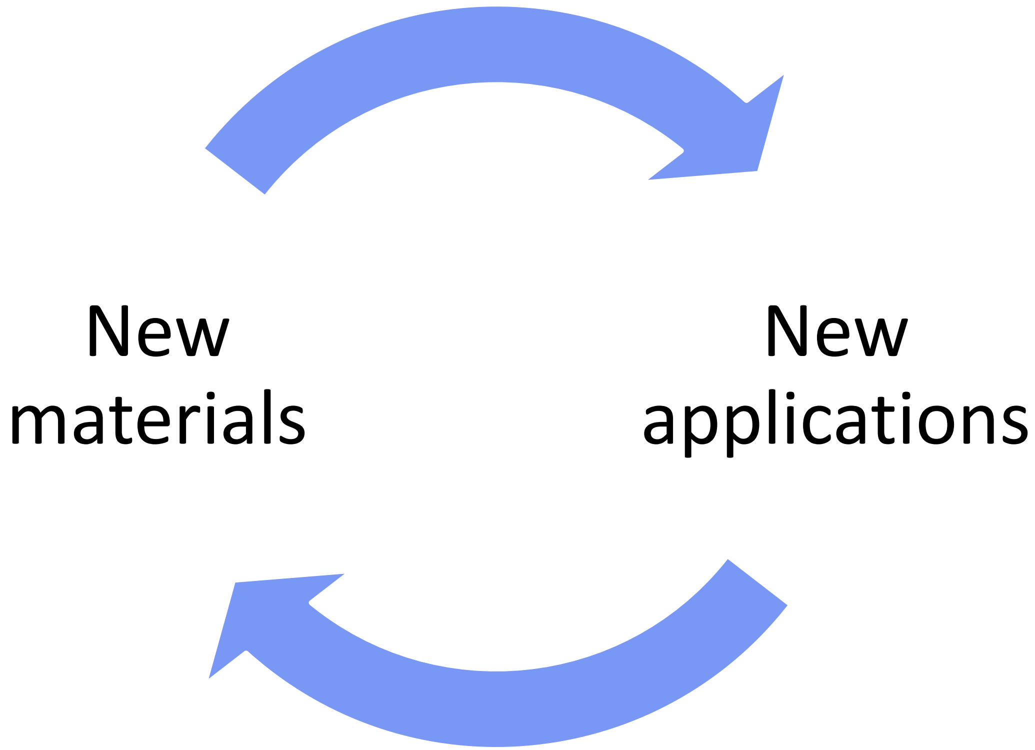
Periodic table of electronegativity (appetite for extra electrons)



Applications of chalcogenide optoelectronic materials



Cycles of new materials and new applications



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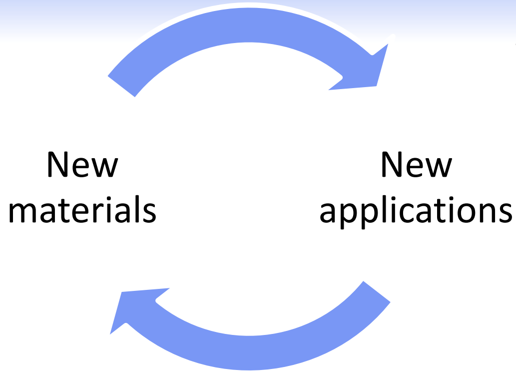
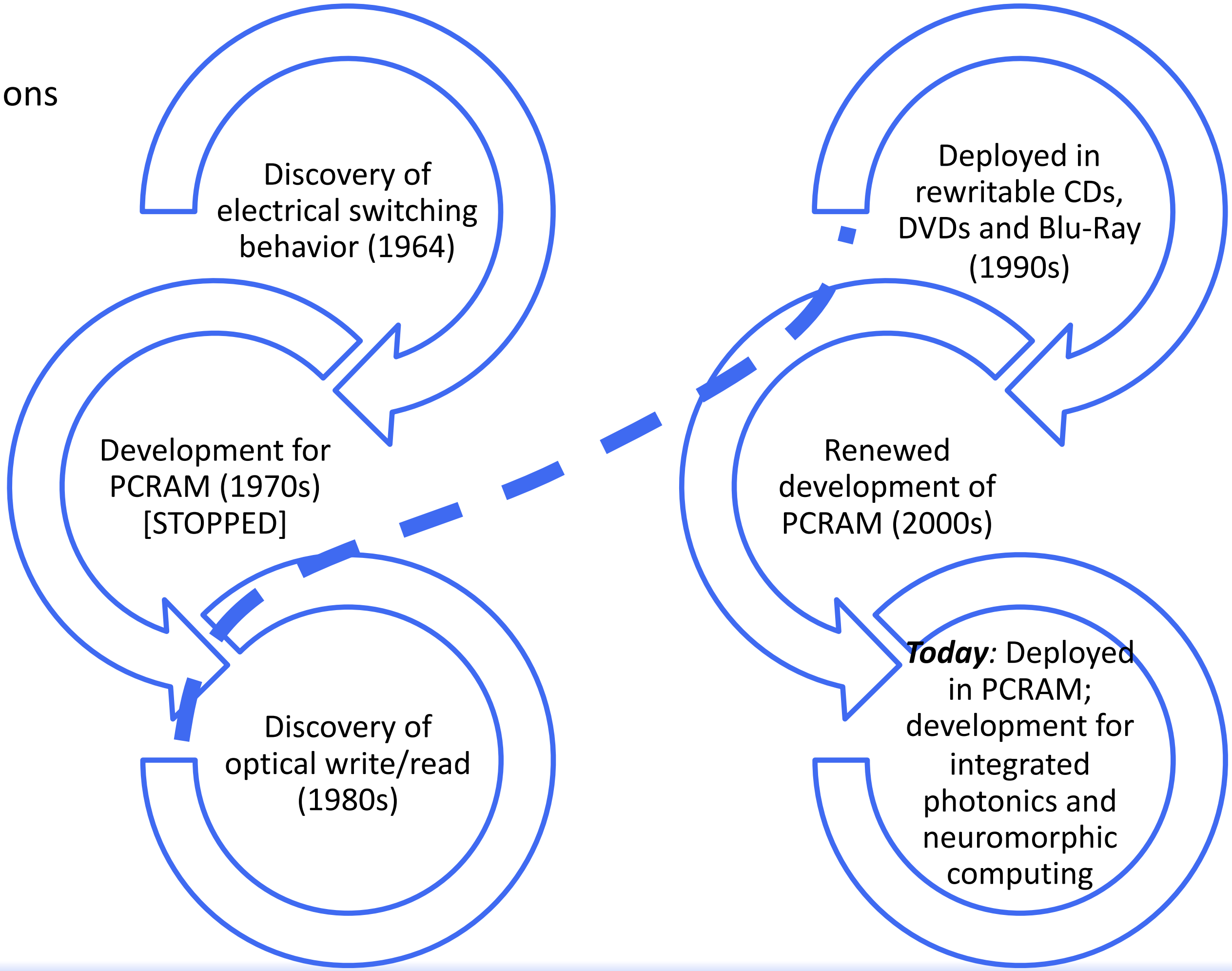
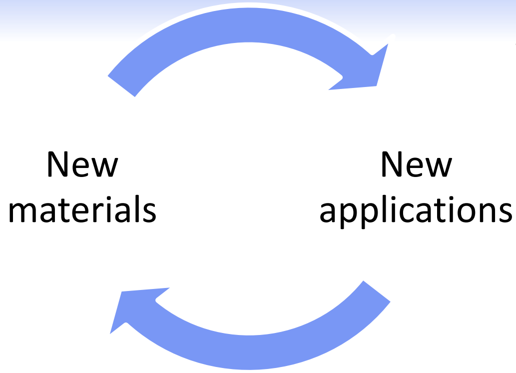


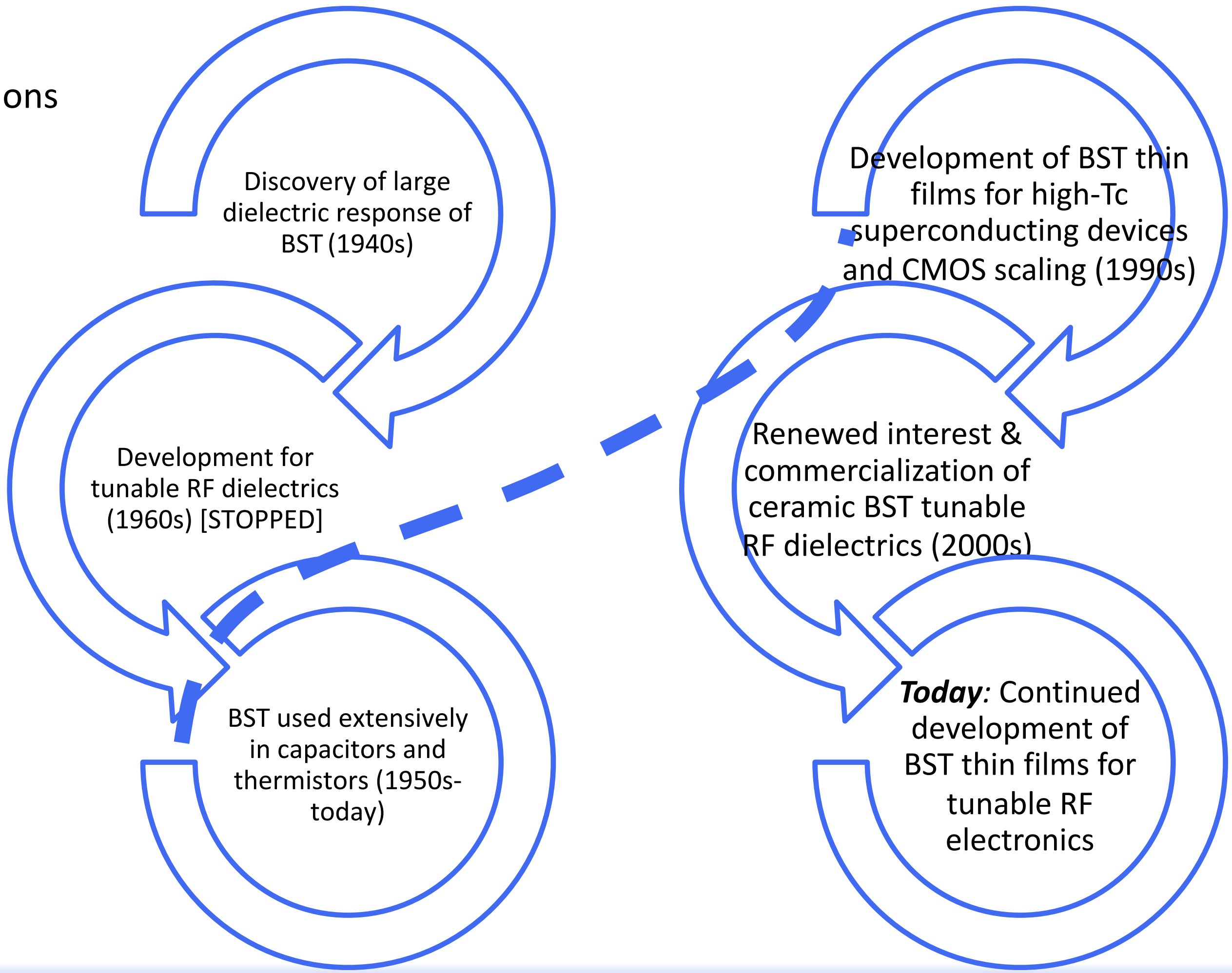
Vignette 1: *History of Ge-Sb-Te (GST) phase-change materials*



Cycles of new materials and new applications



Vignette 2: *History of (Ba,Sr)TiO$_3$ (BST) tunable dielectrics*



Q. What’s different today?

A. Cycles can be kicked-off by theory-guided discovery

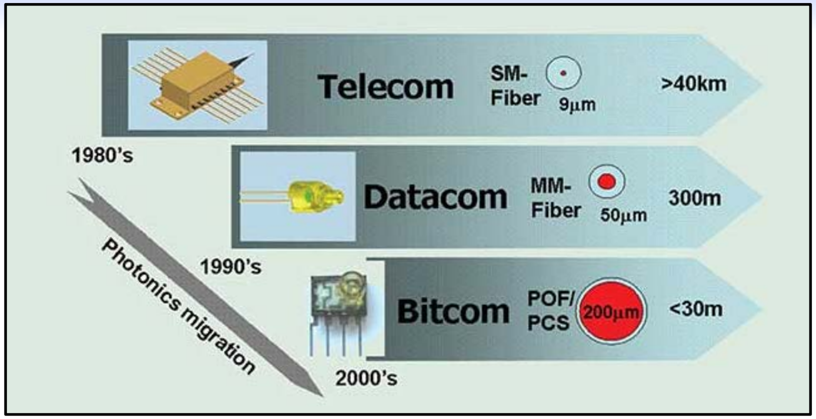
Rest-of-talk

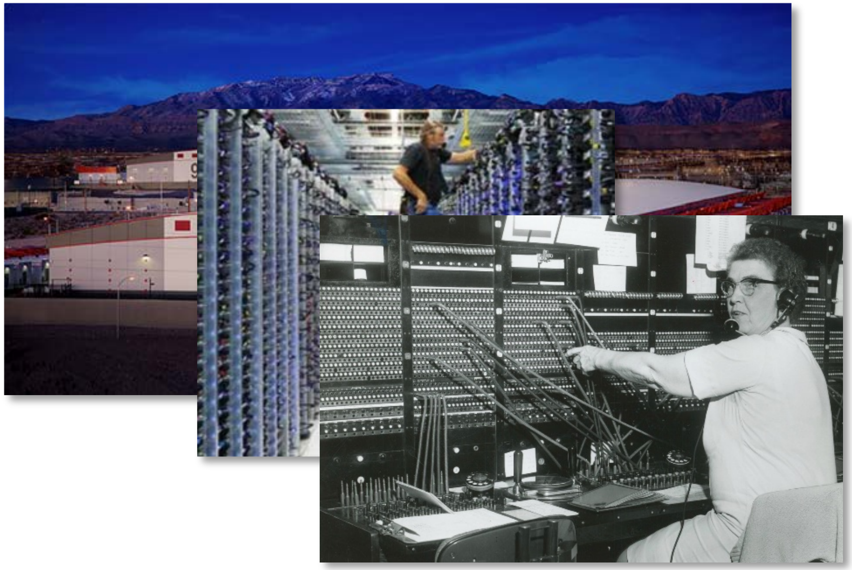
1. New materials and applications: *integrated photonics*
2. New materials: *photovoltaics*
3. Spotlight on chalcogenide materials processing for infrared optics

New materials for integrated photonics

Integrated photonics

- Replacing electrons with photons
  - Increase data transmission rates
  - Reduce power consumption
  - Add functionality
- Telecom to datacom (1980s-present day)
  - Implemented with discrete photonics
  - We're in the vacuum tube era!
  - Integrated photonics is next





Integrated photonics

- Replacing electrons with photons
  - Increase data transmission rates
  - Reduce power consumption
  - Add functionality
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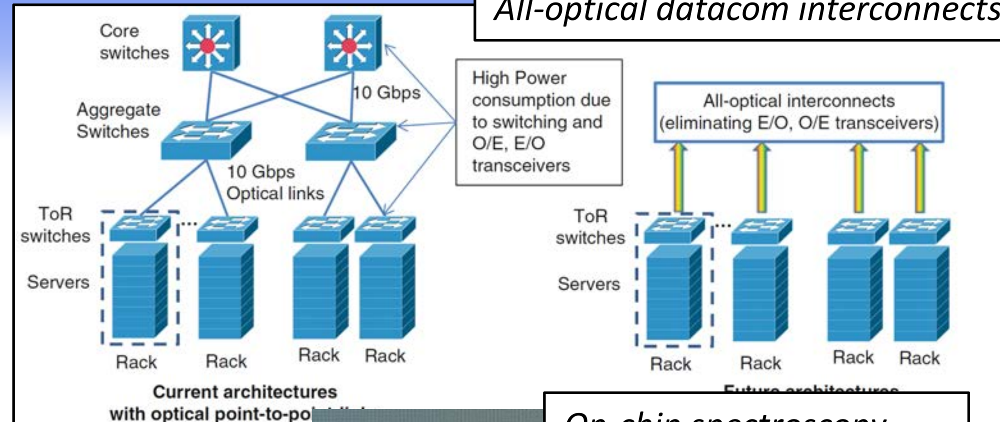
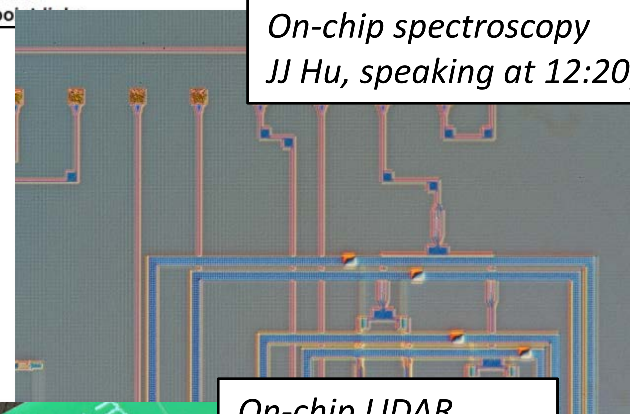
  - We’re in the vacuum tube era!
  - Integrated photonics is next
- Applications
  - Interconnects for data centers
  - Sensors
  - Phased arrays for LIDAR, *etc.*
  - Inter- and intra-core interconnects

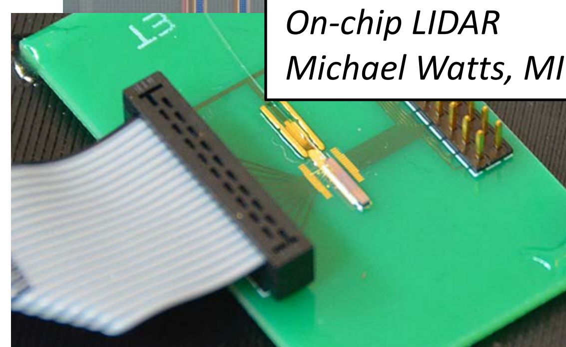
All-optical datacom interconnects



On-chip spectroscopy
JJ Hu, speaking at 12:20p



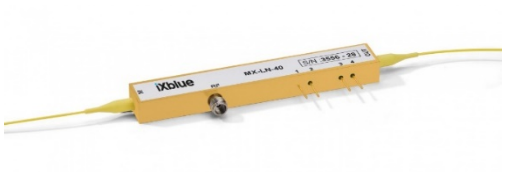
On-chip LIDAR
Michael Watts, MIT



[1] *Optical Interconnects for Future Data Center Networks*, Springer (2013)

Motivation and opportunity

~cm

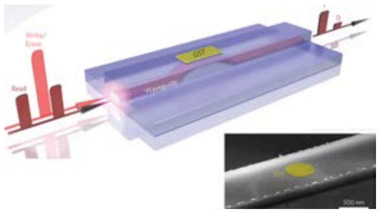


commercial optical modulator

~mm

optical modulator fabricated on $LiNbO_3$ wafer [1]

~μm



GST-based optical switch on a Si3N4/SiO2/Si integrated photonic circuit [2]

- Integrated photonics requires materials that strongly interact and modulate IR light
- Established materials (*e.g*. $LiNbO_3$) interact weakly with light, are difficult to integrate on-chip, or both
- GST phase-change materials proposed and demonstrated, but are lossy and suffer from fatigue

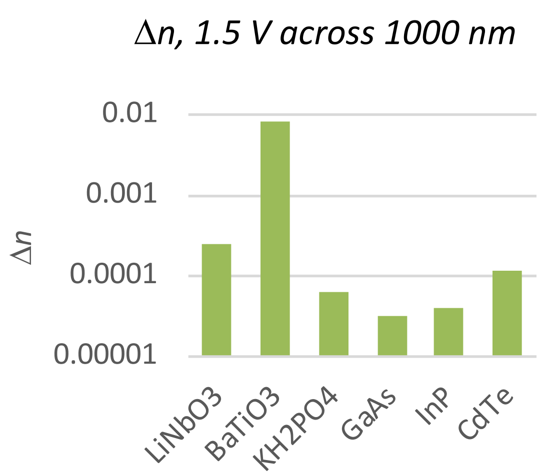
[1] Wang, C. *et al*. *Nature* **562,** 101–104 (2018).
[2] Rios, C. *et al*., Nat. Photon. **9**, 725 (2015).

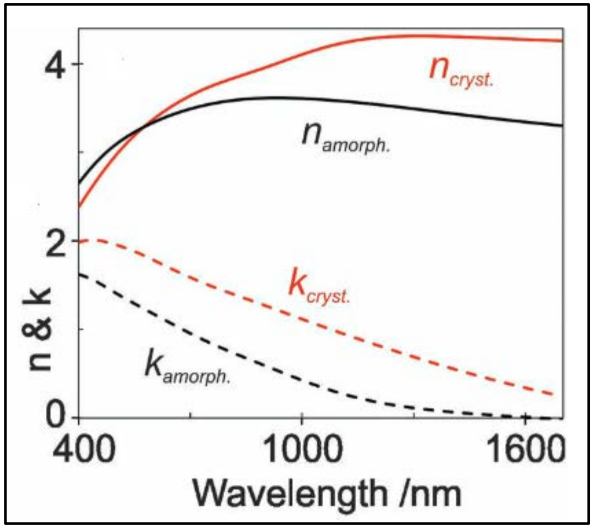
The limits of present-day materials

- Established active photonic materials
  - Electro-optic (EO) or thermo-optic (TO) switching
  - Si, Ge, GaAs, chalcogenide glasses
  - Switching is “perturbative” ($\Delta n \ll n$)
- Phase-change materials
  - GST, VO_2, *etc.*
  - Switching is non-perturbative ($\Delta n \sim n$)
  - One or more phases is lossy

Table I:
Comparison of the elctro-optic figures of merit of several materials of current importance.[3]

	n^3r pm/V	n^3r/ε pm/V
Ferroelectrics		
$LiNbO_3$	320	11
$Sr_{1-x}Ba_xNb_2O_6$	2,460	4.0
$BaTiO_3$	11,300	4.9
KH_2PO_4	86	1.7
Semiconductors		
GaAs	43	3.3
InP	52	4.1
CdTe	152	16
Organics		
2-Methyl 4-Nitroaniline	530	133
m-Nitroaniline	97	29



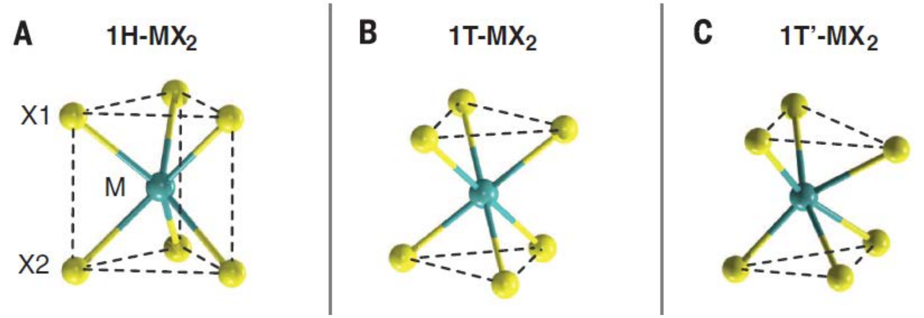


[1] Glass, MRS Bull. **13**, 16-20 (1988).
[2] Gholipour *et al*. Adv. Mater. **25**, 3050-3054 (2013).

New photonic materials by design

- Focus on layered (2D) materials
  - Transition metal dichalcogenides (TMDs)
- Structural phases
  - 2H, semiconducting
  - 1T, metallic
  - 1T', semiconducting (small gap)

Atomic structure of TMD phases
teal = metal, yellow = S/Se/Te



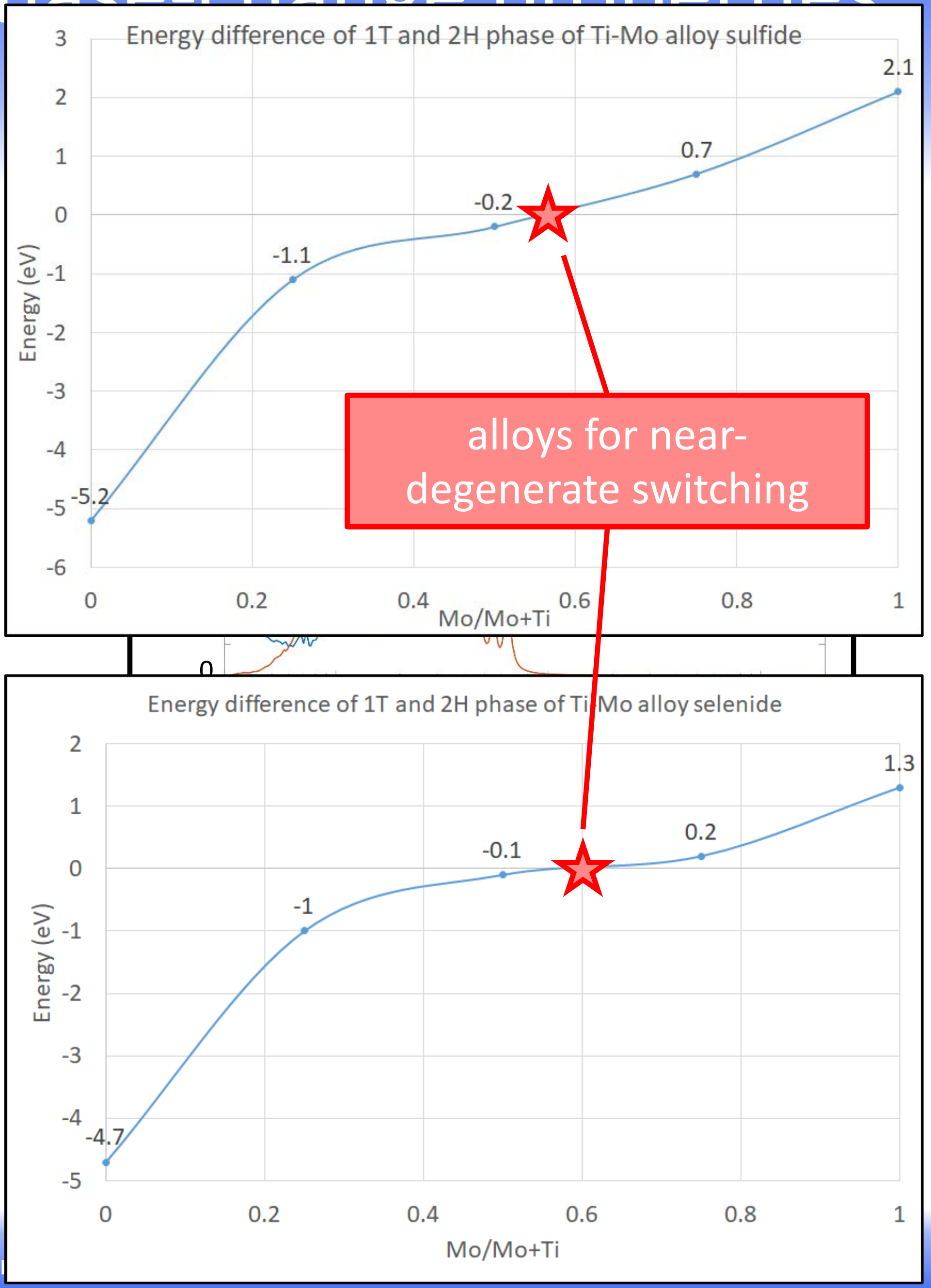
Periodic table of TMD phases: A road map to designer materials

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	1T	2H	1T	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	1T	2H	2H	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	1T	2H	2H	75 Re 186.21	76 Os 190.23	77 Ir 192.22	1T	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)

Qian, X., et al. Science 346, 1344–1347 (2014).

Predicting optical and phase-change properties

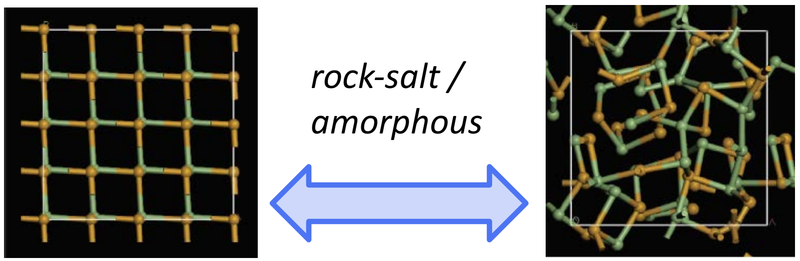
- Promising (n, k) contrast in IR for representative phases
  - MoS_2 in 2H phase
  - TiS_2, ZrS_2 in 1T' phase
- Metal alloying to tune switching energetics
- DFT calculations
  - Collaboration with Prof. Ju Li (NSE / DMSE)

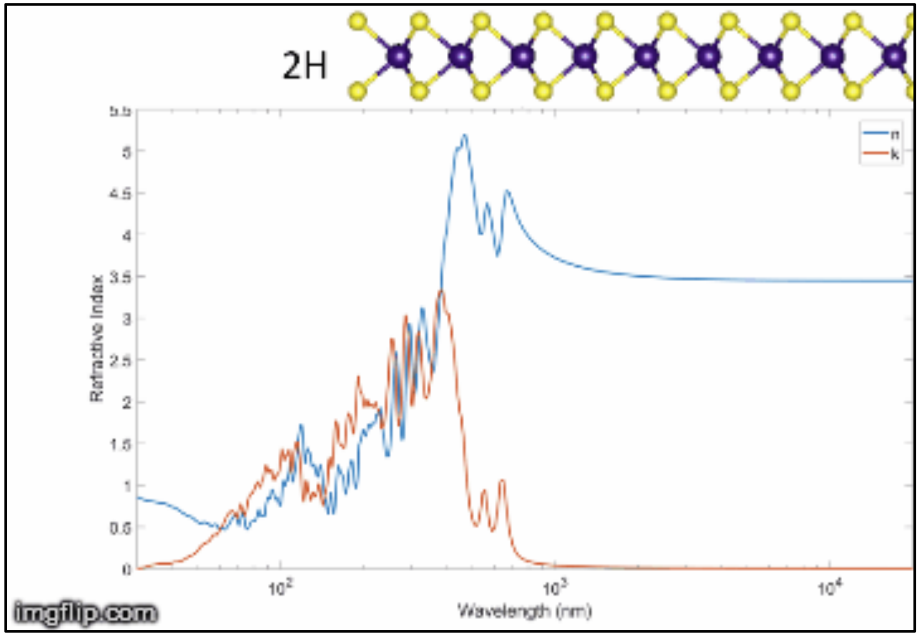


Designing for reliability

- Established phase-change materials suffer from fatigue
  - *e.g.* order-disorder transition in GST
- Design martensitic (order-order) phase transformations for switching light
  - Fast: Timescale of lattice vibrations (ps)
  - Low fatigue: Coherent ("military") atomic motion
  - TMDs: Slip motion of chalcogen planes

GeTe phase-change atomic structure



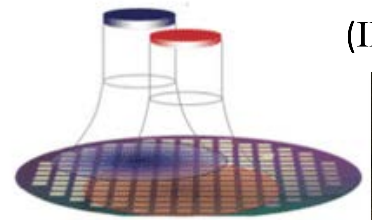


Kolobov, A. V. *et al.* Nat. Chem. **3**, 311-316 (2011).

Work in progress

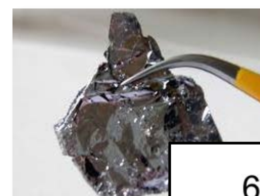
- Make TMD alloy films, guided by theory
  - Metals deposition for well-controlled composition
  - Wafer-scale processes
- Physical property measurements
  - First (*??*) focused study on sub-band gap, IR optical properties of TMDs
- Phase-change measurements
  - IR reflectivity read-out
  - Stimuli: Thermal, optical, electrochemical, mechanical

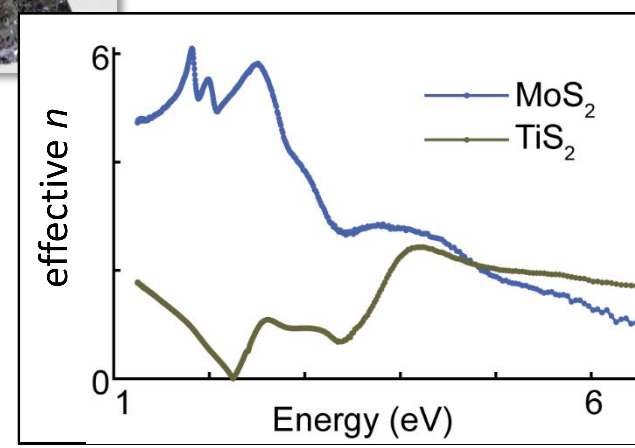
(I) *Combinatorial sputtering*



(II) *Sulfurization/selenization*

Measuring bulk reference crystals

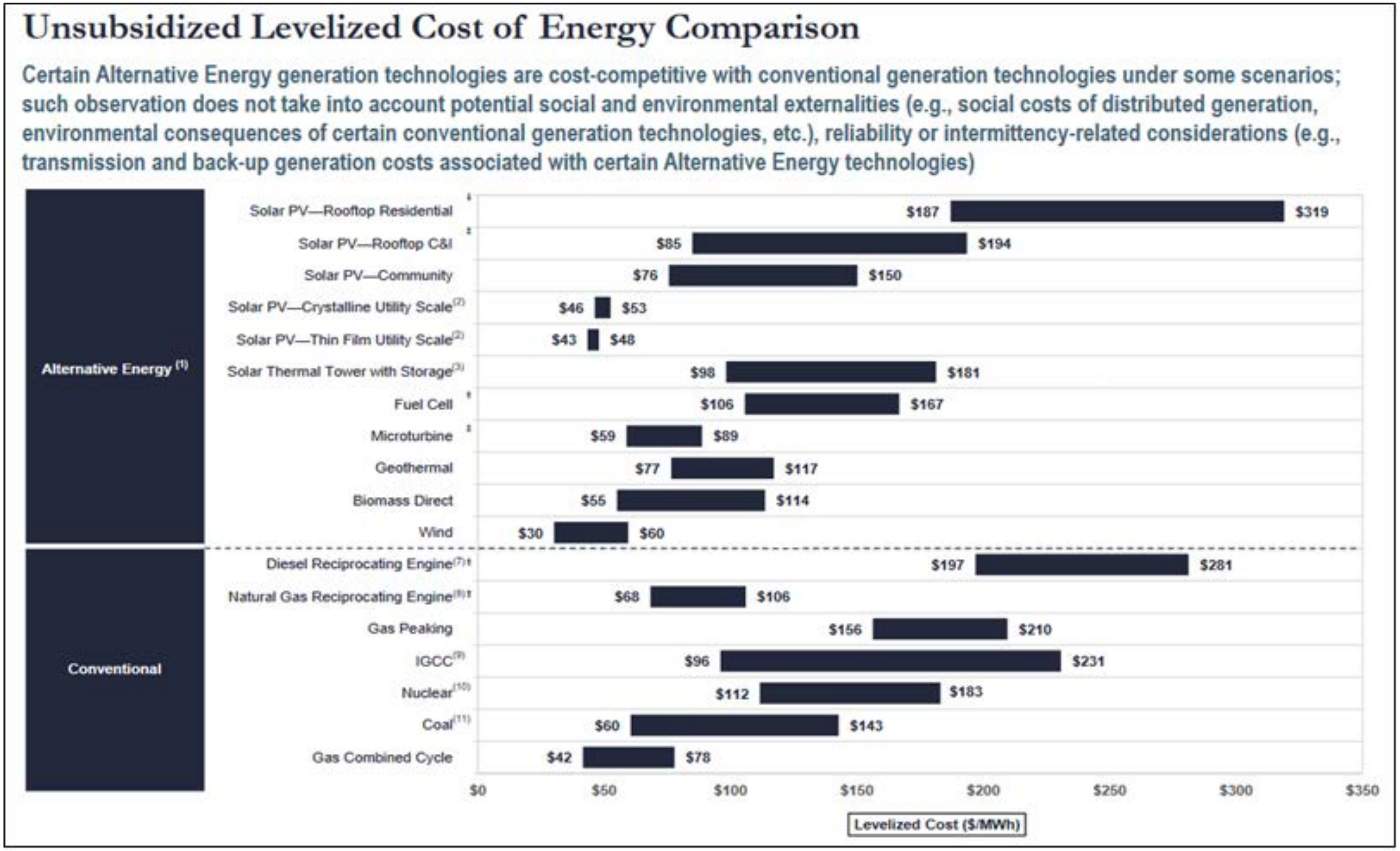




New materials for photovoltaics

Motivation for solar photovoltaic (PV) R&D

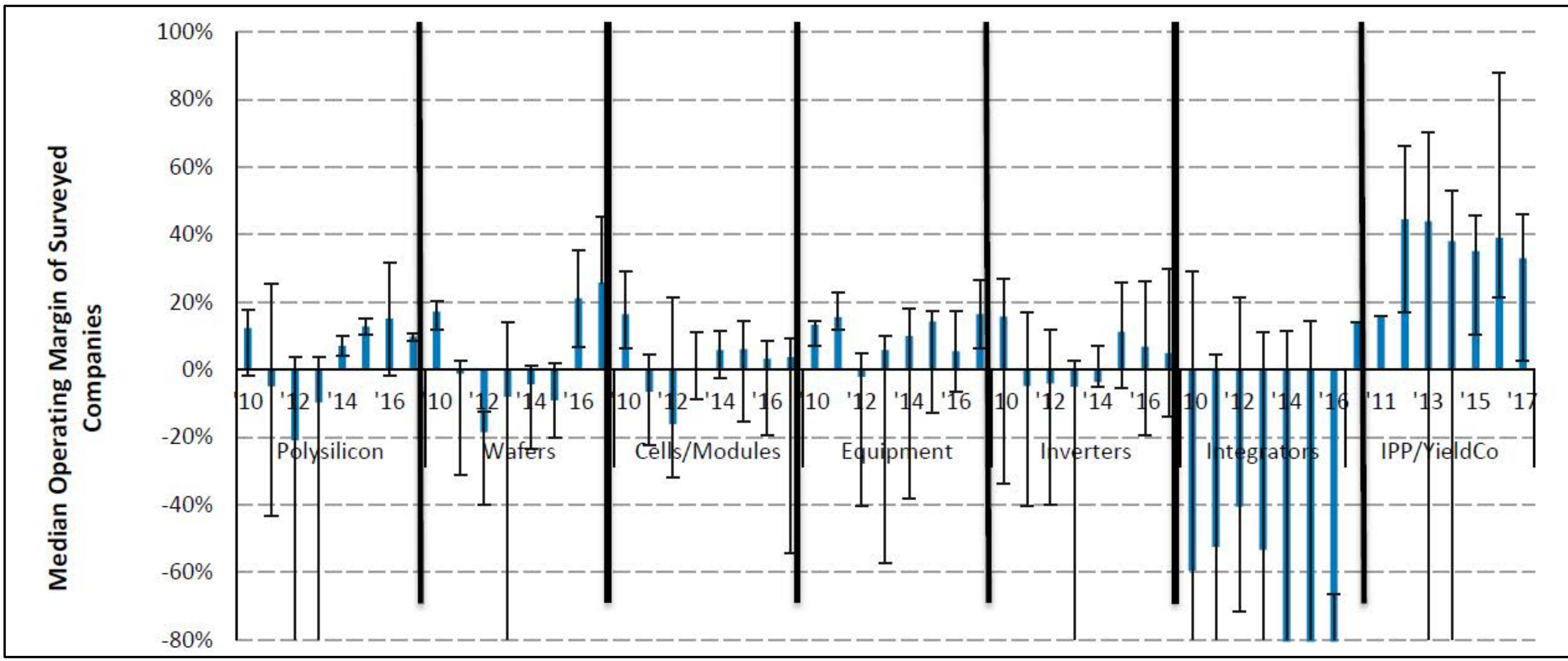
PV is market-competitive



Lazard's Levelized Cost of Electricity Analysis - Version 11.0. (2017).

Motivation for solar photovoltaic (PV) R&D

PV is market-competitive
but margins are low
and volatile

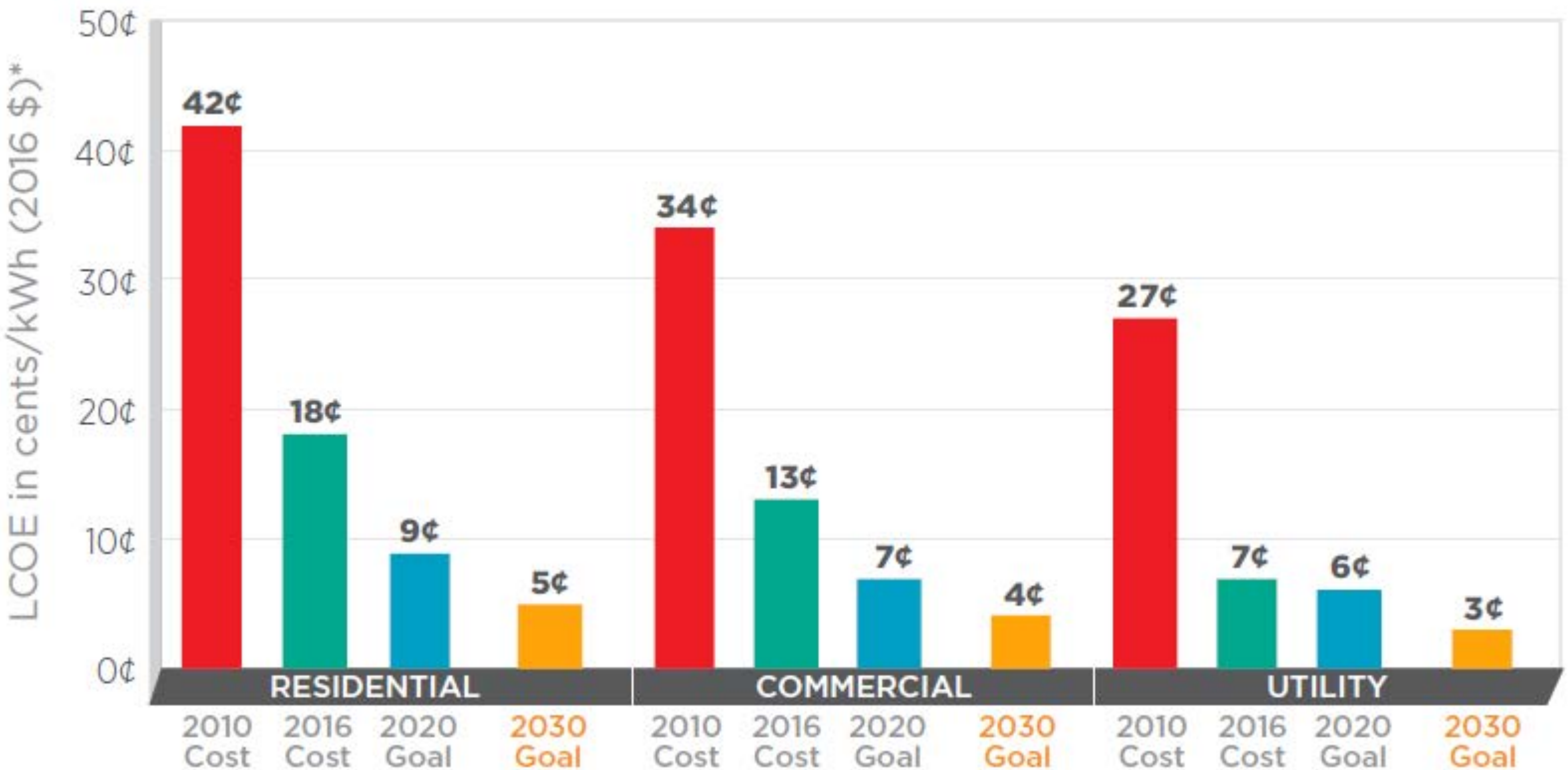


Feldman, D., Hoskins, J. & Margolis, R. *Q4 2017/Q1 2018 Solar Industry Update*. (National Renewable Energy Laboratory, 2018).

Motivation for solar photovoltaic (PV) R&D

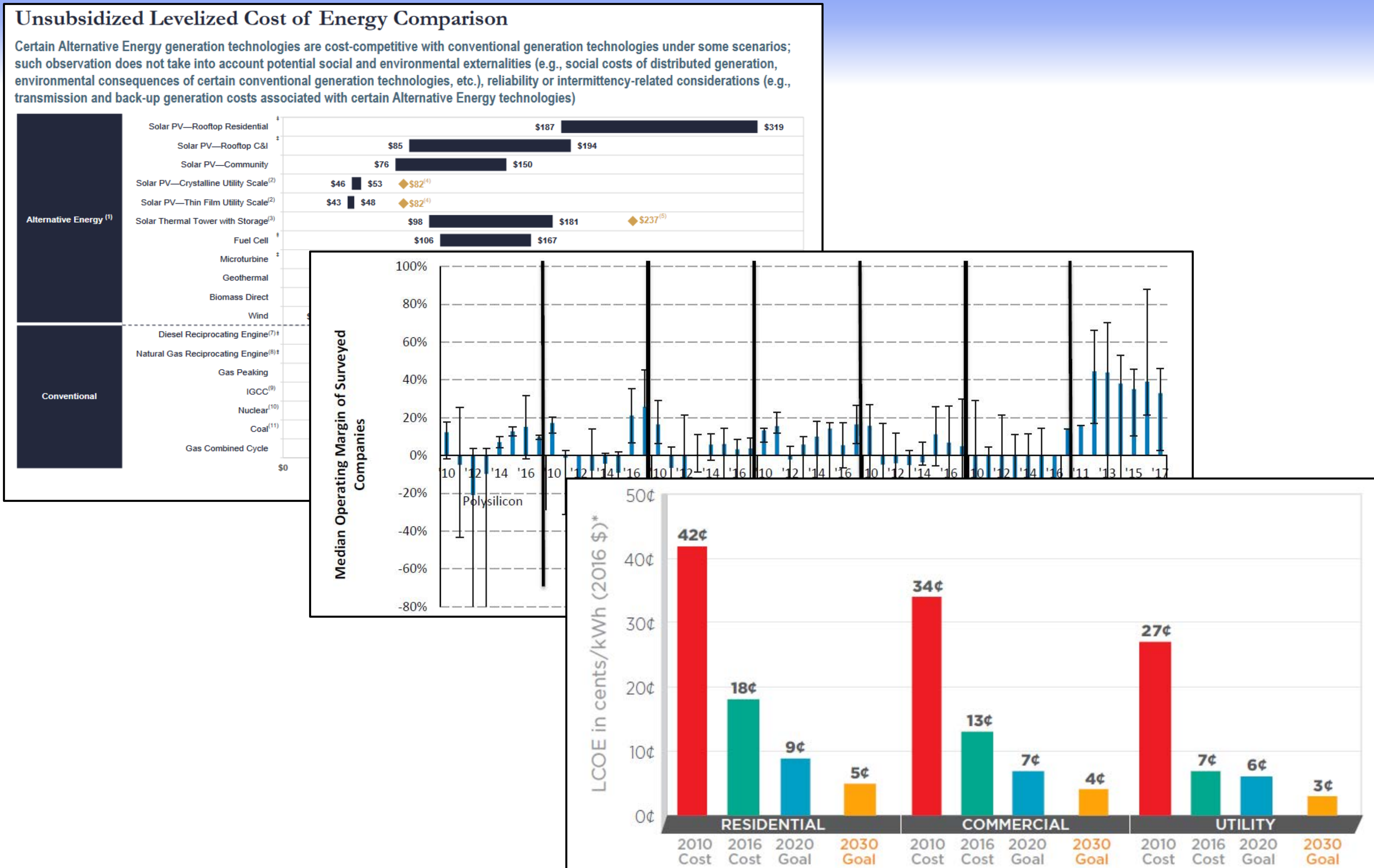
PV is market-competitive

but margins are low and volatile *and* continued explosive growth needs further cost reductions

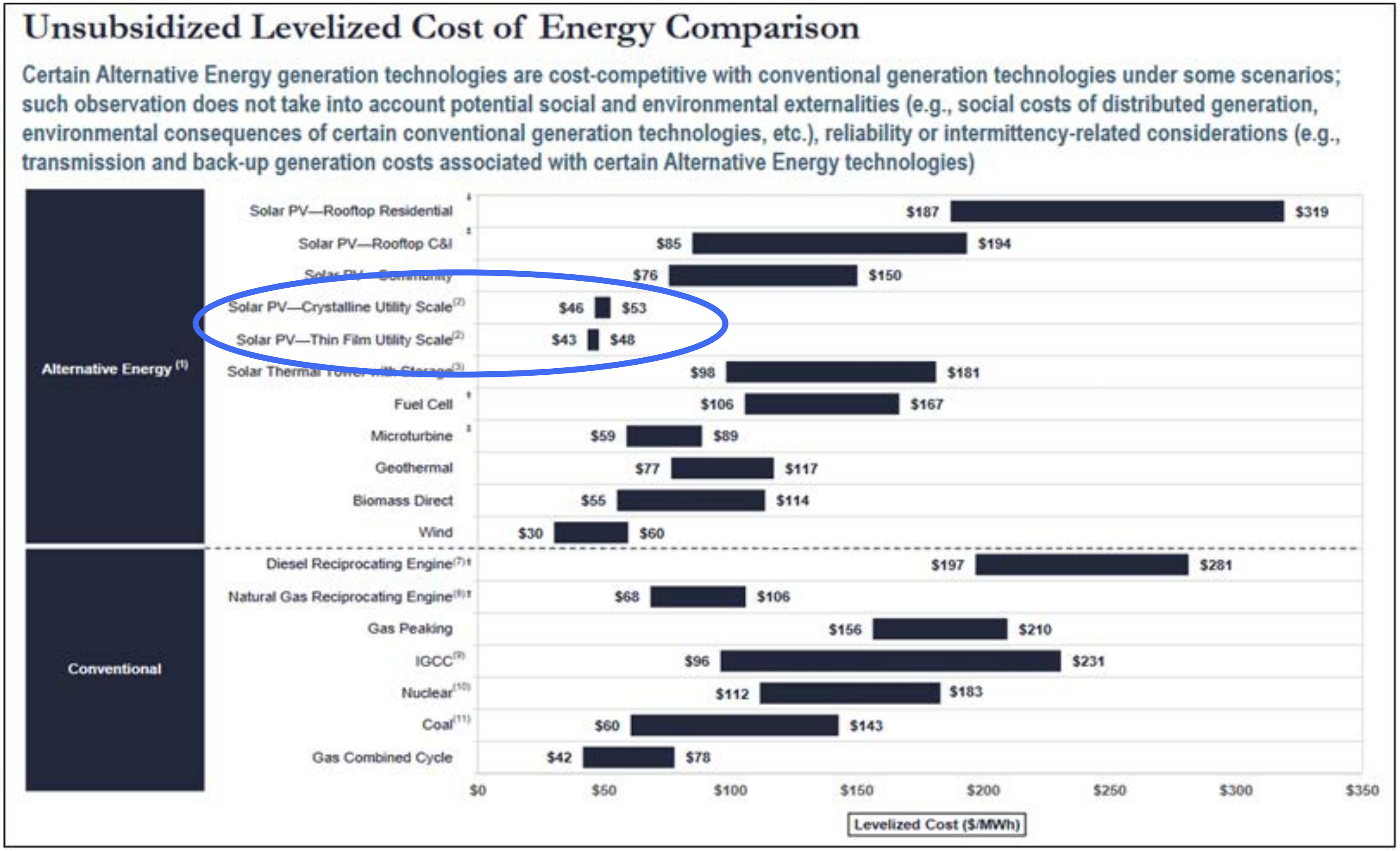


SunShot 2030, U.S. Department of Energy, DOE/EE-1501 (2016)

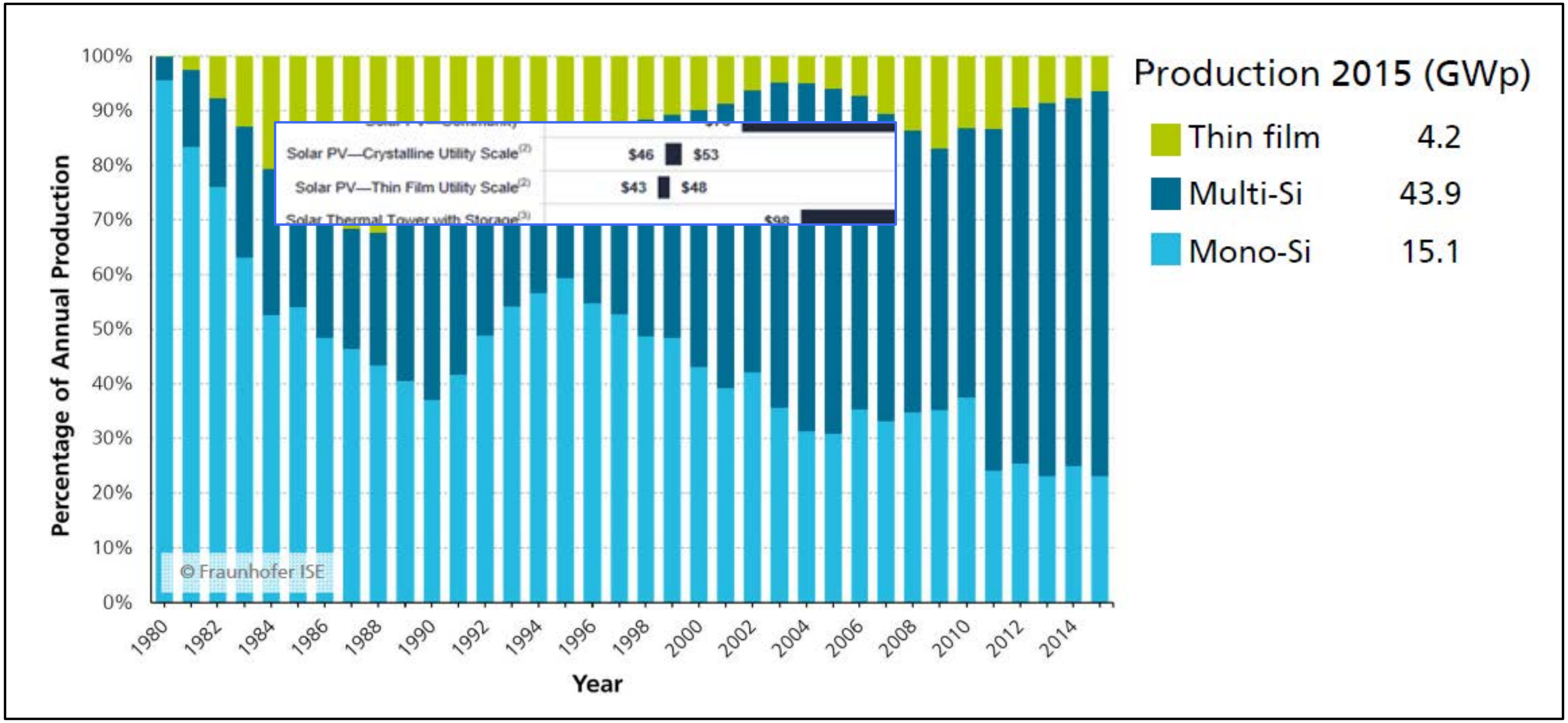
Motivation for solar photovoltaic (PV) R&D



PV technology platforms



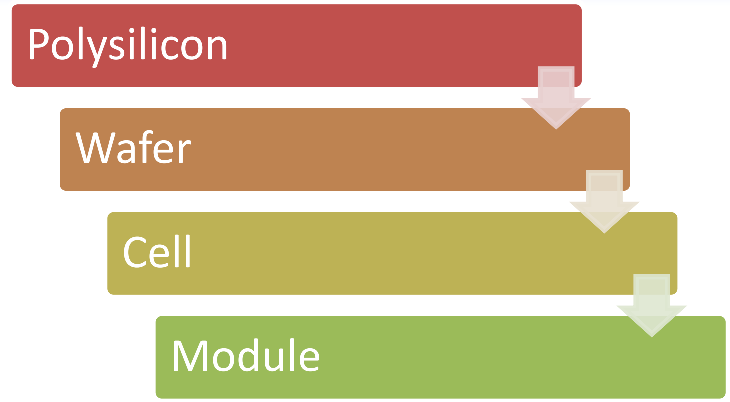
PV technology platforms



Photovoltaics Report, Franhoufer ISE, November 2016.

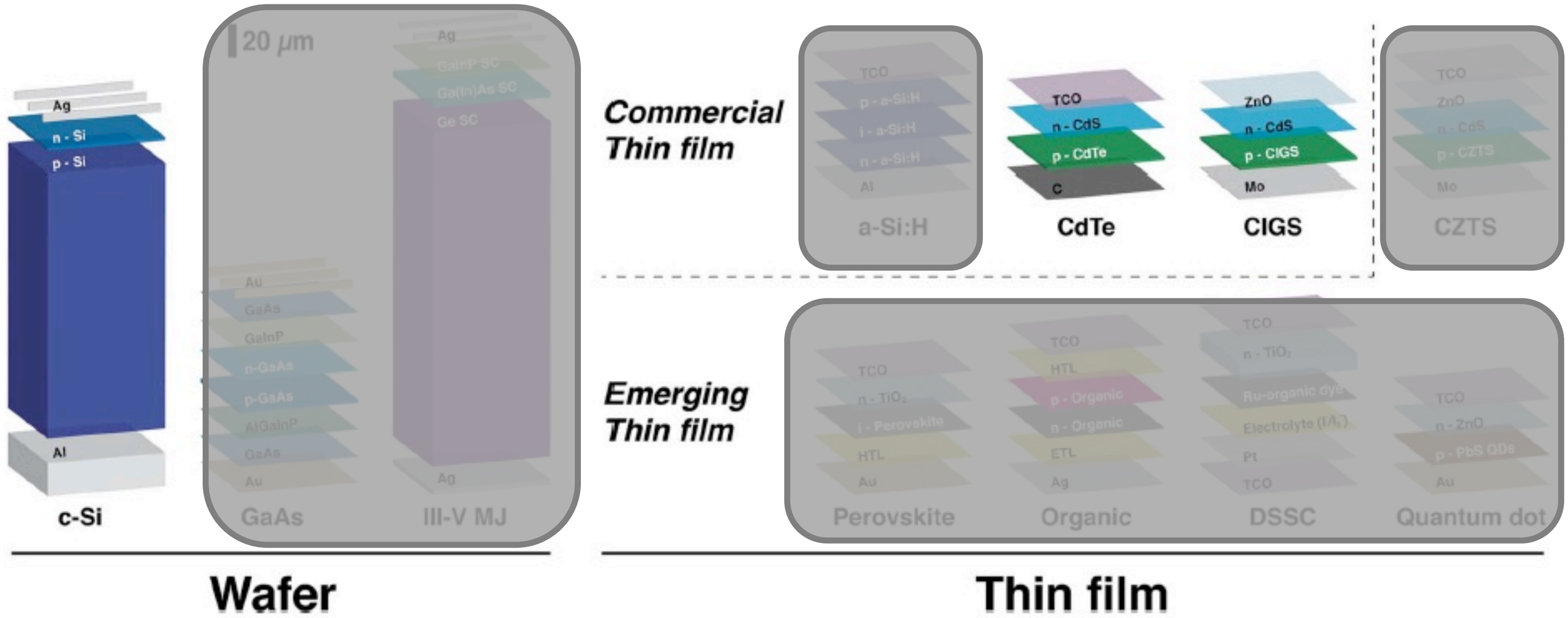
PV technology platforms

- c-Si technologies
  - Mature and reliable
  - Segmented and energy-intensive manufacturing
- Thin film (TF) technologies
  - Significant manufacturing advantages
  - Enable low balance-of-systems (BOS) costs
  - Lag c-Si in performance and reliability

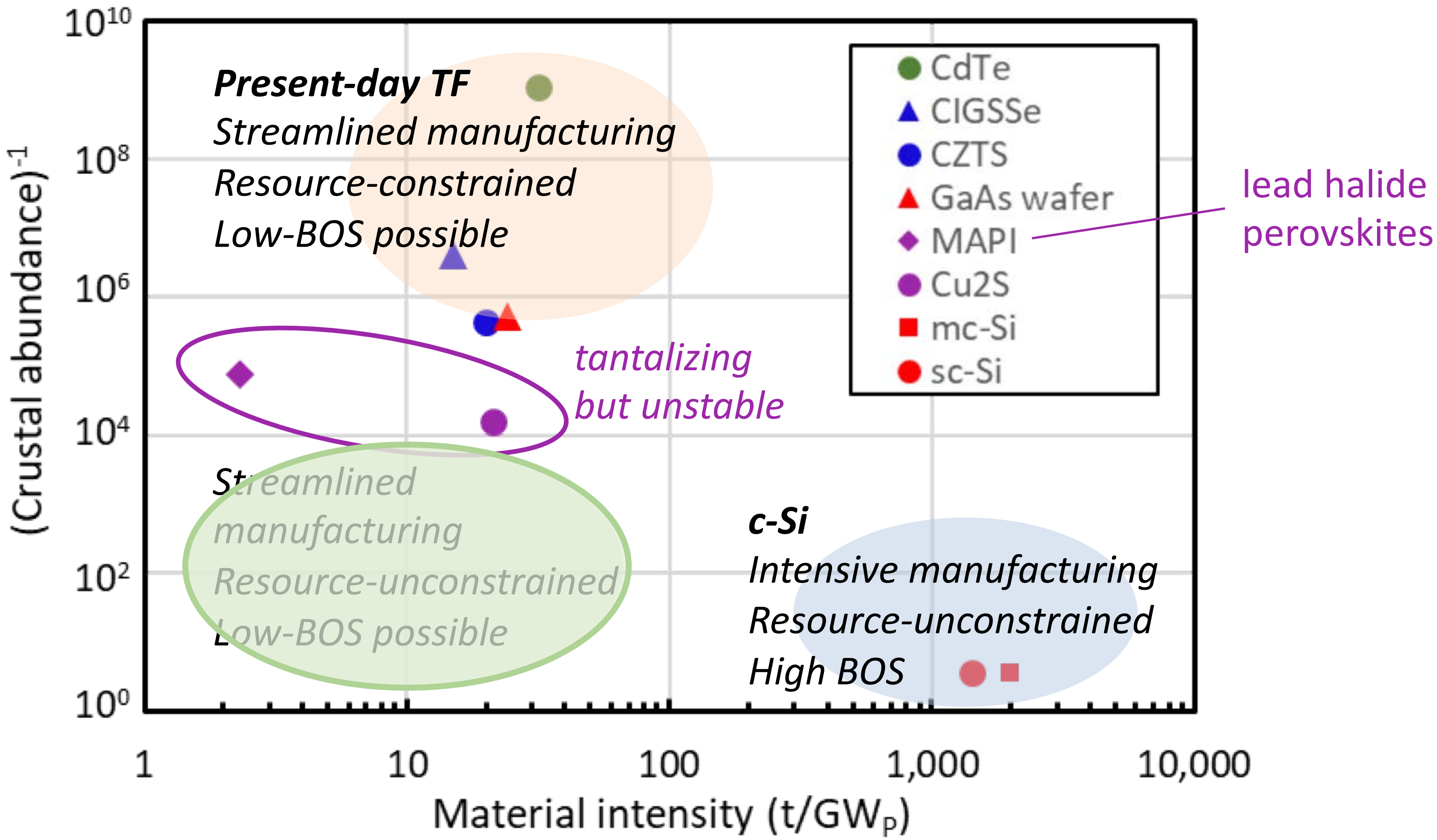


CdTe TF technology
280 MWp/yr factory
First Solar, Ohio (2017)

PV technology platforms



The limits of present-day materials



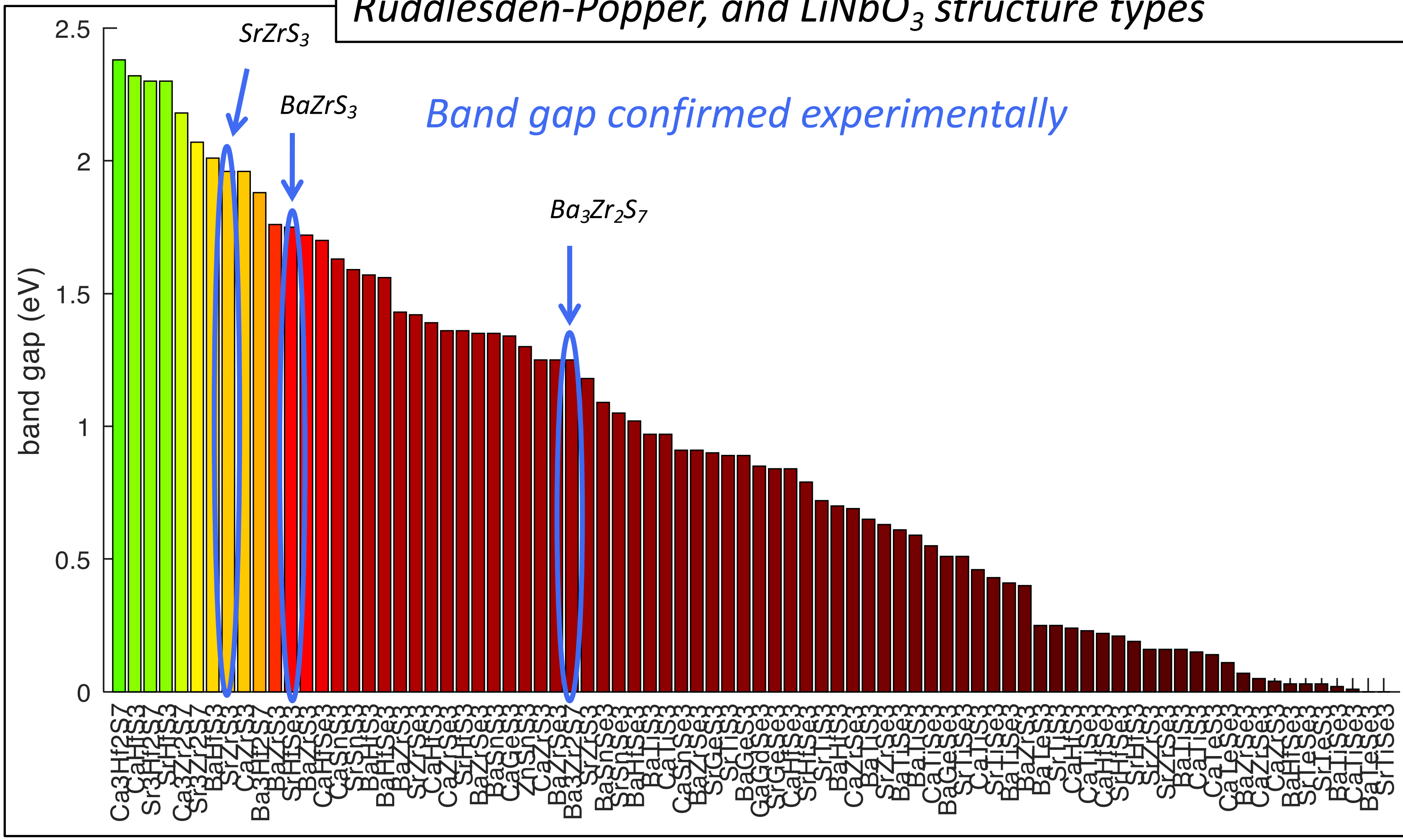
New photovoltaic materials by design

- Chemical intuition inspires theoretical screening of materials that
  - Share structure with high-performing materials (*i.e.* lead halides)
  - Have appropriate band gap
  - Contain non-toxic, abundant elements

Chalcogenide perovskites

New photovoltaic materials by design

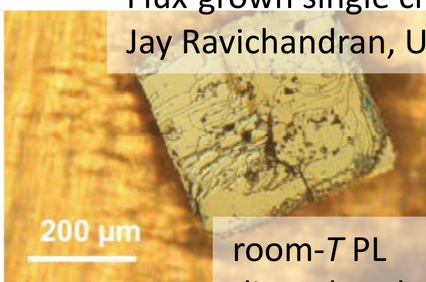
Theoretically-predicted sulfides and selenides in perovskite, Ruddlesden-Popper, and $LiNbO_3$ structure types



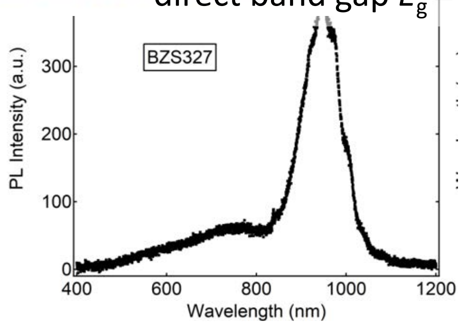
Progress update and outlook

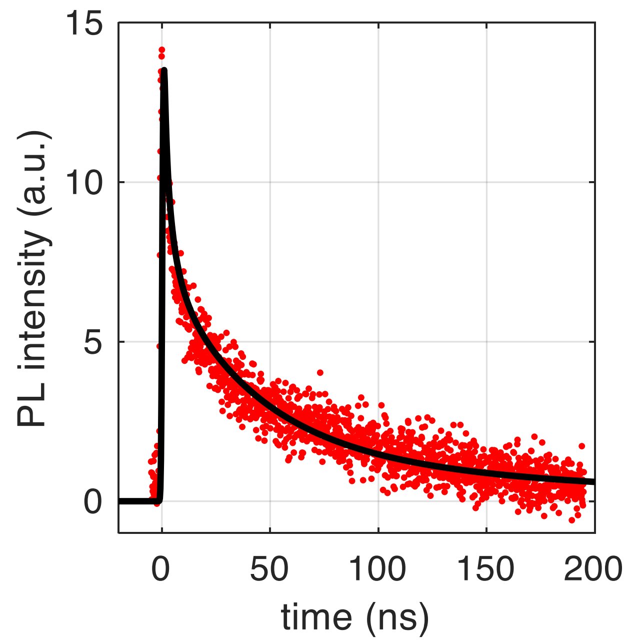
- Studies on bulk & single crystal samples show extremely promising minority carrier lifetime
  - An essential and challenging material metric for PV
- Materials are extremely stable

Flux-grown single crystals
Jay Ravichandran, USC



room-*T* PL
direct band gap E_g = 1.3 eV



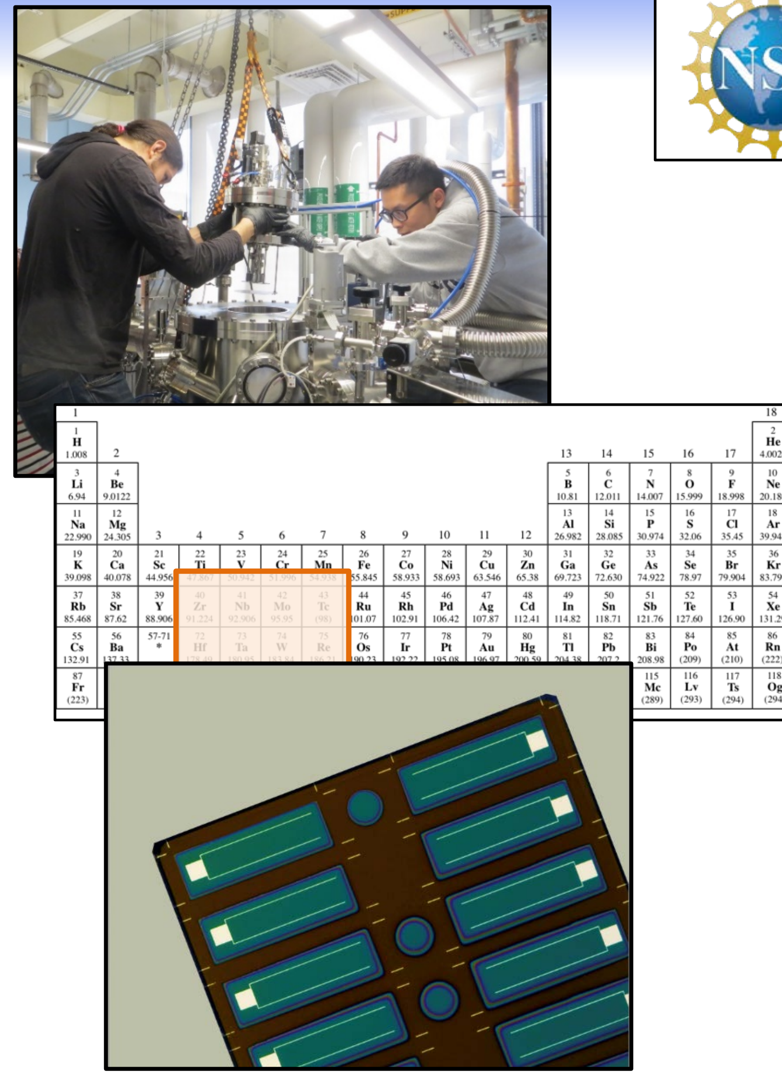


Band-to-band TRPL. Generation-diffusion-recombination model features a bulk minority carrier lifetime τ_0 **= 500 ns**, and SRV ***S*** **= 100 cm/s**.

Niu *et al*., Chem. Mater. **30**, 4882 (2018)

Progress update and outlook

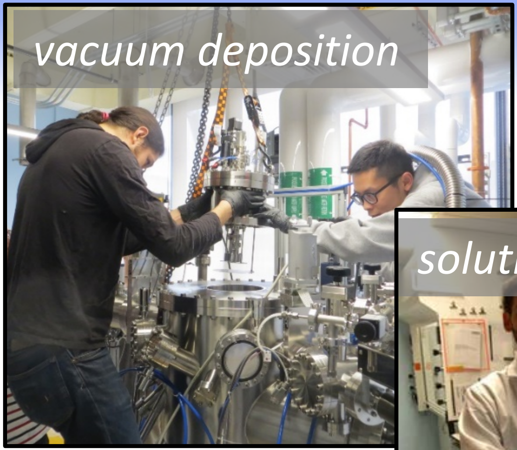
- Making first-of-a-kind chalcogenide perovskite thin films
  - NSF CAREER, 2018-
- Materials processing challenges
  - Sulfurization of refractory metals (*e.g.* Zr)
- Photovoltaics research
  - Looking for support to make & test PV test devices

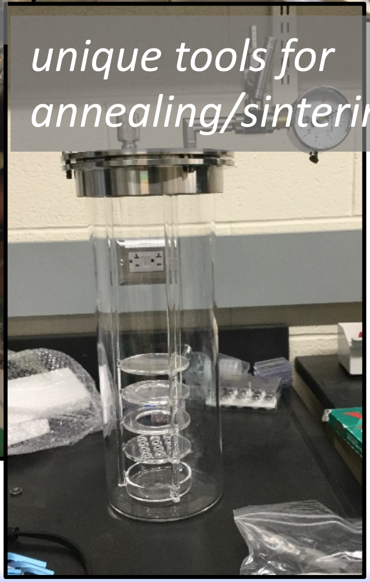


Spotlight on chalcogenide materials processing

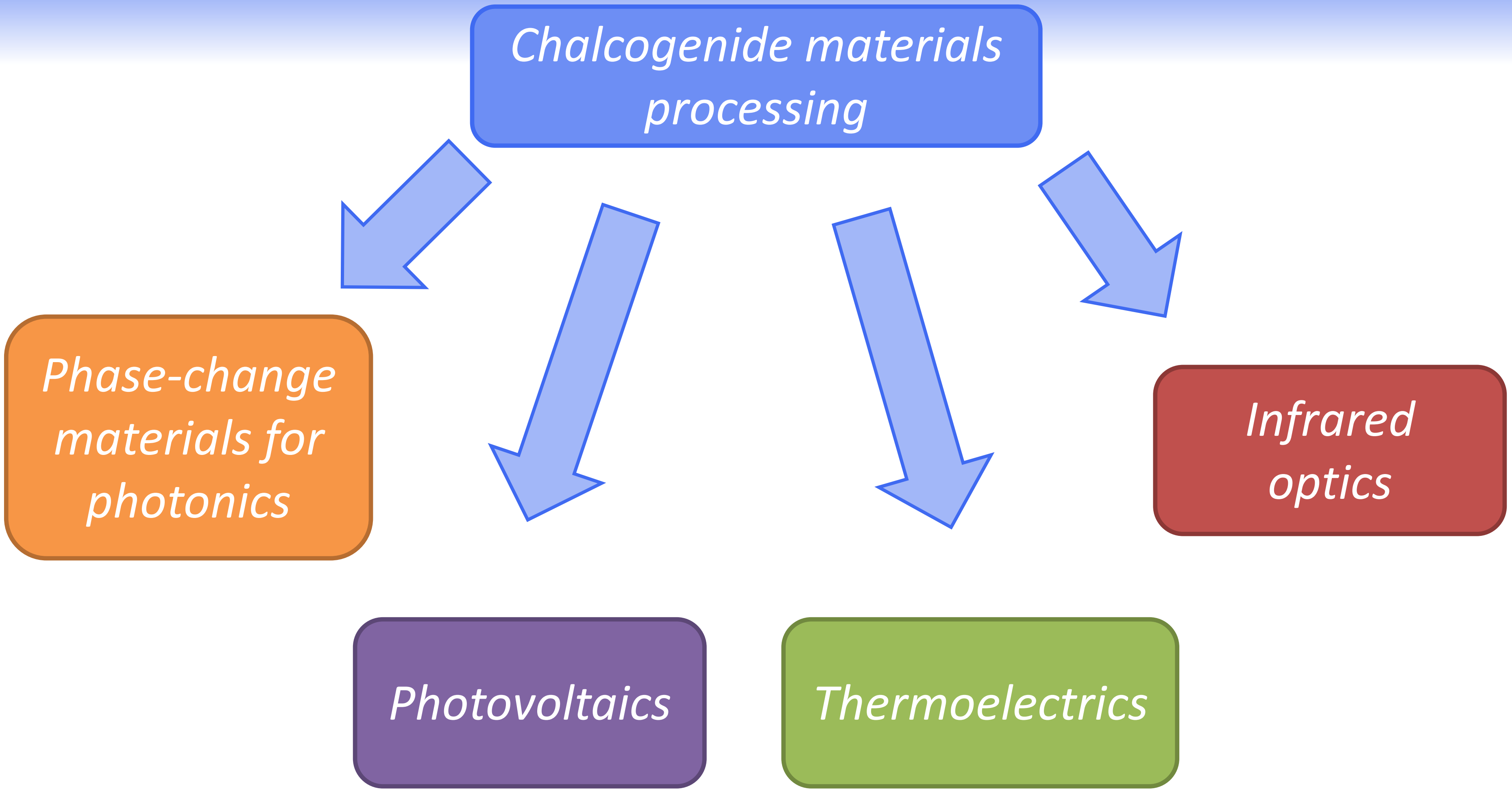
A less-common core competency

- Phase and defect control is essential to enable electronic devices
- Less-mature for sulfides & selenides than for oxides
  - Processing equipment challenges
  - *Stinky ceramics*
- Capabilities at MIT
  - Thin film processing (CVD, MBE, PVD, CBD)
  - Bulk materials processing (sintering, annealing)





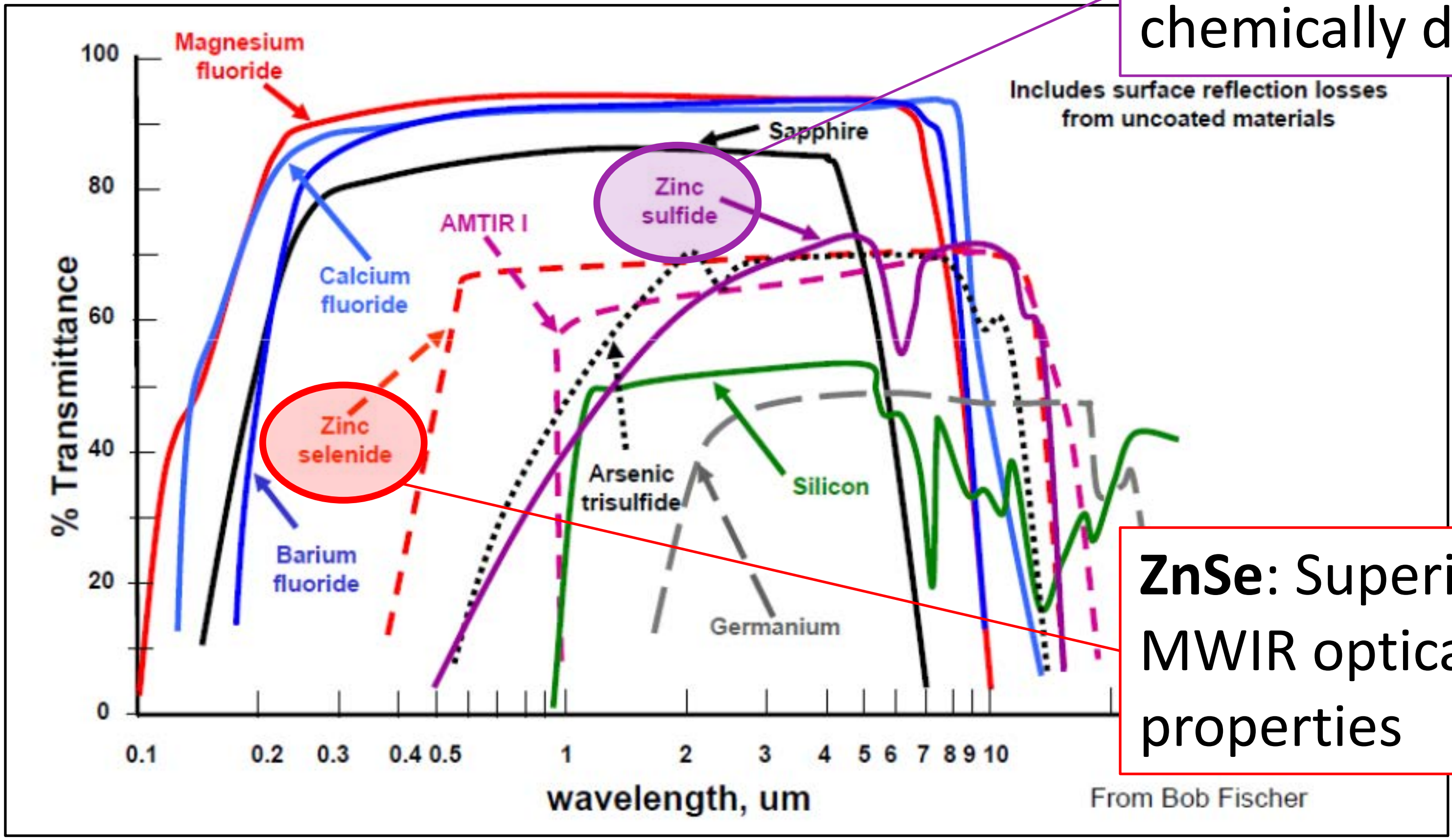
Application areas



Spotlight on: Infrared optics

- ZnS coatings for durable IR optics

ZnS: Mechanically & chemically durable

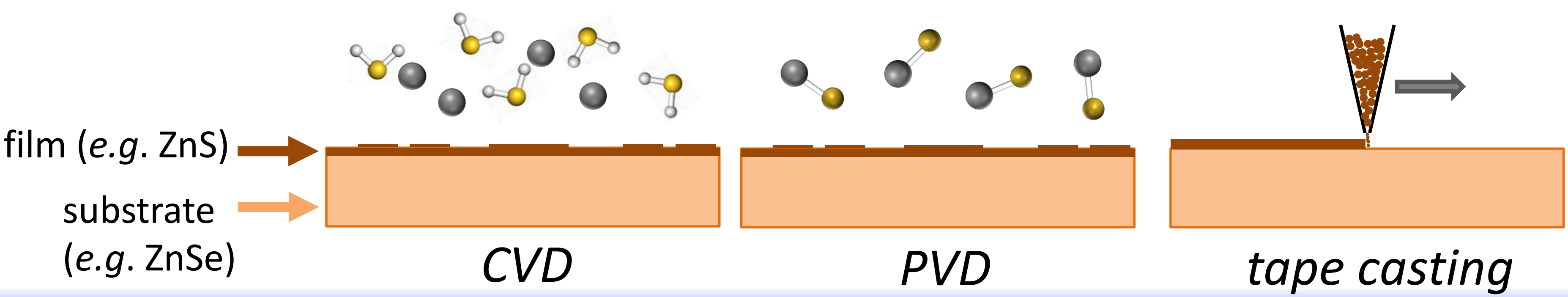


ZnSe: Superior MWIR optical properties

Bob Fischer and Melanie Saayman, University of Arizona

Chalcogenide film coating: Better, faster, cheaper

- *Present-day*: ZnS coatings for IR optics made by chemical vapor deposition (CVD)
  - Slow, expensive, limited availability (*e.g.* Tuftran, by DOW)
- *Traditional alternative*: Physical vapor deposition (PVD)
  - Slow, uncertain quality
- *Proposed alternative*: Tape-casting
  - Fast, inexpensive, provides design flexibility
  - Enabled by advances in nanoparticle and chalcogenide processing capabilities
  - Looking for support to develop this solution



Acknowledgments

Jaramillo research group

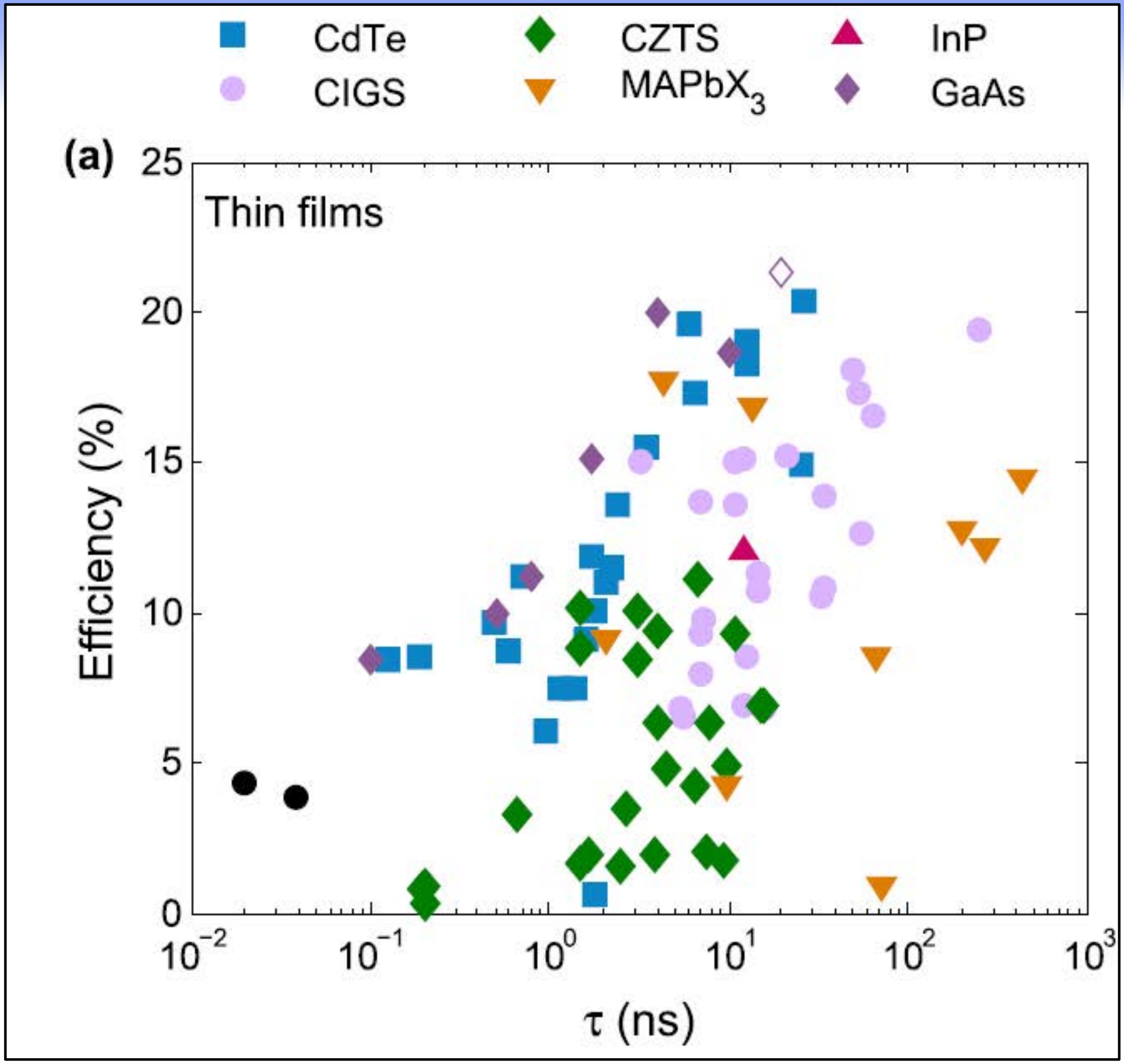
Office of Naval Research
ONR
Science & Technology
USN

NSF

MIT
Skoltech
Program

Thank you for your attention!

Minority carrier lifetime and PV



Jaramillo *et al.*, J. Appl. Phys. **119**, 035101 (2016)