



Development of HVPE-Grown III-V Solar Cells Passivated with AlInP

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PVSC 49 - Philadelphia, PA

Outline

- 1 HVPE Needs AlInP for Low-Cost Potential**

- 2 Challenges of Growing AlInP in HVPE → Solutions**

- 3 Developing AlInP for HVPE Solar Cells**

- 4 Assessing AlInP Passivation → 1J GaAs Solar Cells**

- 5 Implementing AlInP in 2J GaInP/GaAs Solar Cells**

- 6 Progress of HVPE-Grown PV**

- 7 Conclusions & Future Directions**

Low-cost precursors
/high utilization
→ raw material/Wp

→ See Simon *et al.*, *Crystals* 2019
<http://dx.doi.org/10.3390/cryst9010003> for **technoeconomic analysis of production-scale HVPE**

High throughput
→ wafers/h; MW/tool

→ See Simon *et al.*, *Crystals* 2019
<http://dx.doi.org/10.3390/cryst9010003> for **production-scale HVPE concept**

Low-cost substrate
→ reuse via spalling

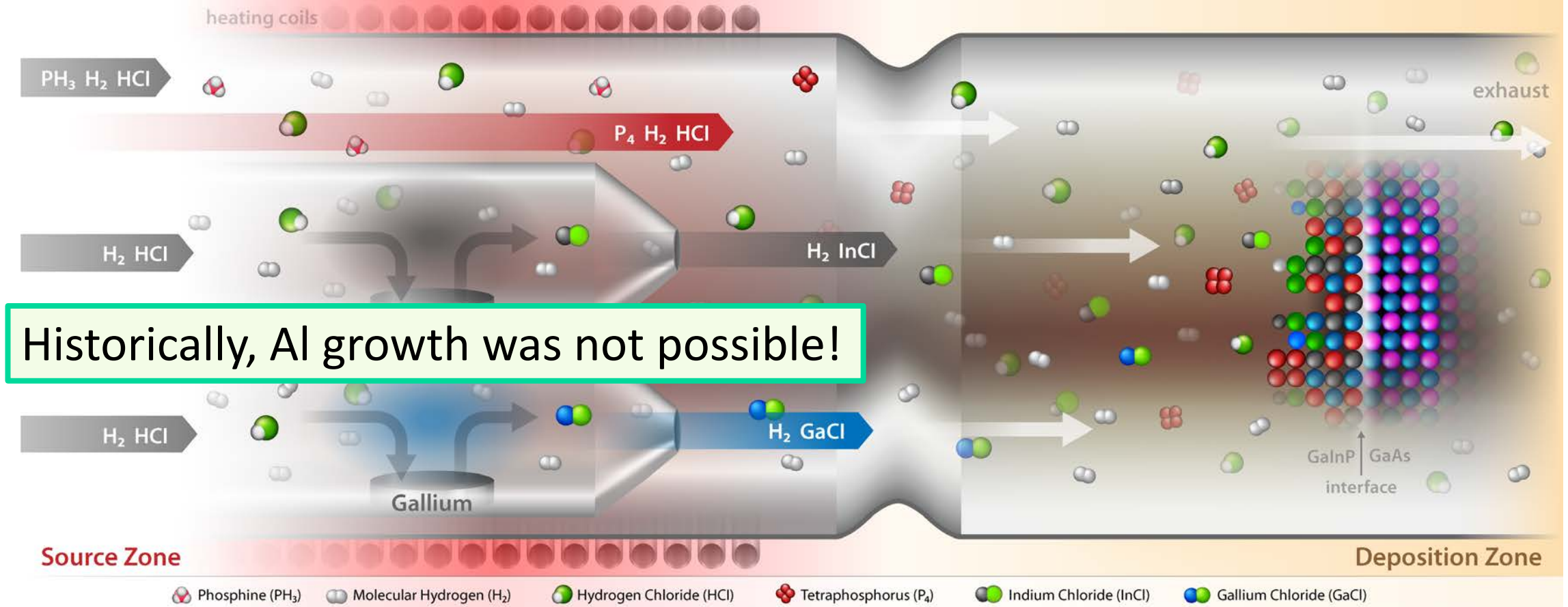
→ See John Mangum – next talk: “High Efficiency solar cells grown on spalled germanium without polishing”
→ See Anna Braun at 9:30a: “Planarizing HVPE growth on GaAs substrates produced by controlled spalling”

Parity efficiency with state-of-the-art
(OMVPE-grown PV)

→ This talk: achieving passivating AlInP removes last barrier(s) to parity efficiencies

What is needed to produce III-V PV at low cost?

→ Hydride Vapor Phase Epitaxy (HVPE) can address these



Historically, Al growth was not possible!

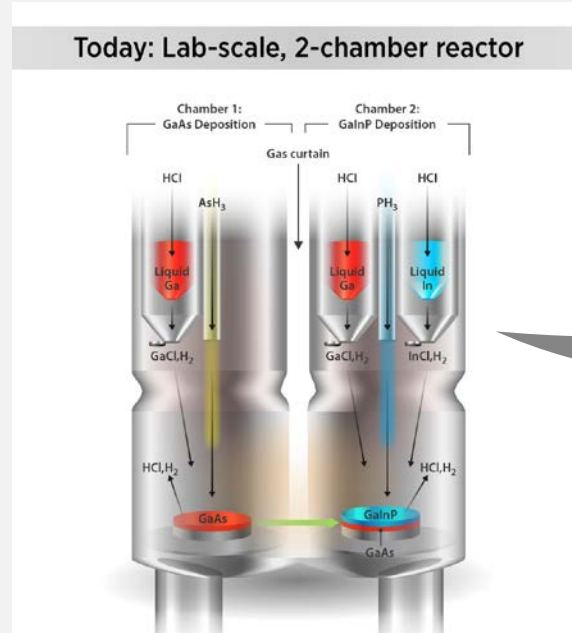
HVPE enables low-cost precursors

- Hot wall, atmospheric pressure epitaxial deposition
- Group V via hydride; Group III transport via chloride
- High precursor utilization (low V/III)
- Low-cost precursors (10x lower cost than organometallics)
- High growth rates (~530 μm/h)*

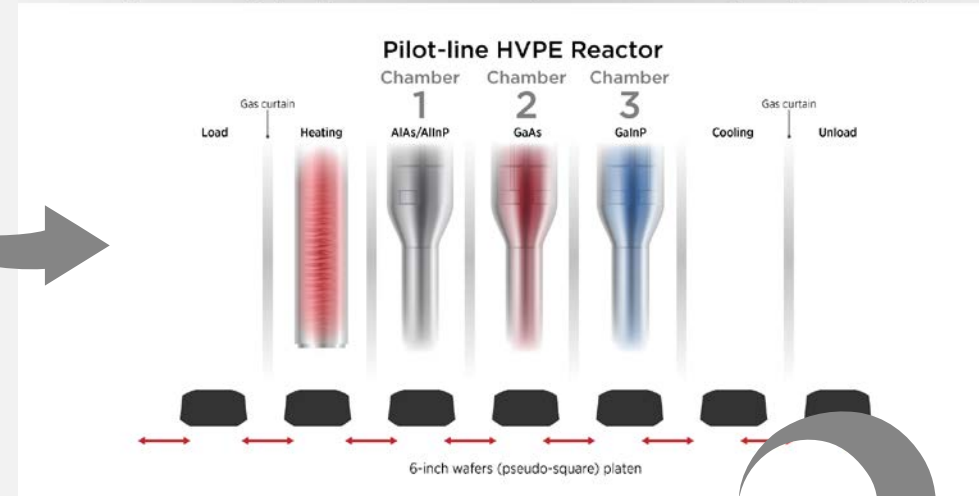
*McClure et al., Appl. Phys. Lett. **116**, 182102 (2020)

Towards High Throughput: Future HVPE reactor scale-up plans

High R_{growth} ($\mu\text{m}'\text{s}/\text{min}!$)
 +
 In-line tool design
 =
 high throughput
 ≈ 70 OMVPE's!



Stage 1: Throughput per tool: 11 wafers/h Production capacity: 250 kW/year

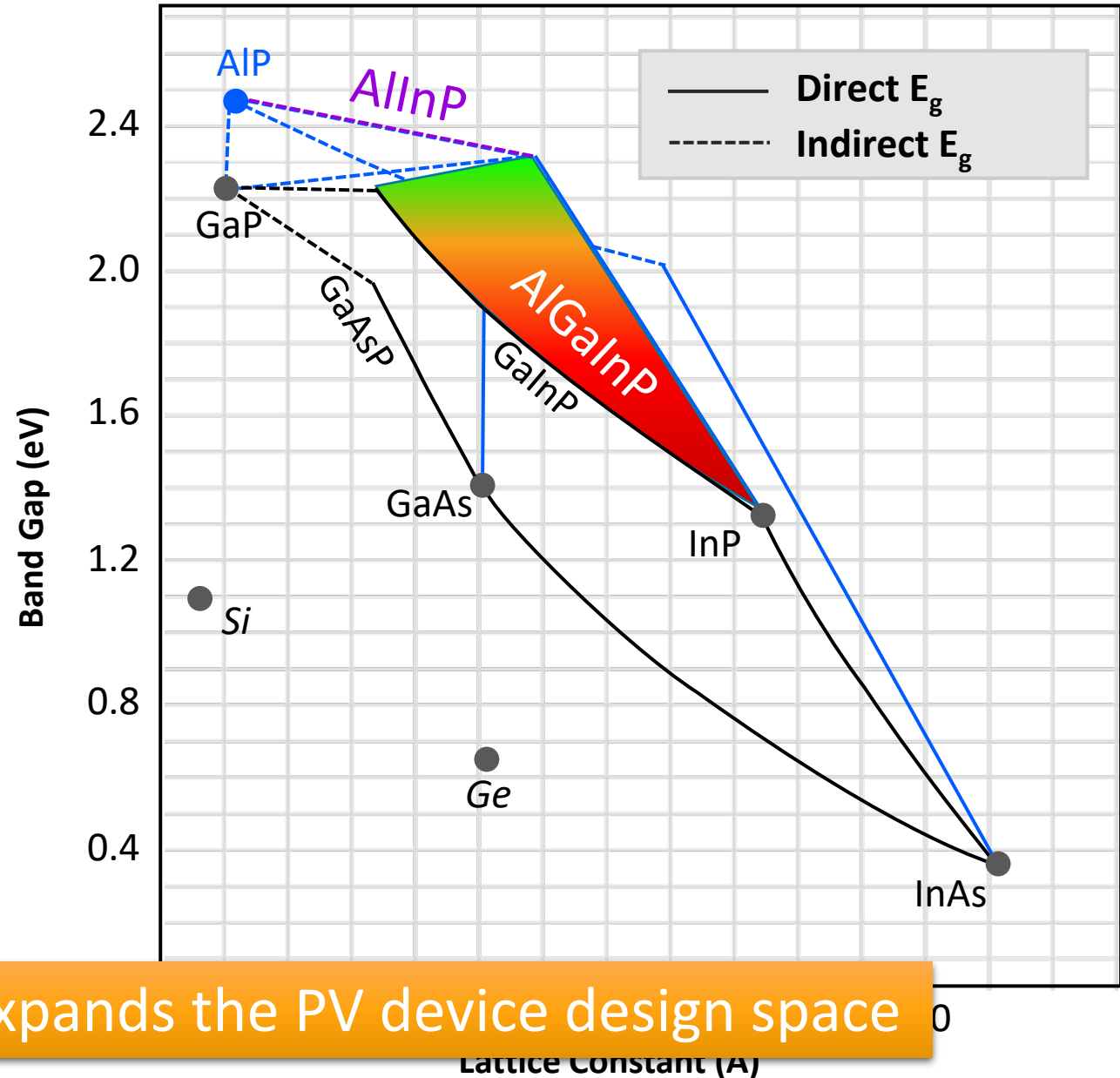


Stage 2: Throughput per tool: 75 wafers/h Production capacity: 2 MW/year



Benefits of Al-containing III-V materials

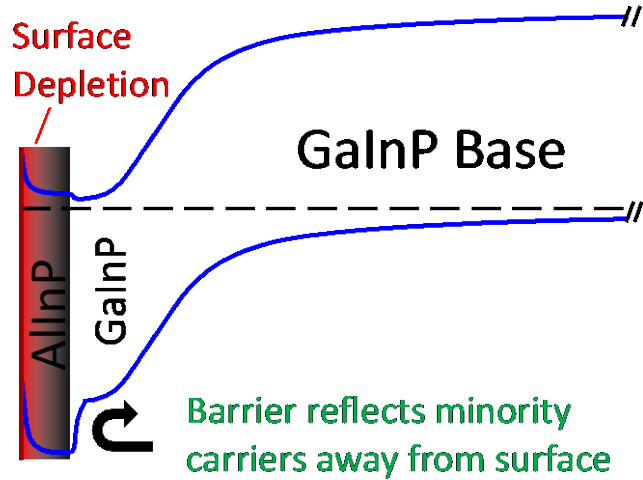
- Al greatly expands III-V As/P material palette
- AlInP enables widest E_G @ GaAs lattice constant
- AlGaInP has large region of tunable direct E_G



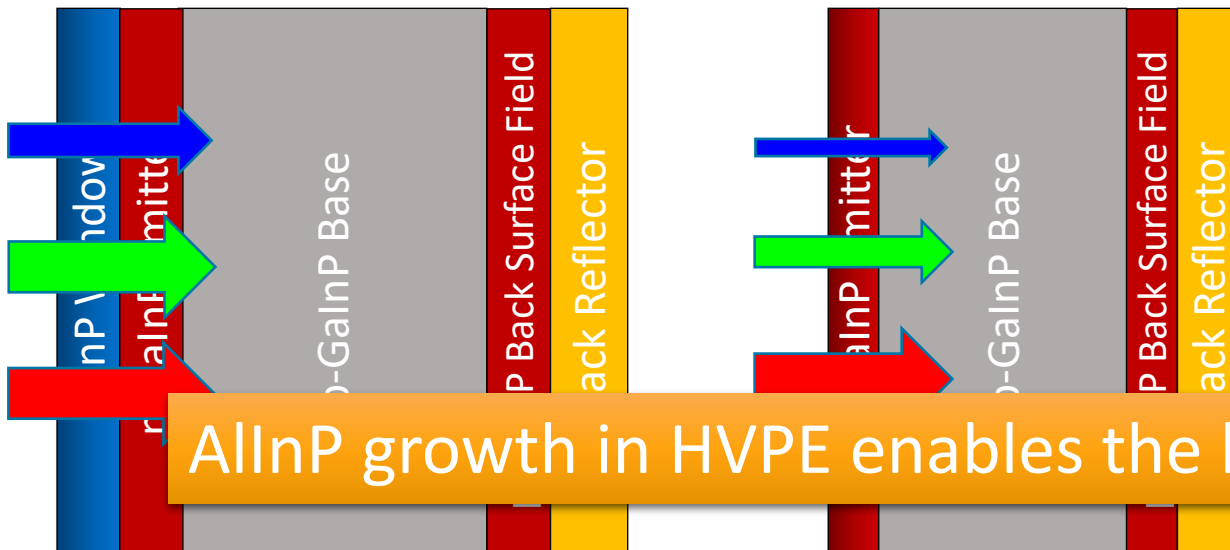
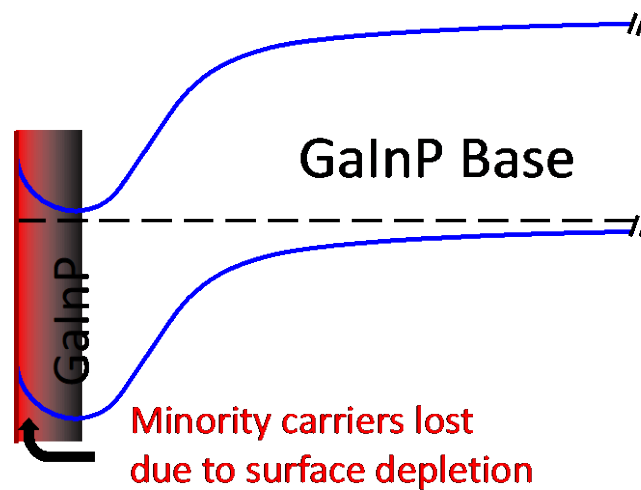
Adding Al to HVPE expands the PV device design space

Need for AlInP – Passivated Solar Cells

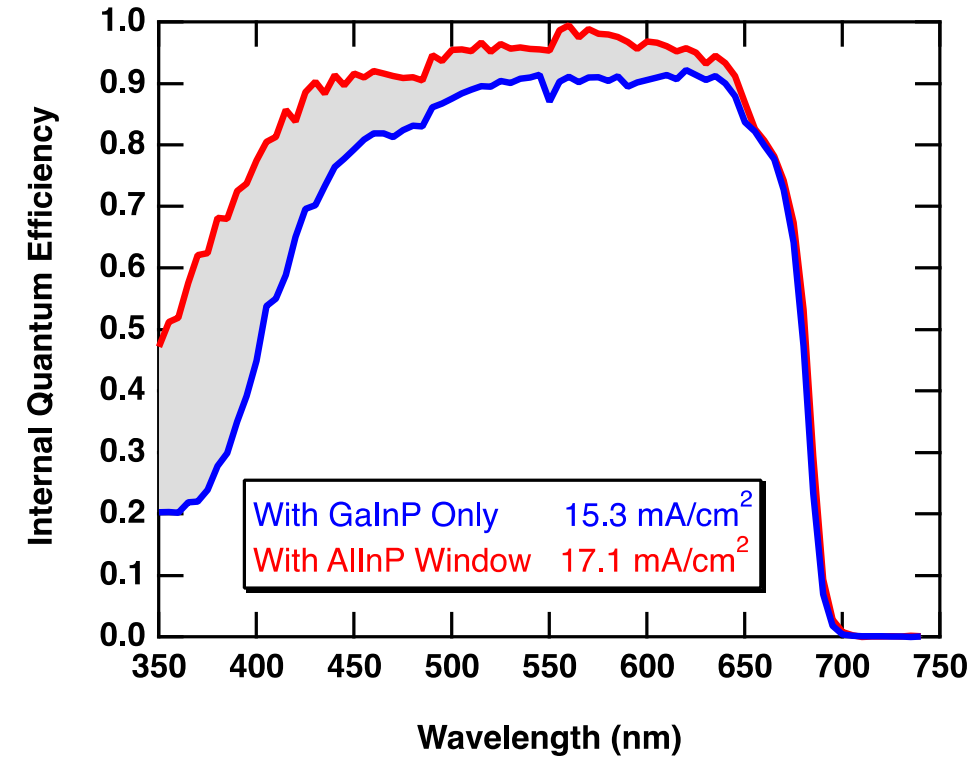
AllnP-passivated



GaInP-'passivated'



OMVPE GaInP Solar Cells



AllnP growth in HVPE enables the highest efficiency potential of PV

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1 Need for AlInP in Hydride Vapor Phase Epitaxy (HVPE)

2 Challenges and Solutions for AlInP growth in HVPE

3 Developing HVPE-AlInP for Solar Cells

4 Assessing Passivation of AlInP in 1J GaAs Solar Cells

5 Implementing AlInP in 2J GaInP/GaAs Solar Cells

6 Progress of HVPE-Grown PV

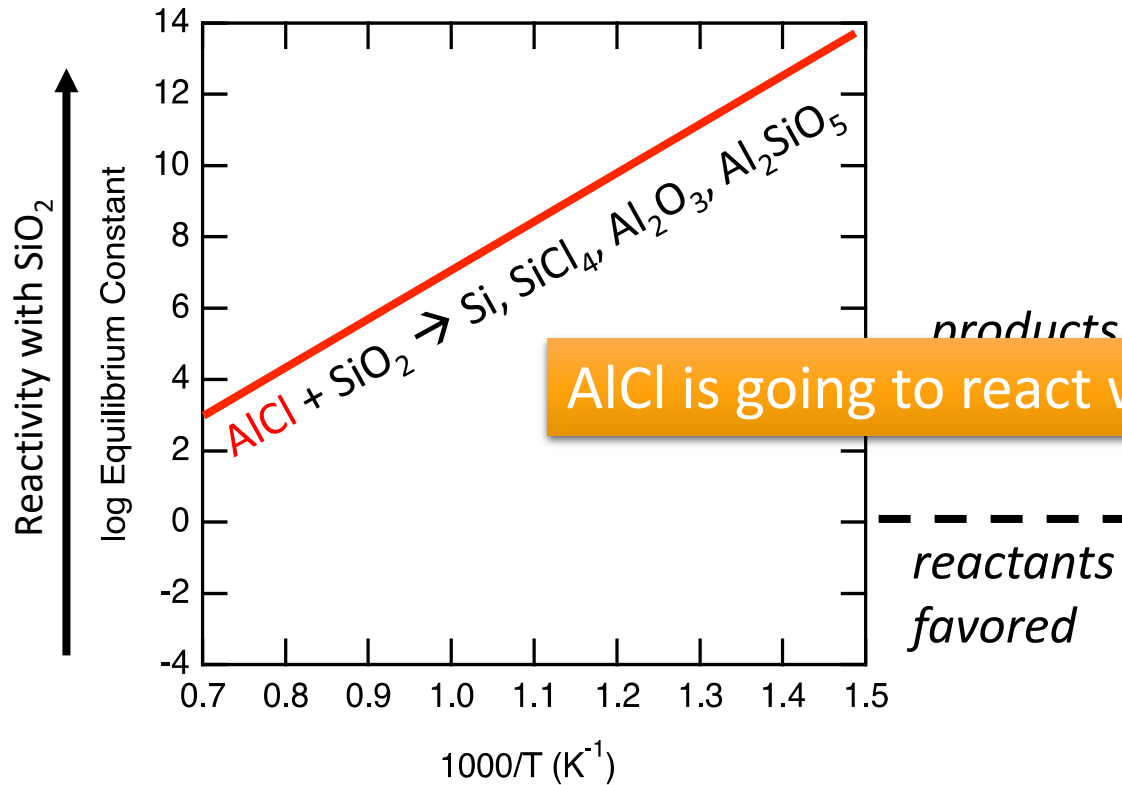
7 Conclusions & Future Directions

Challenge of Growing Al-Containing Materials by D-HVPE

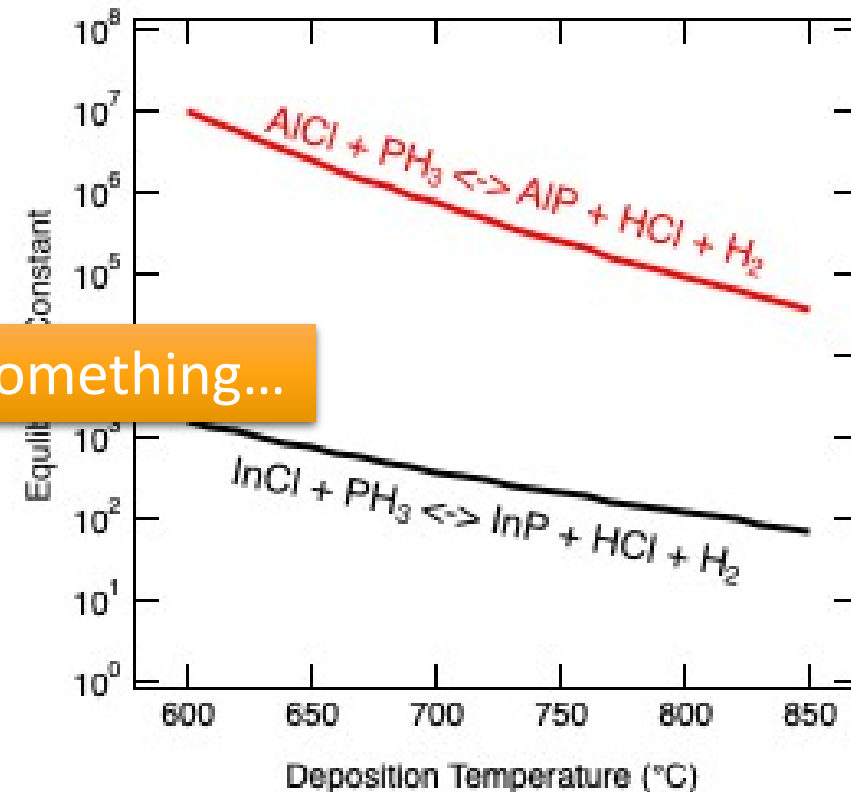
Al(Ga)InP thought to be impossible by HVPE

“Likewise, (HVPE) growth of all Al containing alloys is also **practically impossible** due to the chemistry of the chlorides of Al, the large Al distribution coefficient and the extremely reactive nature of Al chlorides. Thus, it was recognized that AlGaInP alloys would be grown only using either molecular beam epitaxy (MBE) or organometallic vapor phase epitaxial (OMVPE)...”

Yuan and Stringfellow, et al., J. Appl. Phys. **57**, 1380 (1985)



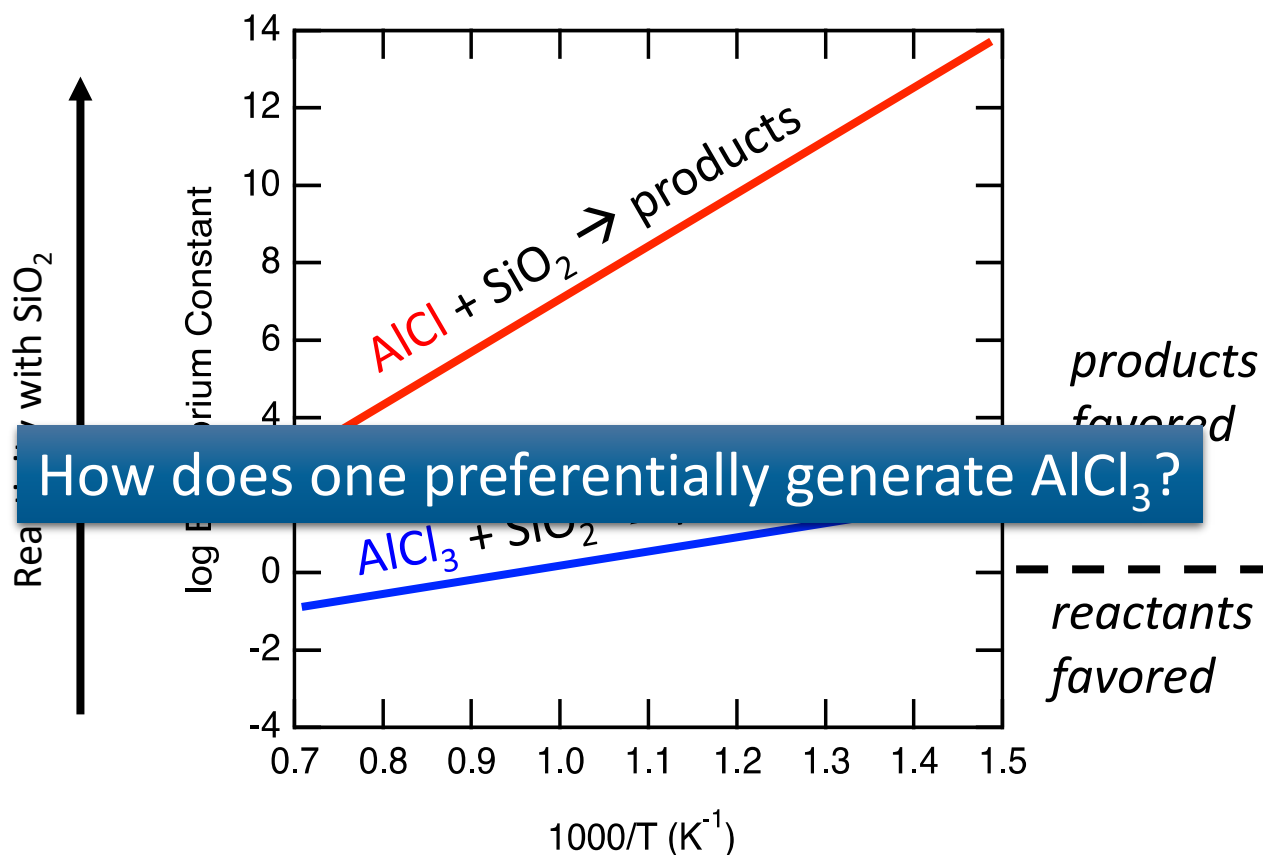
AlCl is going to react with something...



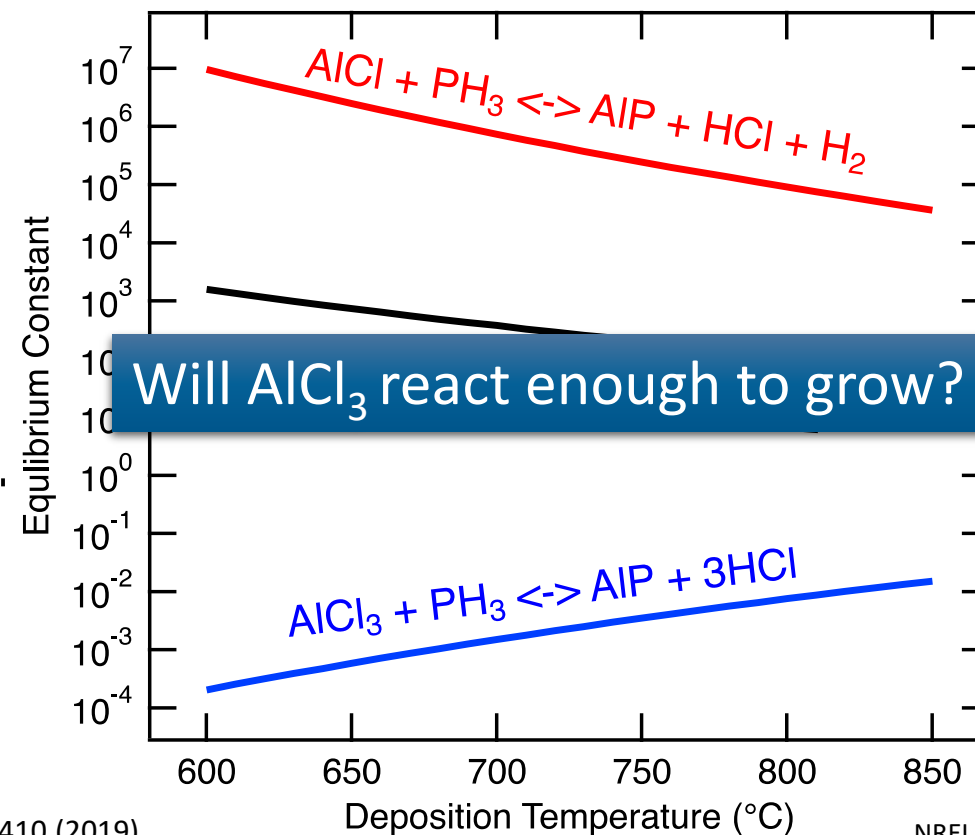
AlCl₃ – A Less Reactive Al Precursor

AlCl₃ - 'good' precursor
→ low reactivity with reactor quartz

AlCl - 'bad' precursor
→ high reactivity with reactor quartz
→ Can contribute to Si and O impurities



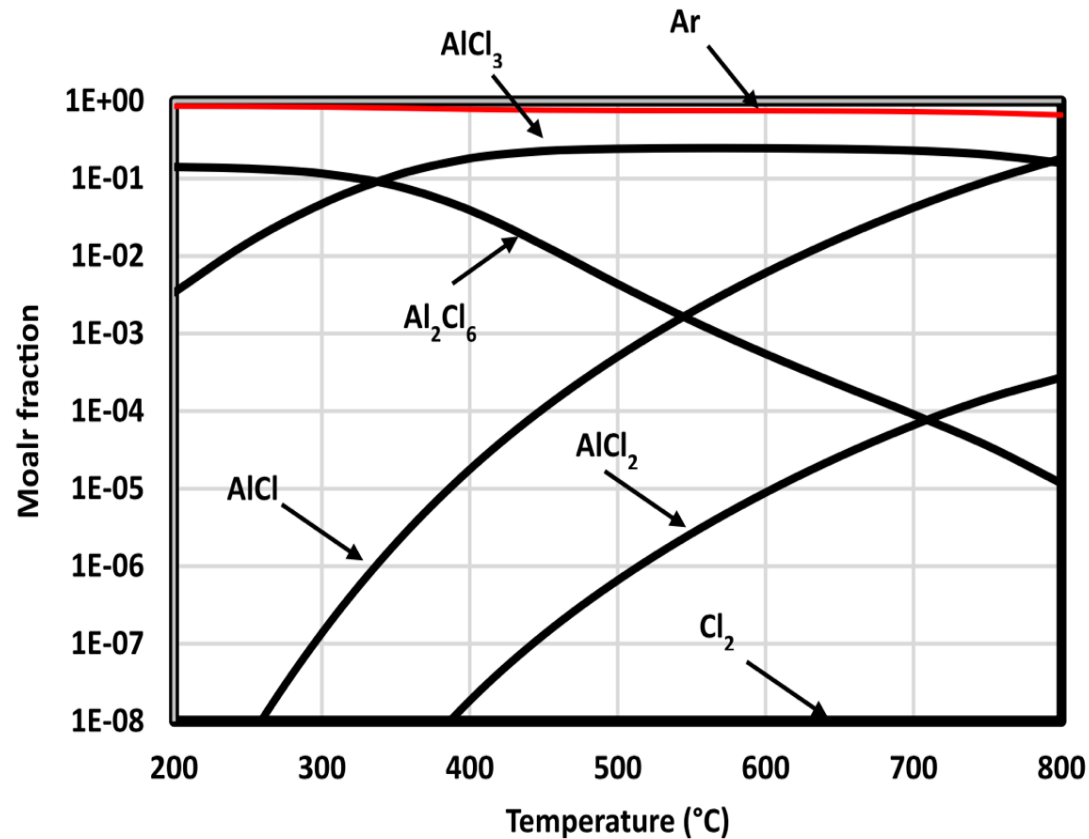
How does one preferentially generate AlCl₃?



Will AlCl₃ react enough to grow?

Solution: Generate AlCl_3 without AlCl at lower temperature

Molar fraction of Al-chlorides generated from HCl



Ex-Situ AlCl_3 Source

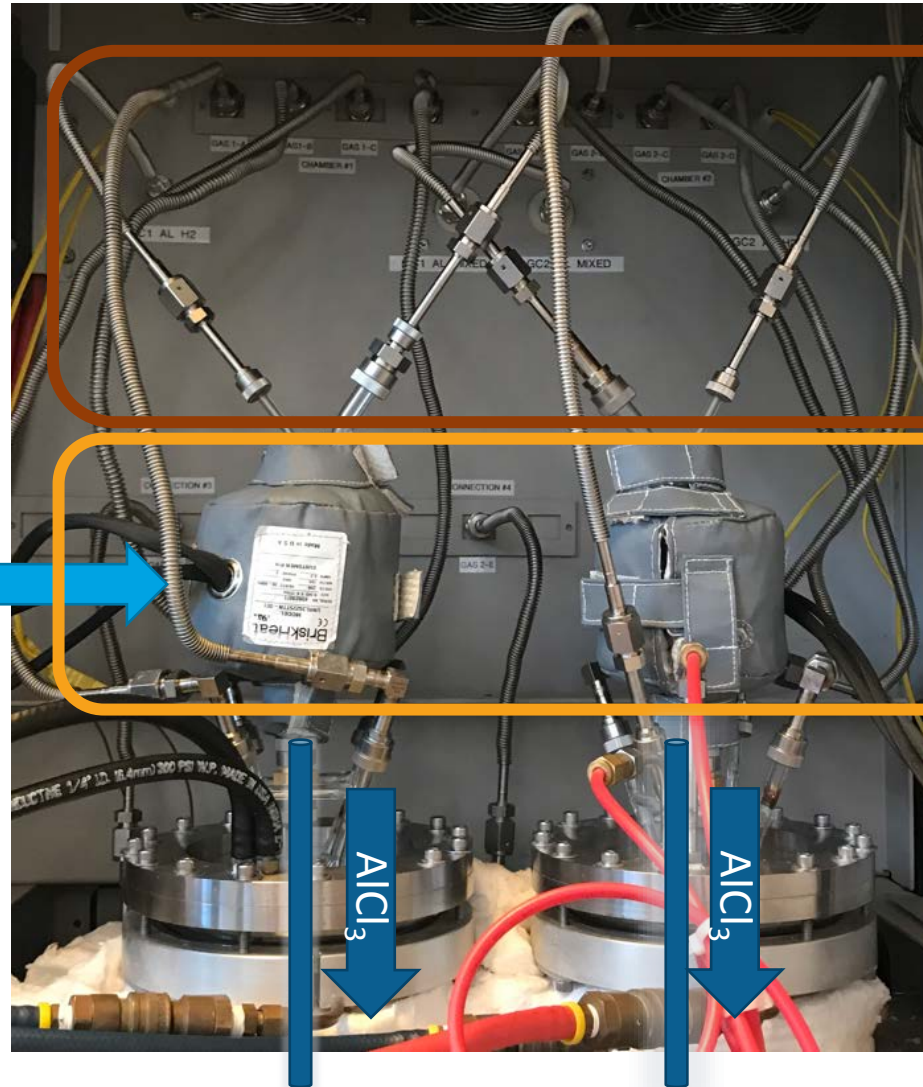
- React Al and HCl @ 400°C to favor AlCl_3 generation
- 4 orders of magnitude less AlCl

Solution: Generate AlCl_3 without AlCl at lower temperature



Ex-Situ AlCl_3 Source

Generate AlCl_3 just above reactor at colder temperature



HCl and H_2
gas inlets

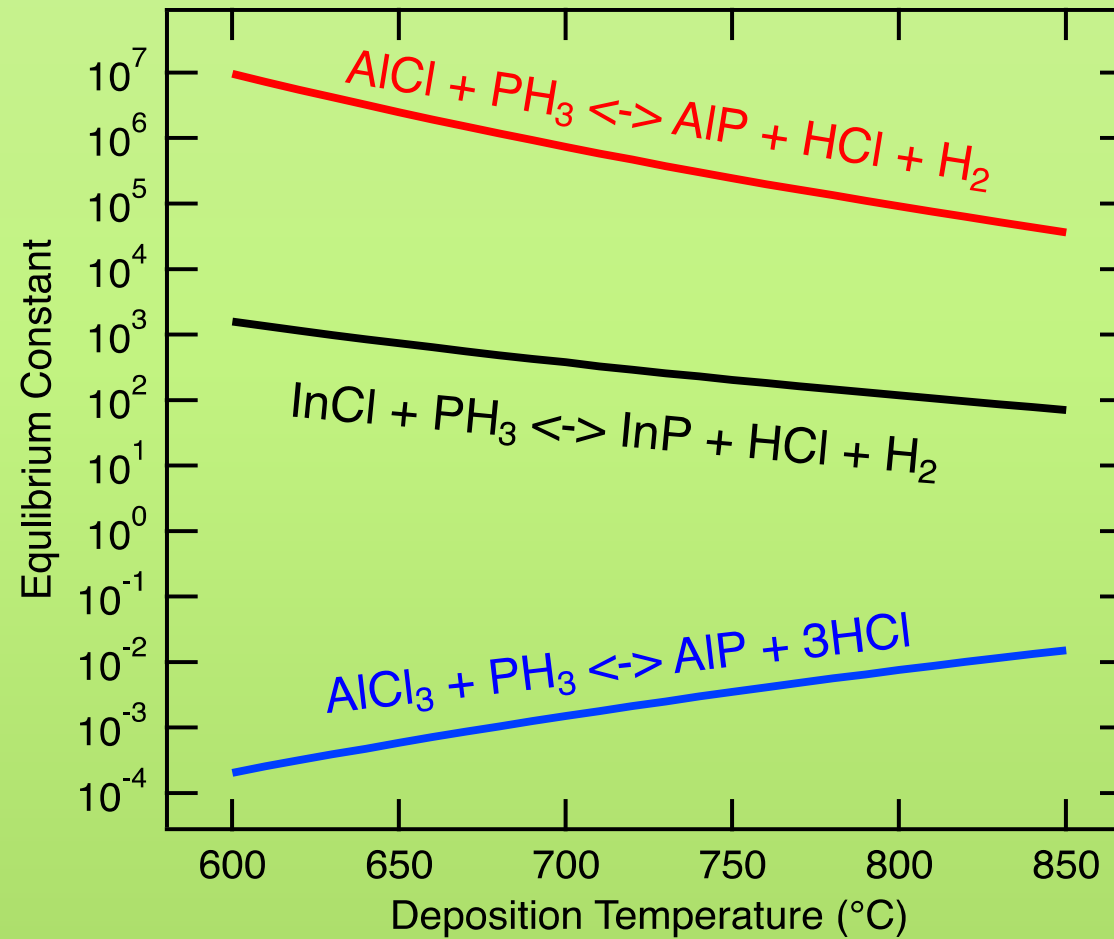
Heaters held
at 400°C

Quick flow AlCl_3 in
quartz tube past
 800°C source zone

Al ampoule renovated – closer to reactor for easier operation with less maintenance

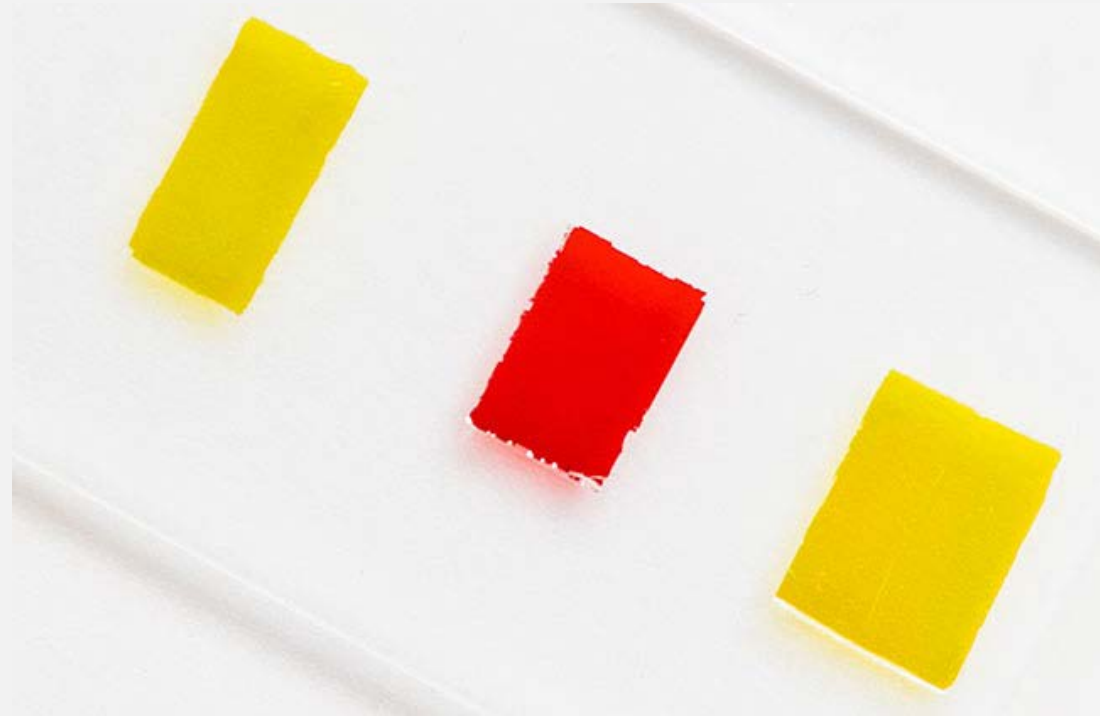
Solution: Use Uncracked Hydrides and AlCl_3 to Grow AlInP

Thermodynamics predicts AlCl_3 is too stable to grow AlInP

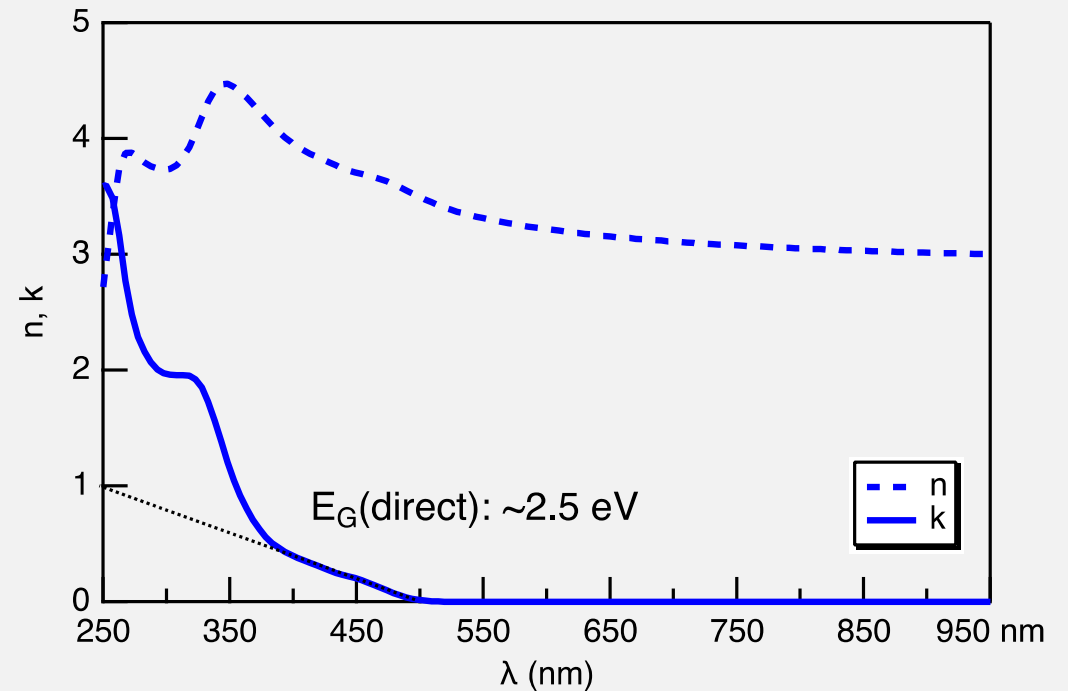


Solution: Use Uncracked Hydrides and AlCl_3 to Grow AlInP

Transmission Samples – HVPE $\text{Al}(\text{Ga})\text{InP}$



Spectroscopic Ellipsometry – HVPE AlInP



Verified that we have wide bandgap material commensurate with $\text{Al}(\text{Ga})\text{InP}$!

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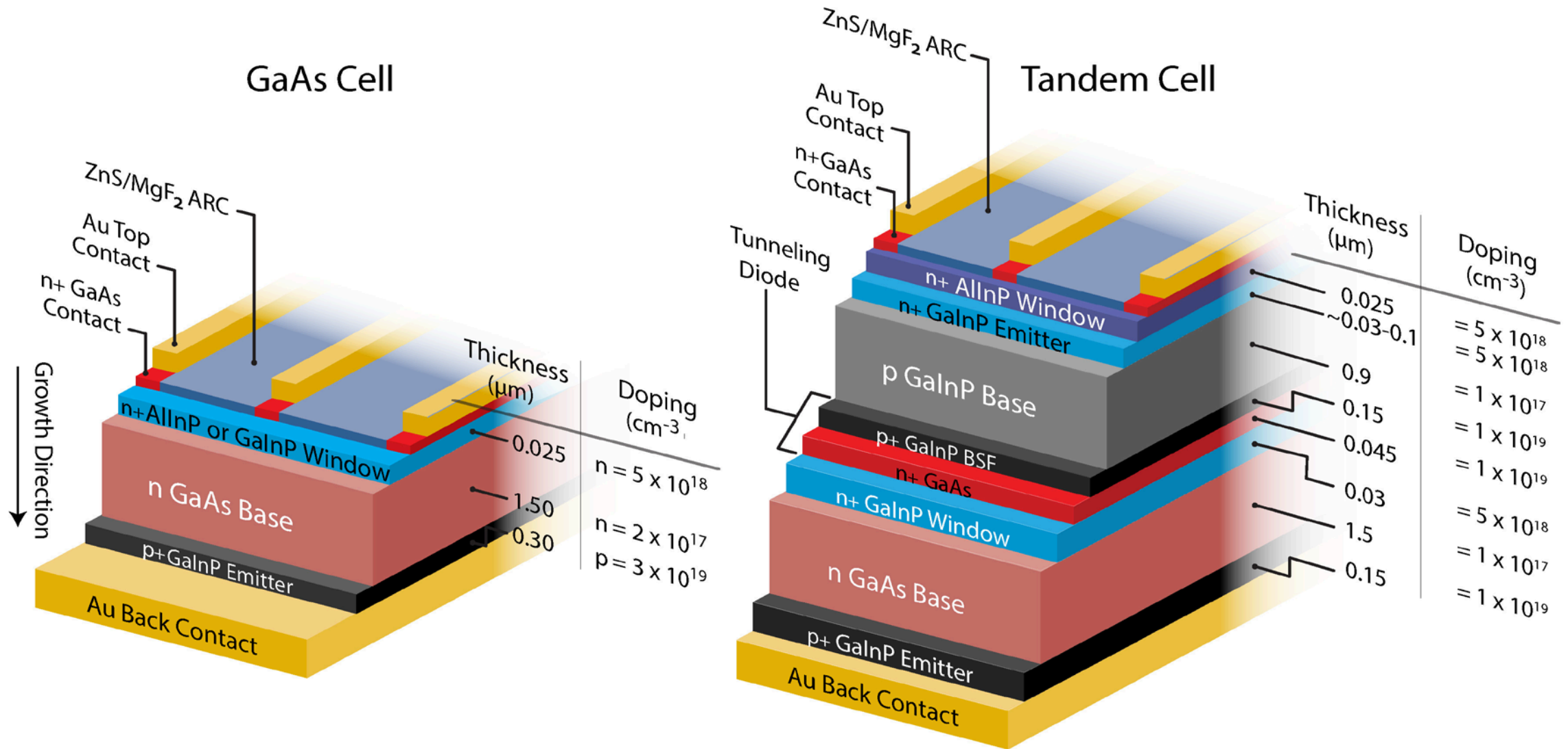
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5 Implementing AlInP in 2J GaInP/GaAs Solar Cells

6 Progress of HVPE-Grown PV

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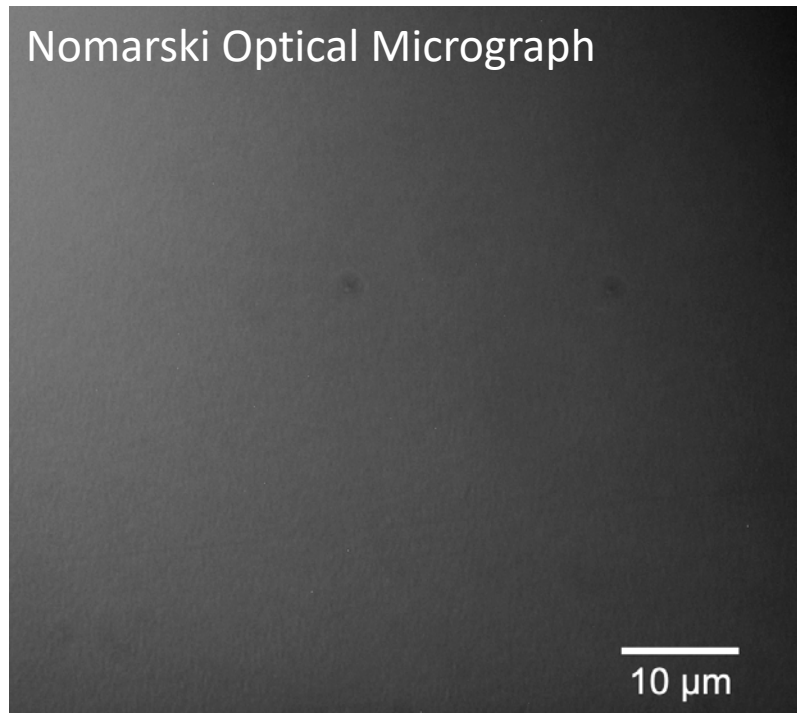
AlInP in HVPE-Grown PV Device Structures

AlInP window requirements:

- Smooth morphology for inverted growth
- Doping to $n = 5 \times 10^{18} \text{ cm}^{-3}$ or higher

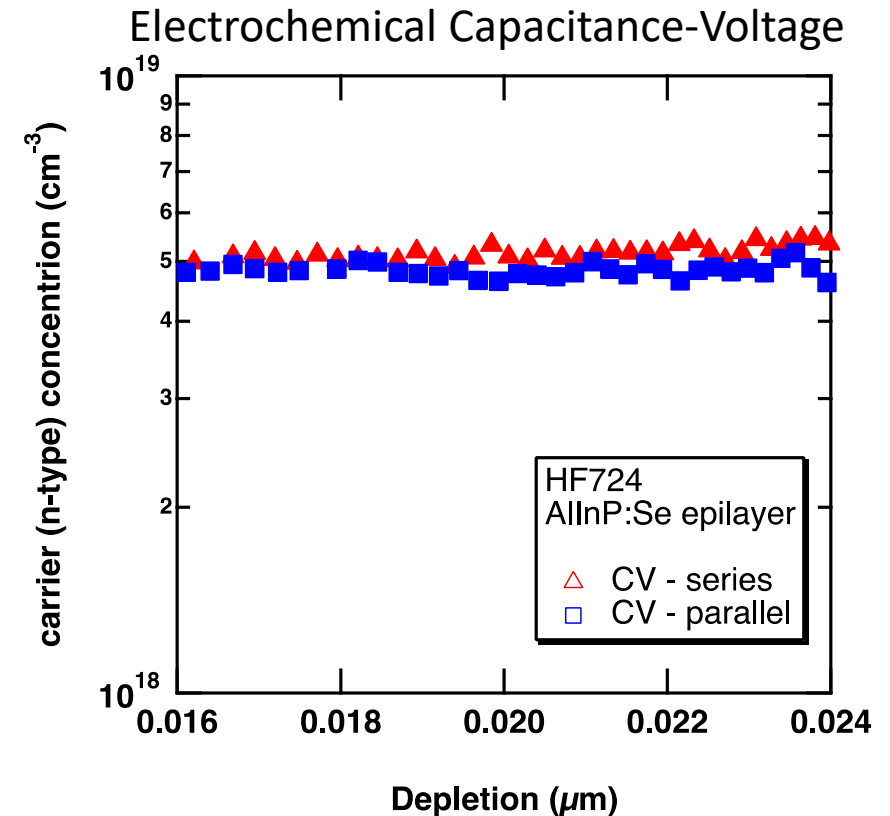
Surface Morphology

- Smooth morphology good for inverted devices (grown before active layer)
- R_q : 1.66 nm from 5x5 μm atomic force micrograph



Carrier Concentration

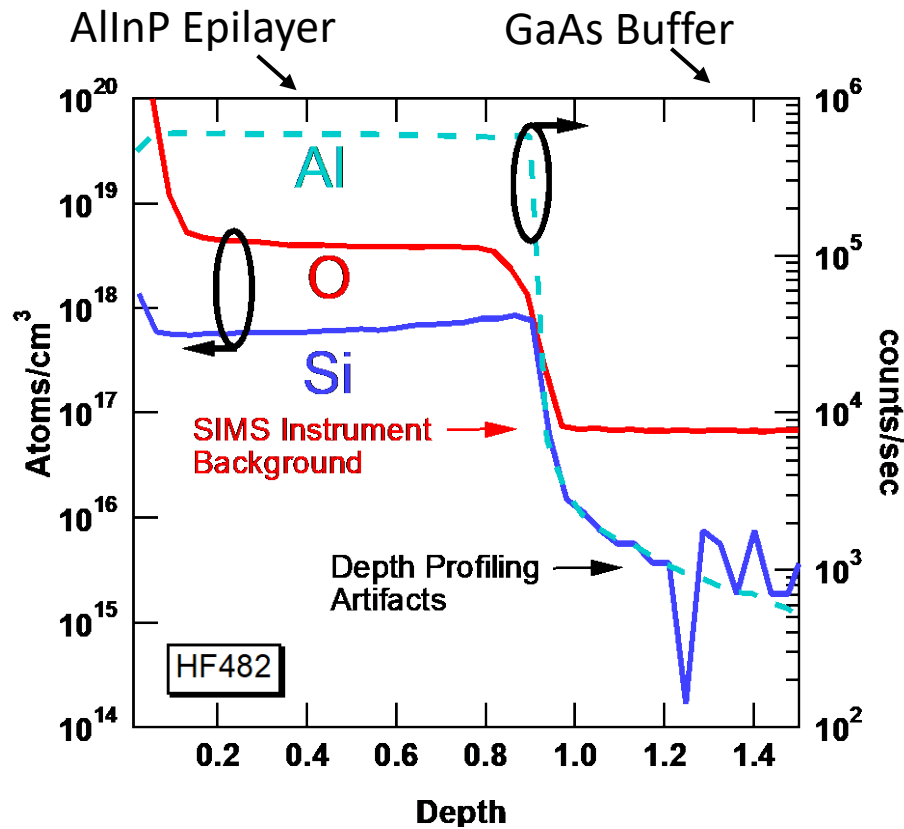
- N -type doping at $5 \times 10^{18} \text{ cm}^{-3}$ achieved with H_2Se



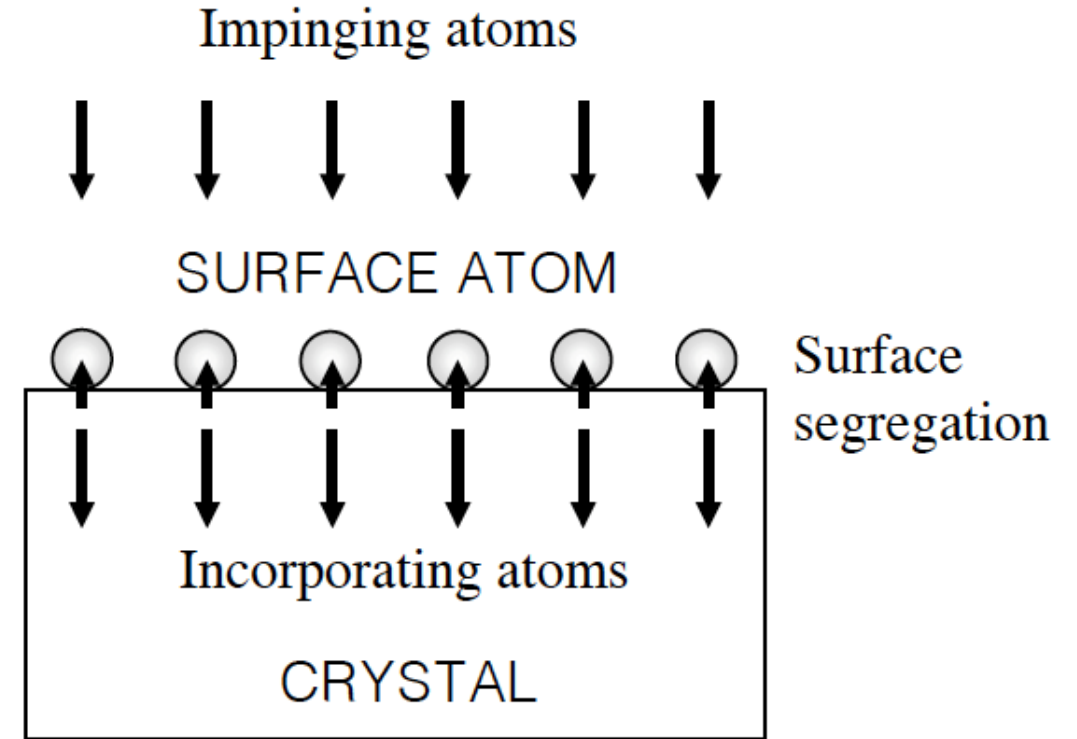
Towards Implementing
AlInP in PV Devices

- Achieved smooth AlInP with target doping for use as window layers

Thick AlInP epilayer



Surface [O] saturates after ~100 nm of growth
 → O incorporation rate = O impingement rate



Dynamic Secondary Ion Mass Spectrometry

- Significant [Si] and [O] observed in AlInP
- AlInP growth has minimal effect on other layers
- Less [O] in thinner layers – surface segregation likely

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4 **Assessing Passivation of AlInP in 1J GaAs Solar Cells**

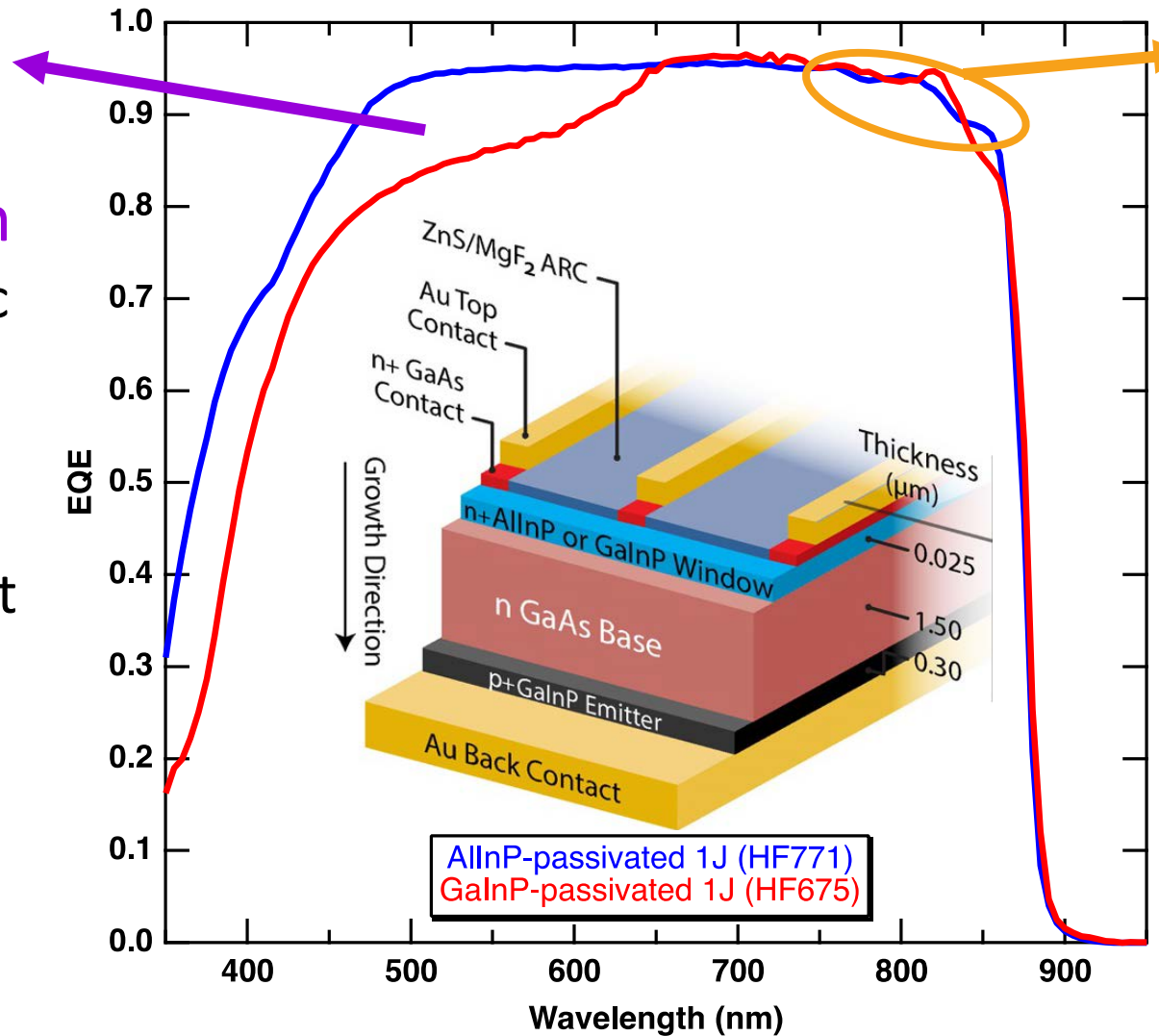
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Improved short wavelength current collection

- Reduced parasitic absorption of AlInP window
- Accounts for 1.3 mA/cm² boost

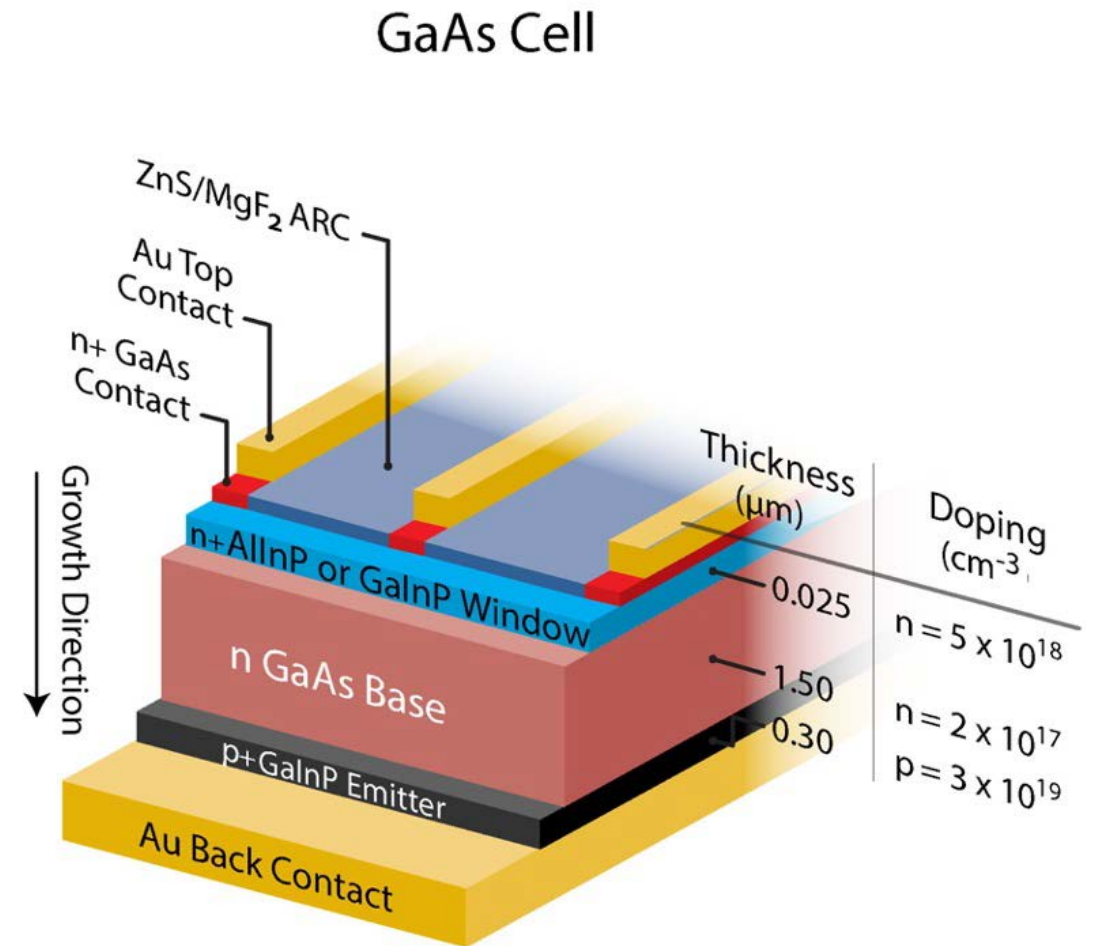
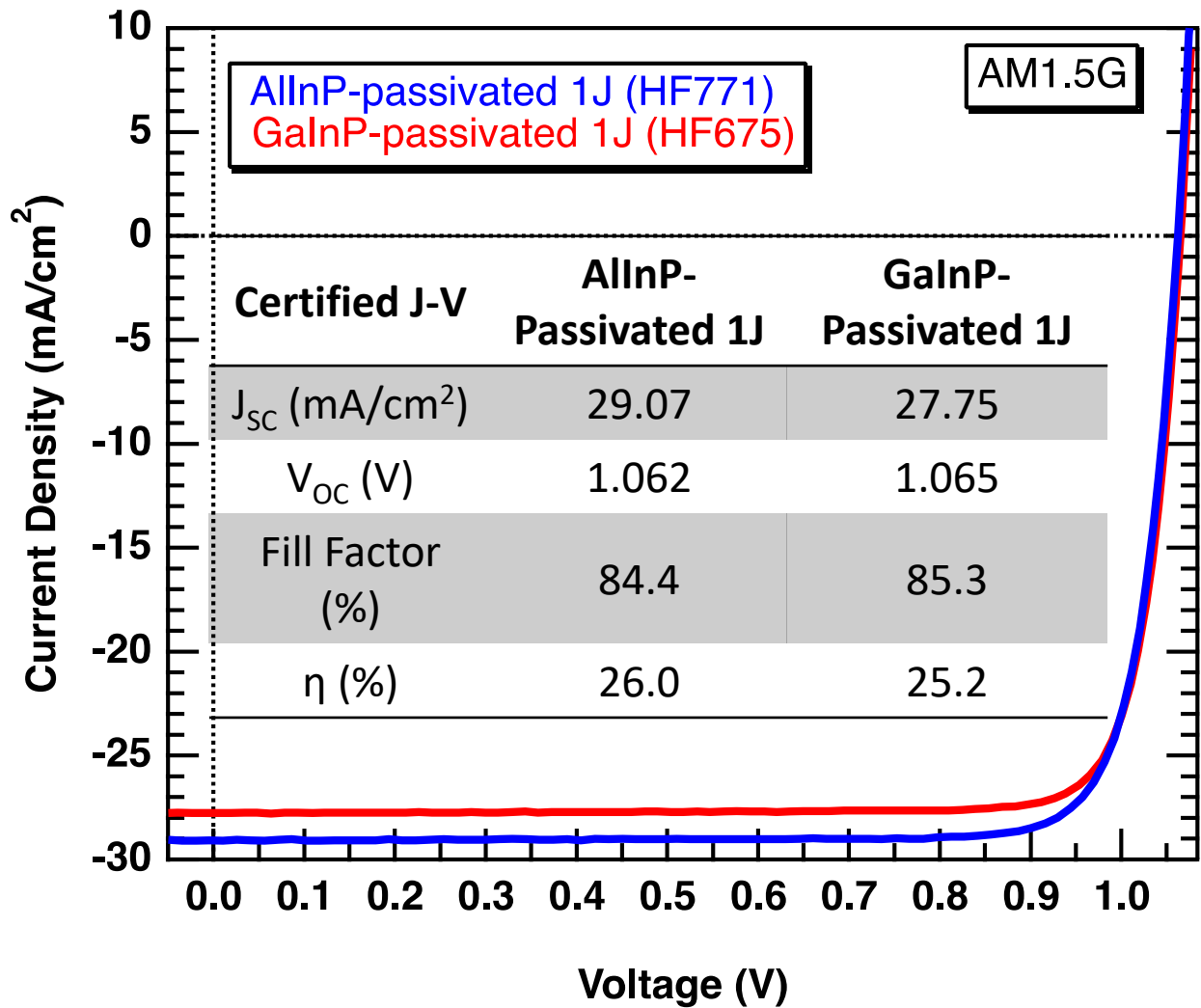


Unchanged long wavelength current collection

- Equivalent passivation & no degradation of other layers
- Rear junction cells especially sensitive to passivation

GaAs Solar Cells with AlInP Passivation

- Unchanged EQE at long wavelengths demonstrates equivalent passivation ability of AlInP
- Short wavelength EQE accounts for J_{SC} boost



GaAs Solar Cells with AllnP Passivation

- GaInP previously demonstrated good passivation; no O or Si impurities
- AllnP passivation improves J_{sc} & η ; no change in V_{oc} & FF

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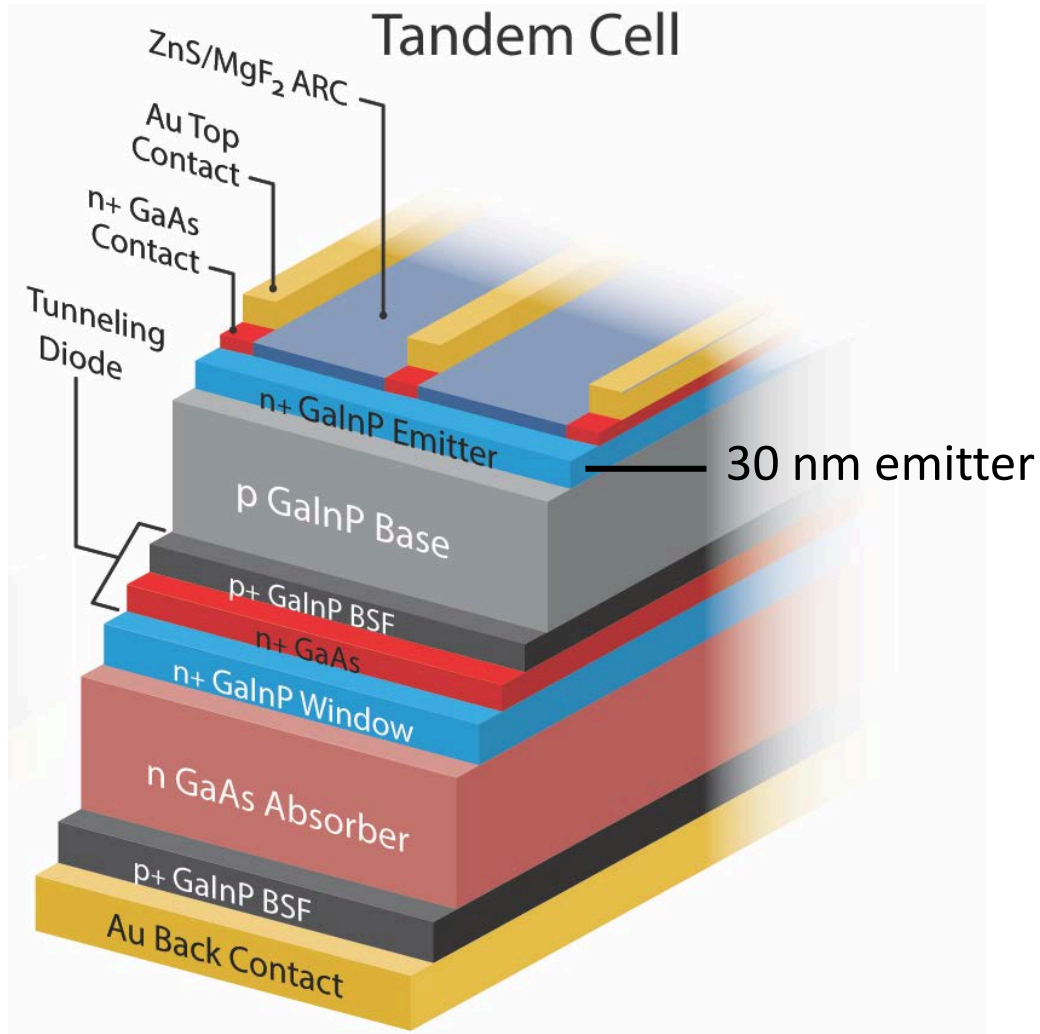
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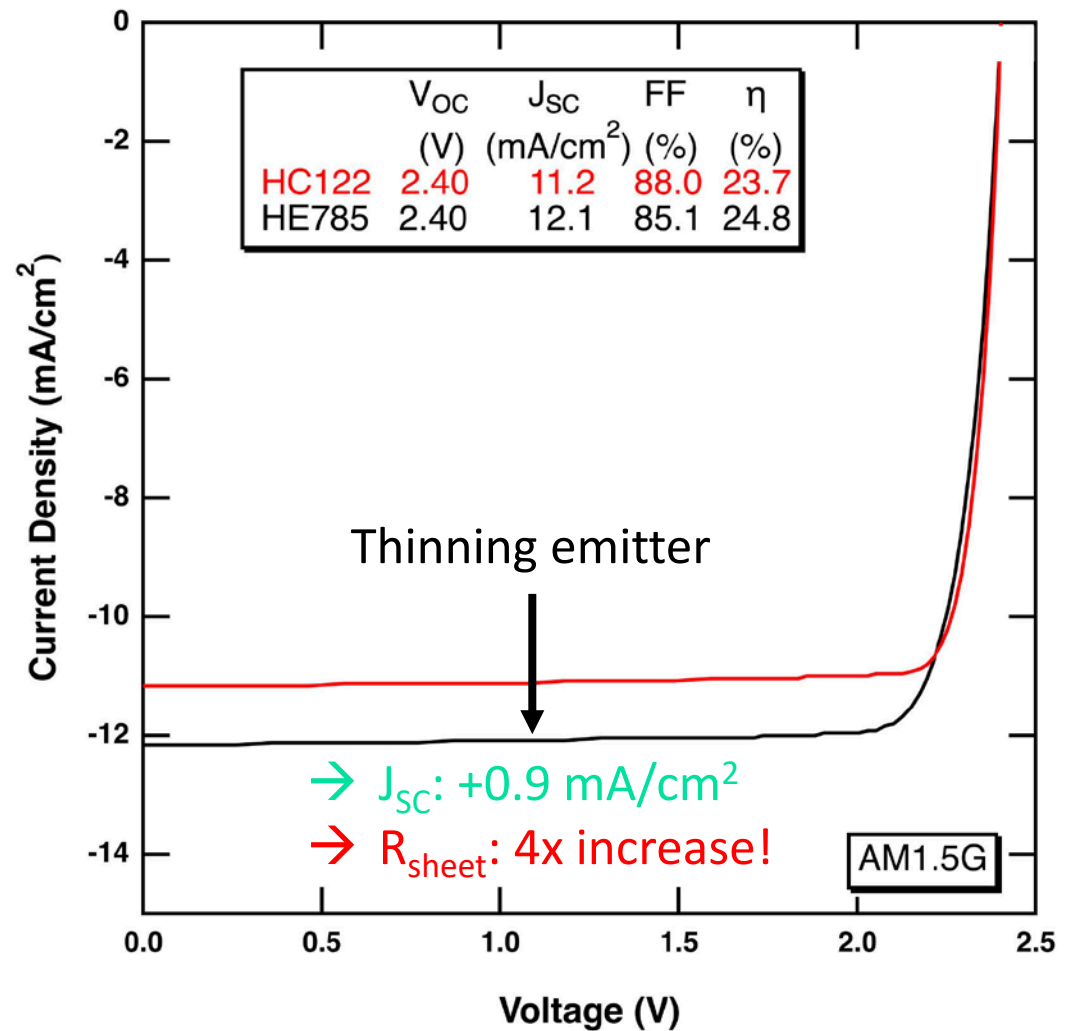
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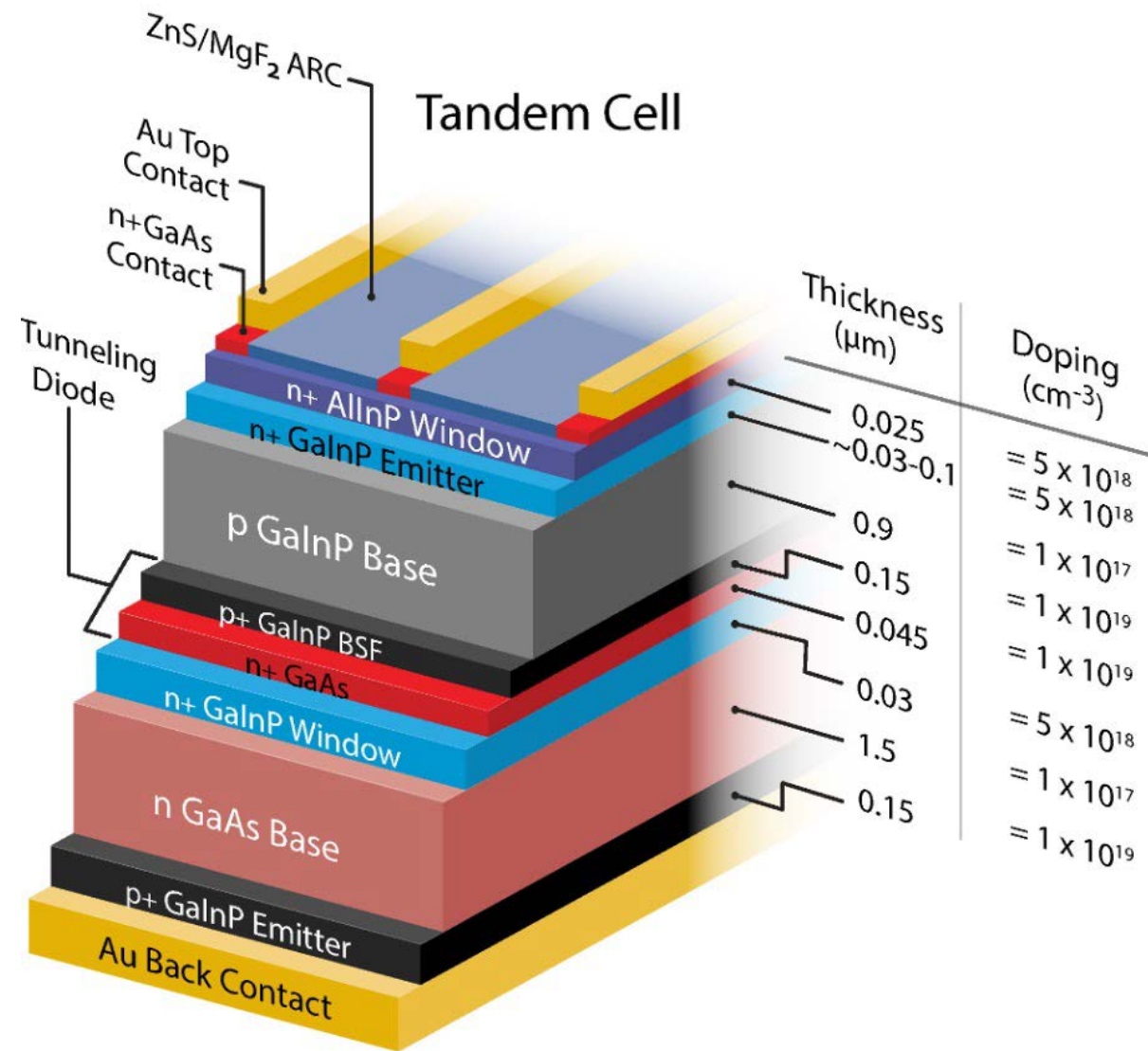
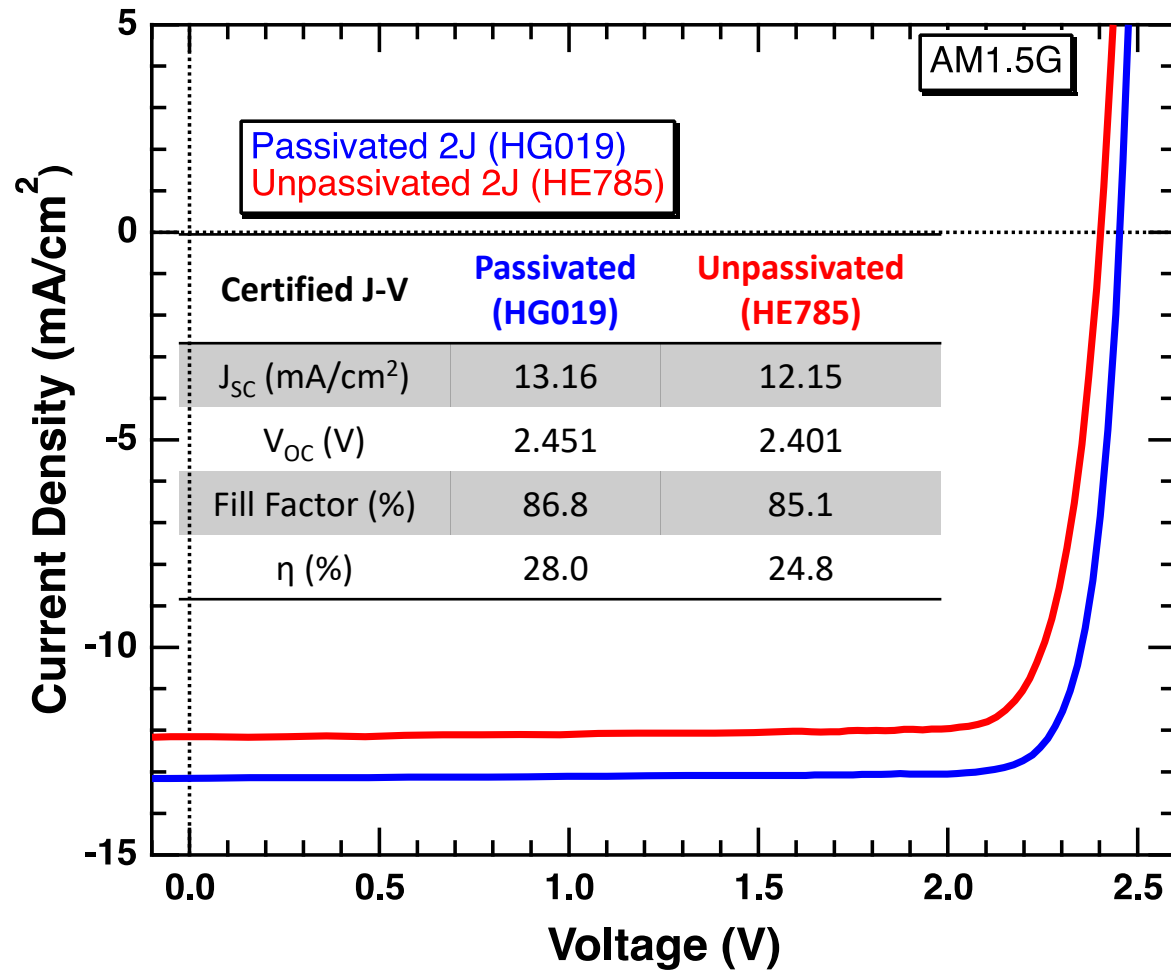
Roberts et al., *JPV*, **11**, 5 (2021)

Schulte et al. *Prog Photovolt Res Appl*. 26:887–893 (2018)



Unpassivated GaInP/GaAs (2J) Solar Cells

- Without AlInP, use thin 30 nm emitter to optimize current collection, lose R_{sheet}



AllnP Passivated GaInP/GaAs (2J) Solar Cells

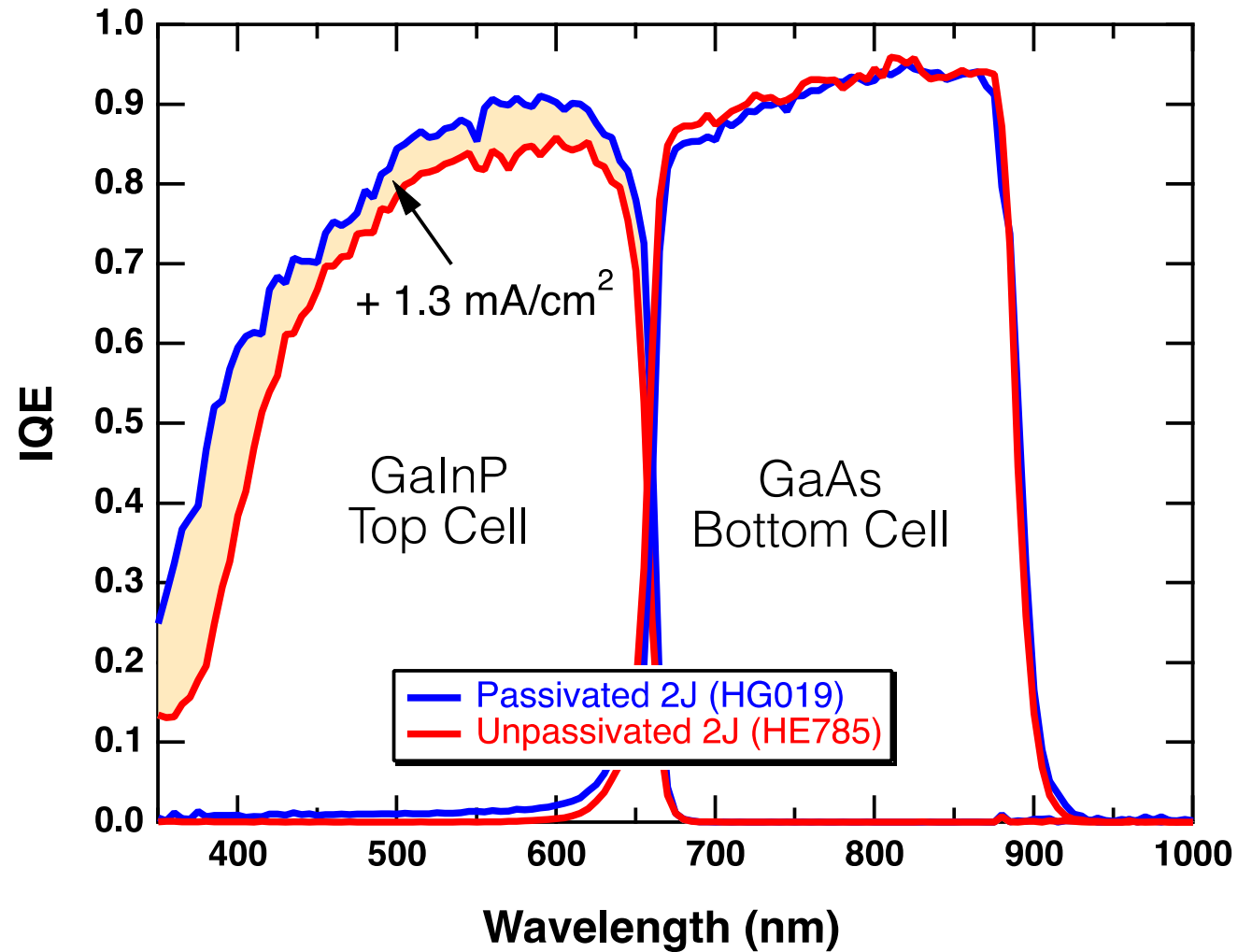
- Passivated 2J: → 28.0% efficiency, certified AM1.5G

GaInP/GaAs (2J) Solar Cells with AlInP Passivation

Subcell IQE

- AlInP improves top cell current potential by 1.3 mA/cm²
- Bottom cell is unchanged, no effect on layers grown after
- Slope suggests some parasitic absorption from TJ – add Al to future 2J

Adding passivation improves top cell current at **all wavelengths**

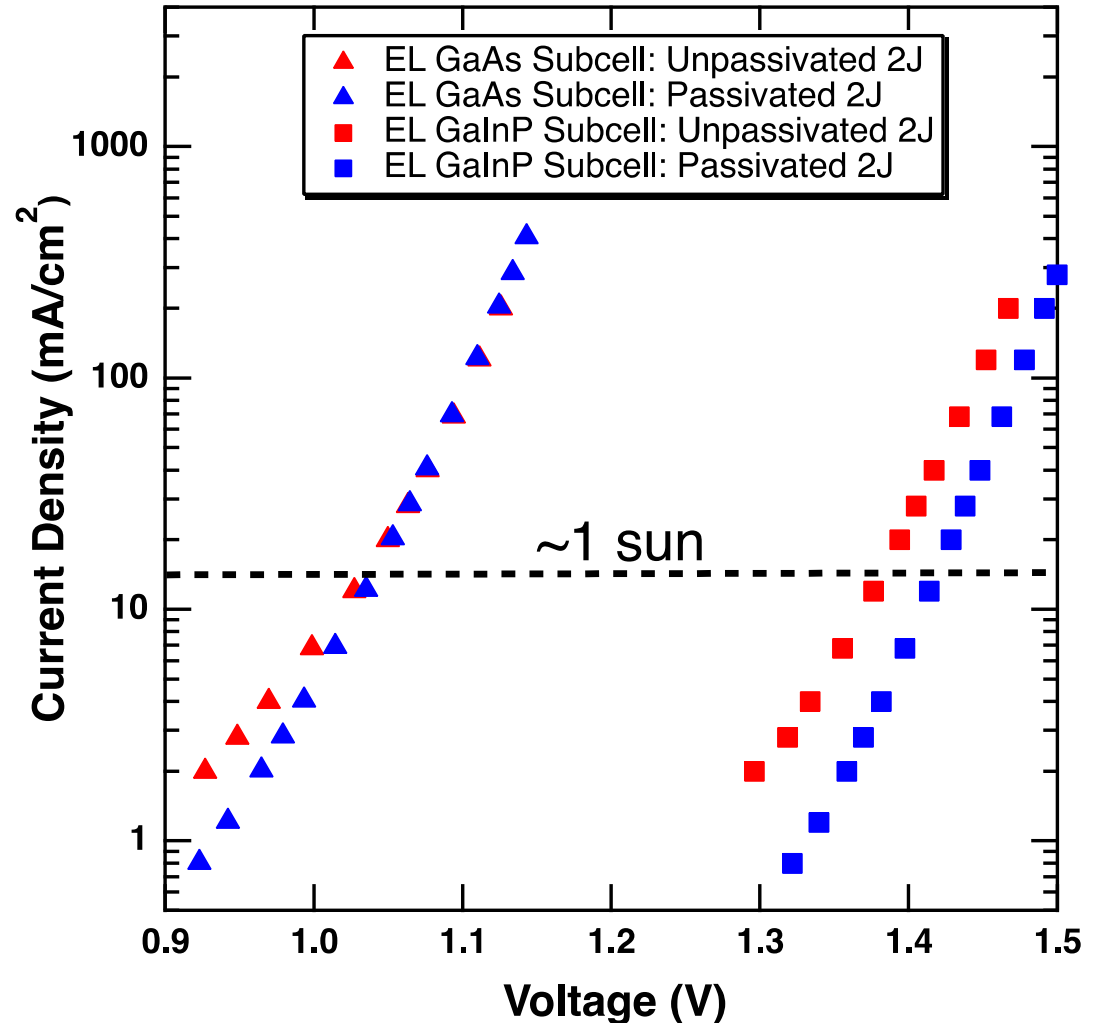


GaInP/GaAs (2J) Solar Cells with AlInP Passivation

Subcell Electro- luminescence (EL)

- AlInP Passivation improves top cell V_{oc} by 40 mV – majority of V_{oc} boost

Subcell:	GaAs Bottom Cell		GaInP Top Cell	
Device:	Unpassivated 2J	Passivated 2J	Unpassivated 2J	Passivated 2J
V_{oc} (V)	1.027	1.037	1.376	1.416

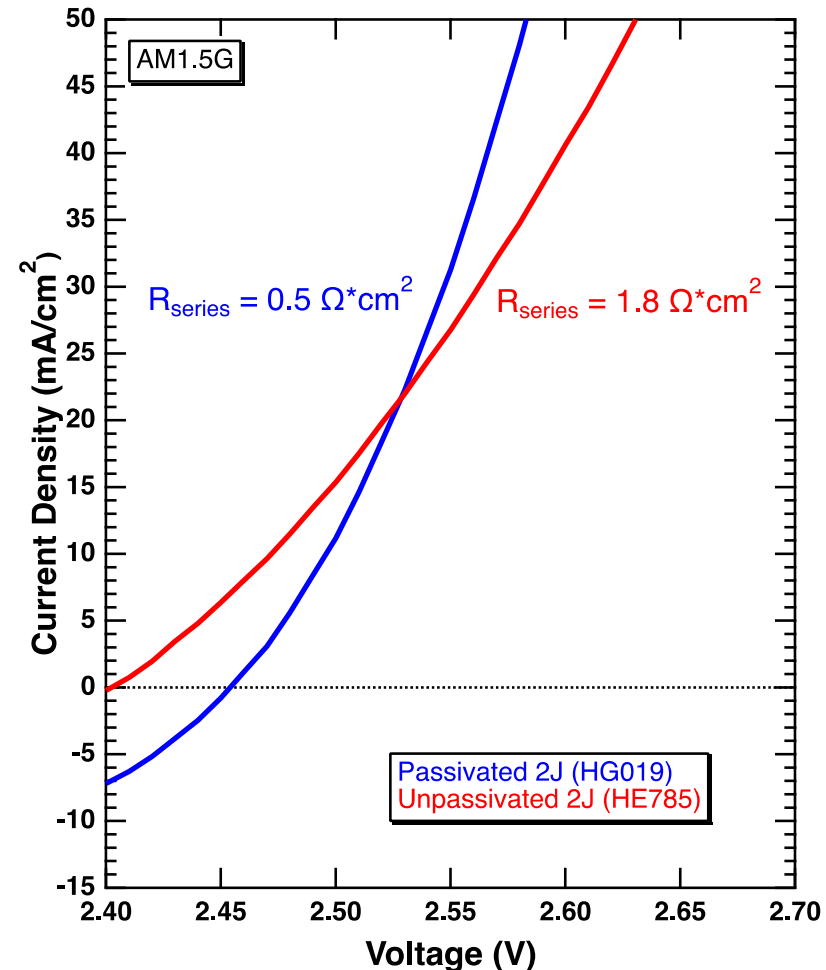


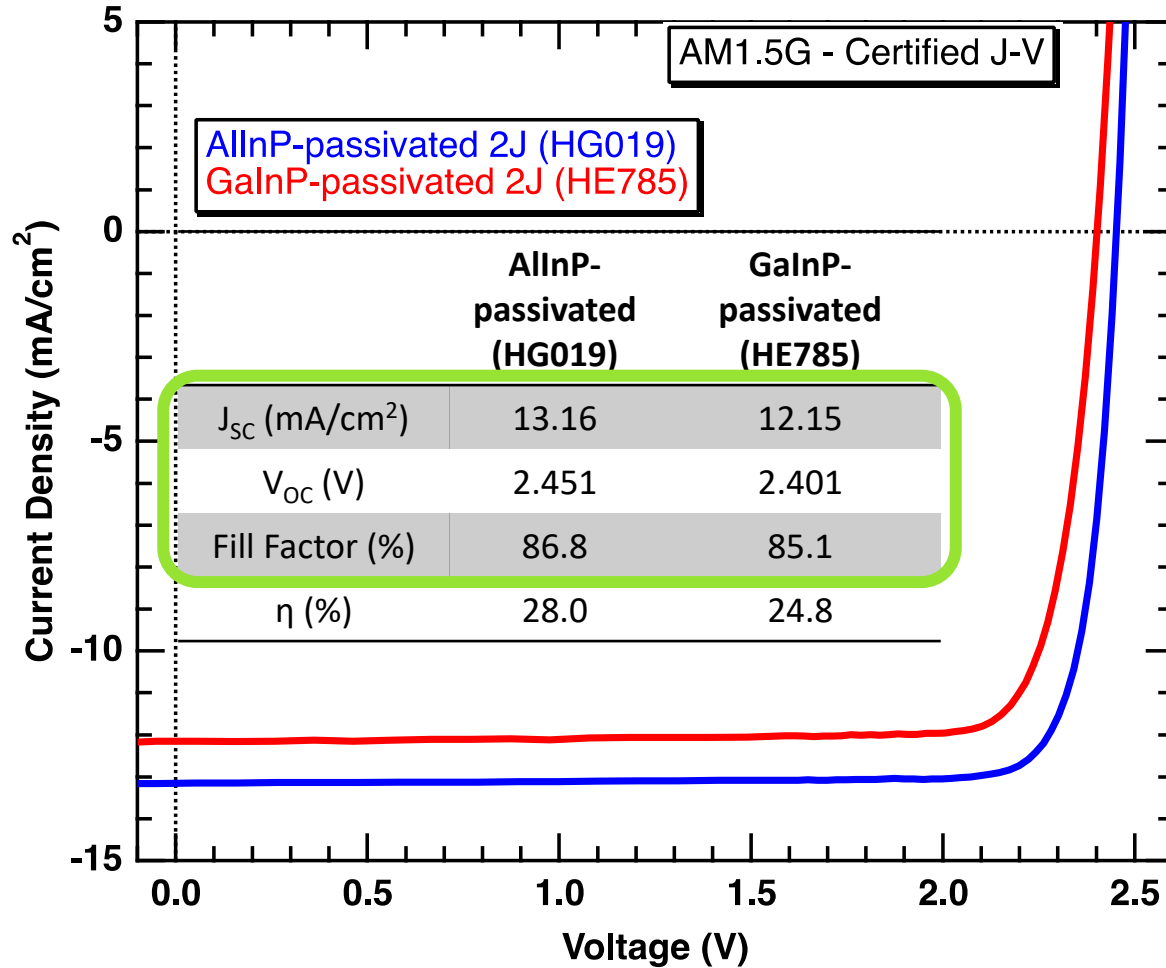
GaInP/GaAs (2J) Solar Cells with AlInP Passivation

J-V @ diode turn on

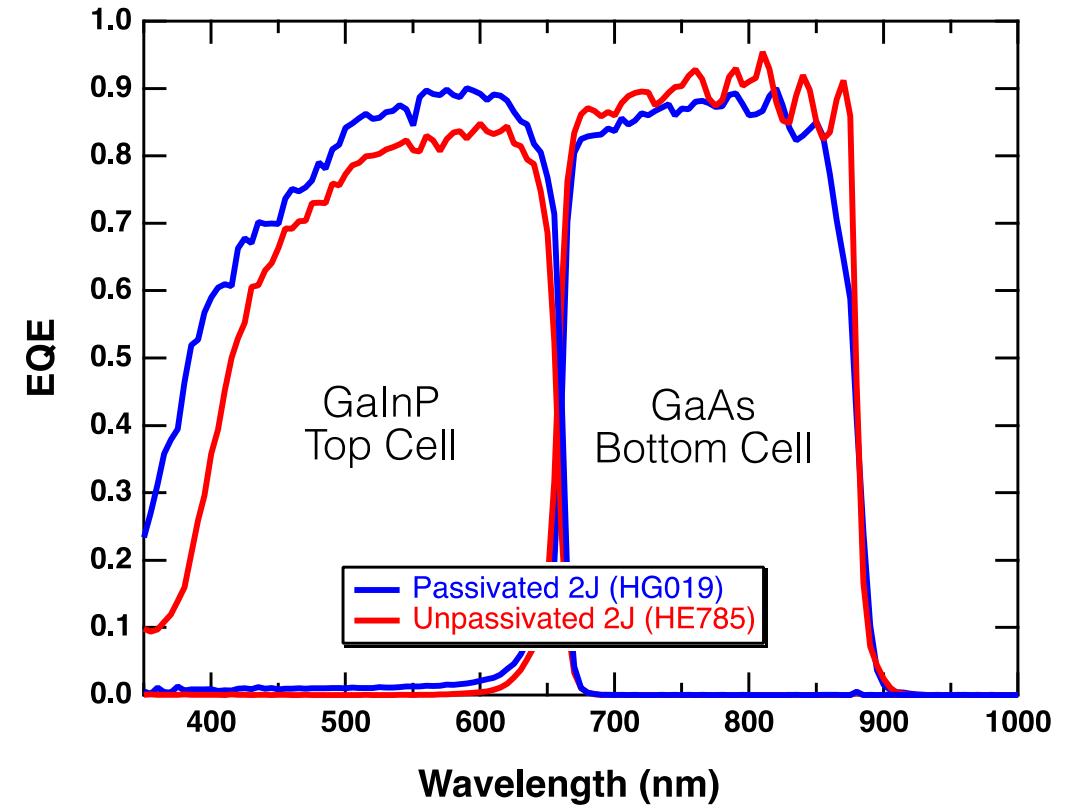
- Increased emitter thickness possible with AlInP passivation
- Fill factor improvement due to reduced R_{series} and R_{sheet}

	Passivated 2J (HG019)	Unpassivated 2J (HE785)
J_{SC} (mA/cm ²)	13.16	12.15
V_{OC} (V)	2.451	2.401
Fill Factor (%)	86.8	85.1
η (%)	28.0	24.8





AllnP enables:
+1 mA/cm²; +50 mV; +1.7% FF



GaInP/GaAs (2J) Solar Cells with AllnP Passivation

- J_{sc} , V_{oc} , FF improved with AllnP passivation
→ 28% efficiency, certified AM1.5G

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2 Challenges and Solutions for AlInP growth in HVPE

3 Developing HVPE-AlInP for Solar Cells

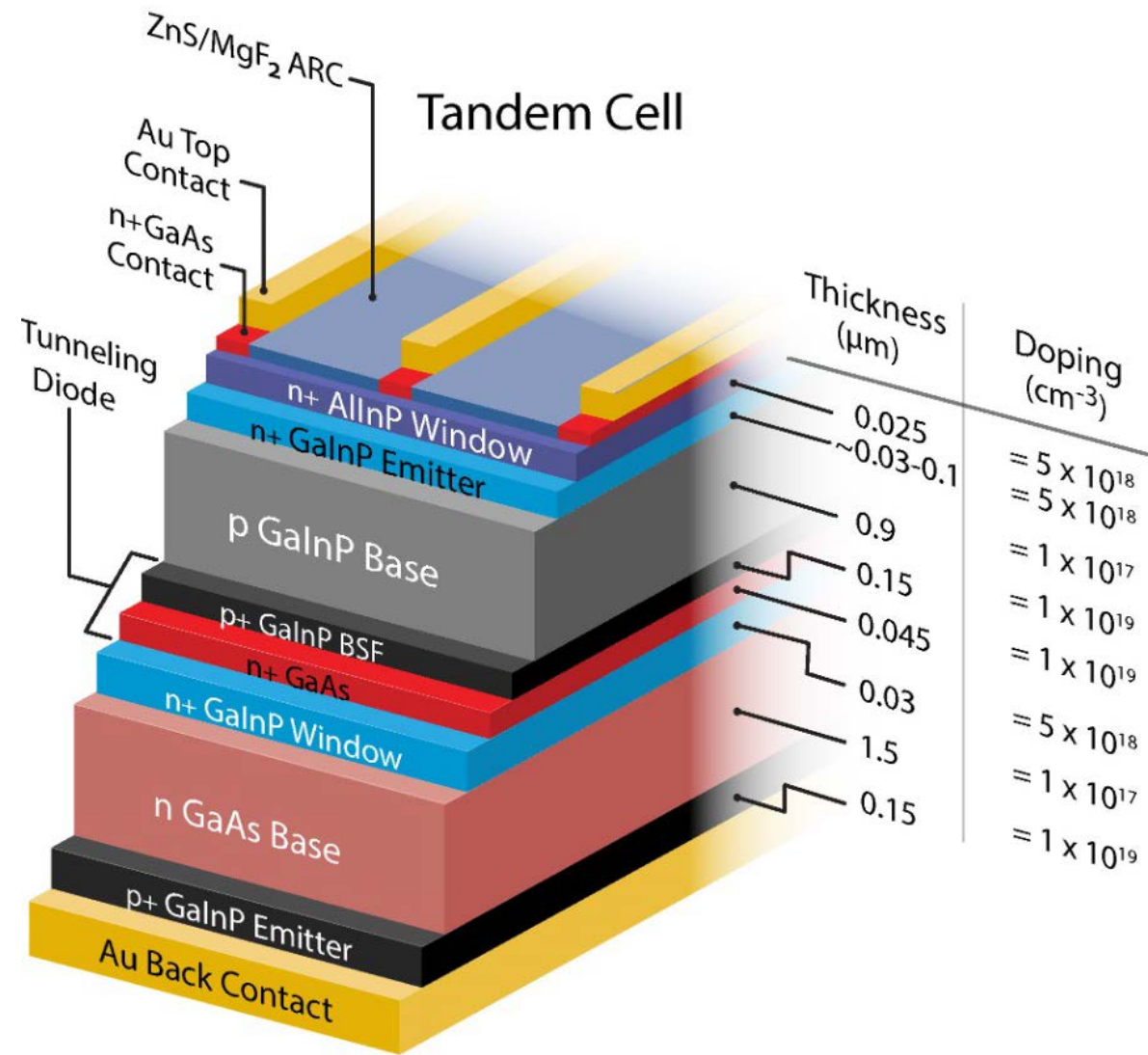
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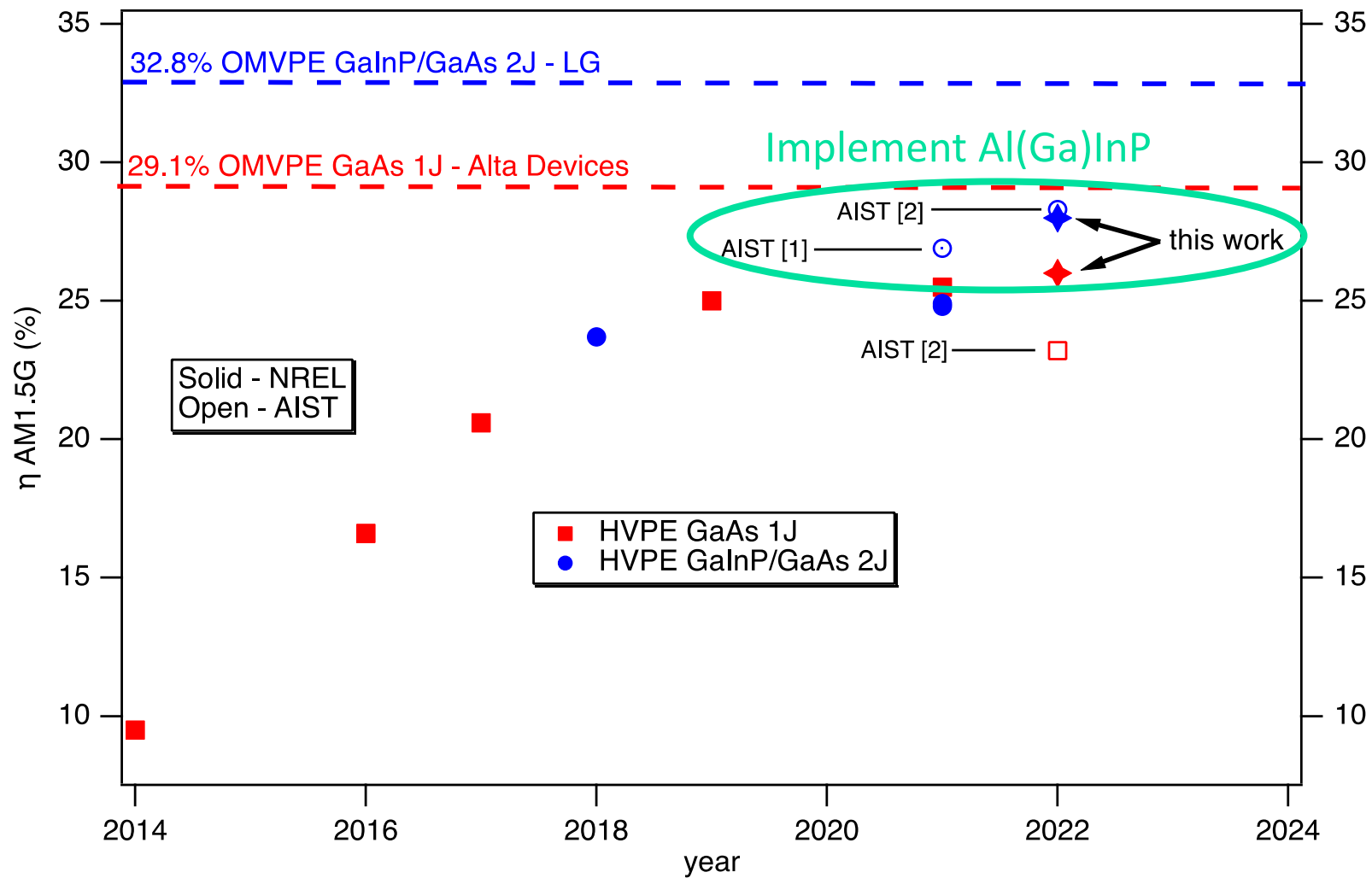
- Initial demonstration of AlInP within PV by HVPE reaches 26%(1J)/28%(2J)
- Add Al to other layers, top cell BSF and tunneling diode
 - *Shoji et al. already demonstrated V_{OC} boost by using AlGaInP BSF*
- Optimize GaInP with passivation



Y. Shoji, et al., *Solar RRL*, p. 2100948, Dec. 2021

Pathways toward higher η

- Room to expand upon this initial demonstration with AlInP



[1] Y. Shoji, et al. *Prog Photovolt Res Appl*, pip.3454, Jul. 2021

[2] Y. Shoji, et al., *Solar RRL*, p. 2100948, Dec. 2021

Learning curve of PV grown in D-HVPE

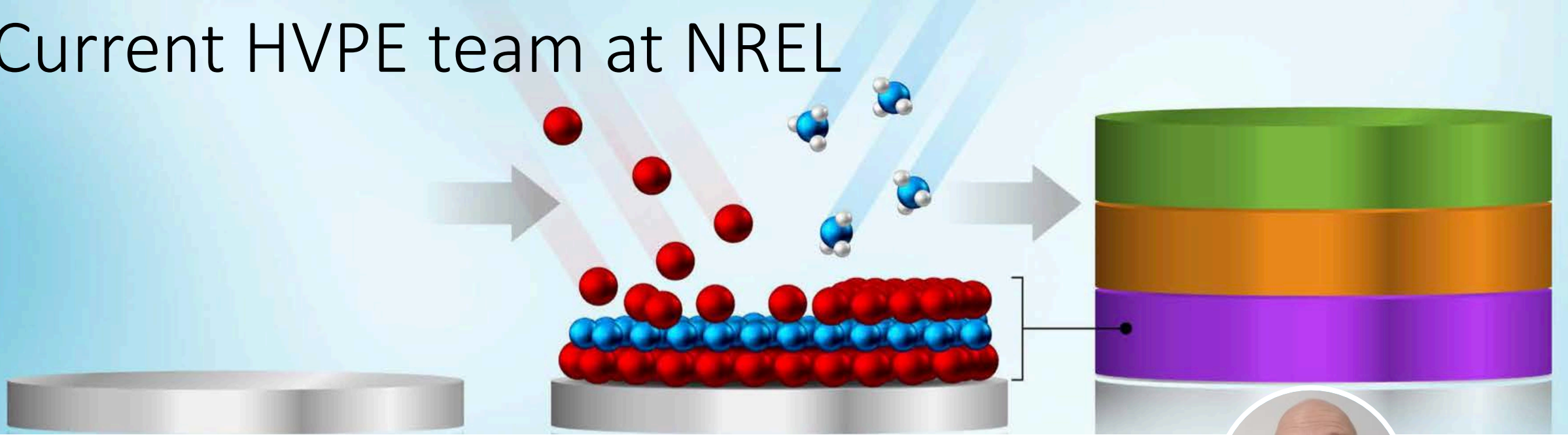
- Steady progress in D-HVPE-grown PV
- AlInP enables further growth

Conclusions & *Further Directions*

- *Incorporate Al in other layers within PV structure to increase transparency*
- *Understand origin and incorporation of O/Si impurities*
- *Exploring Al generation temperature, carrier flow rates, V:III, etc.*

- Initial demonstration of HVPE-PV with AlInP reaches 26% (1J Record) and 28% (2J) with room to improve
 - Current AlInP material yields the anticipated cell improvements without any degradation or barriers to further development
- Addresses last major barrier to achieving D-HVPE-grown PV at parity efficiency with state of the art III-V PV**

Current HVPE team at NREL



Anna Braun



Dennice Roberts



John Simon



Kevin Schulte



Jacob Boyer



Evan Wong



Allison Perna



David Guling

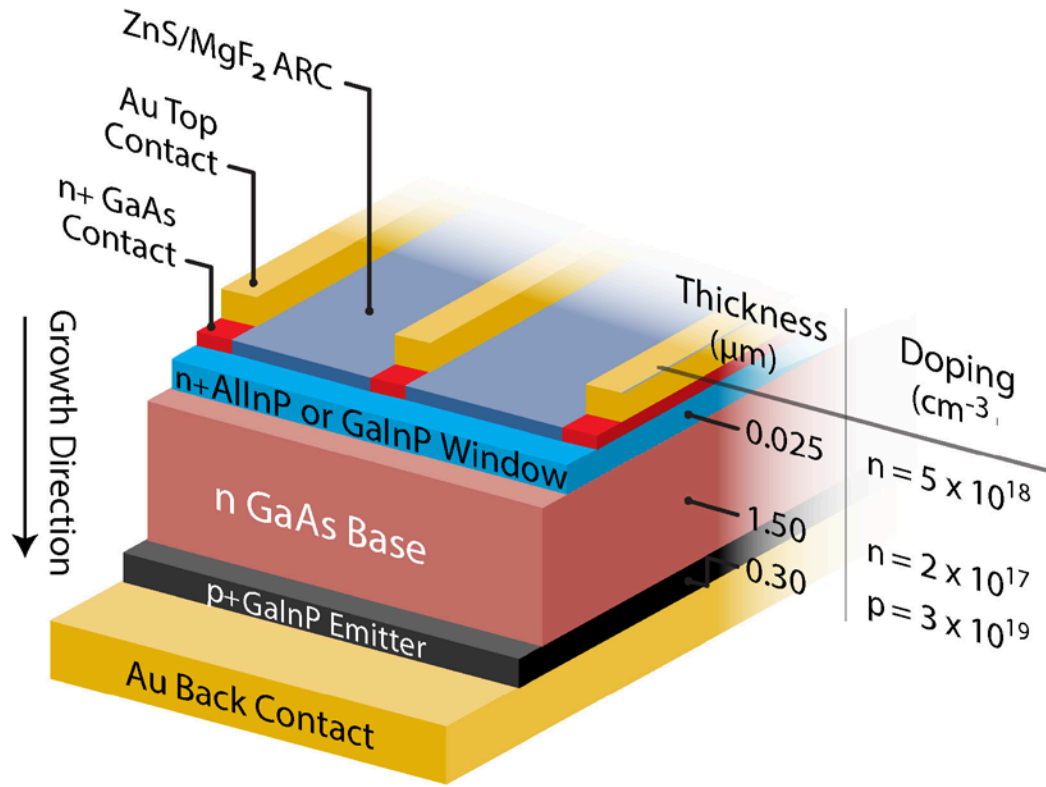
- **The authors would like to acknowledge David Guiling for materials growth and Evan Wong for cell processing.**
- This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. The information, data, or work presented herein was funded by the DOE's Office of Energy Efficiency and Renewable Energy (EERE) under Solar Energy Technologies Office (SETO) Agreement Number 34358. NREL acknowledges support from the Operational Energy Capability Improvement Fund (OECIF) of the U.S. Department of Defense (DOD). The authors wish to thank R. Darling of the Office of the Undersecretary of Defense for Acquisition and Sustainment, Arlington, VA, USA for guidance and support. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

Questions?

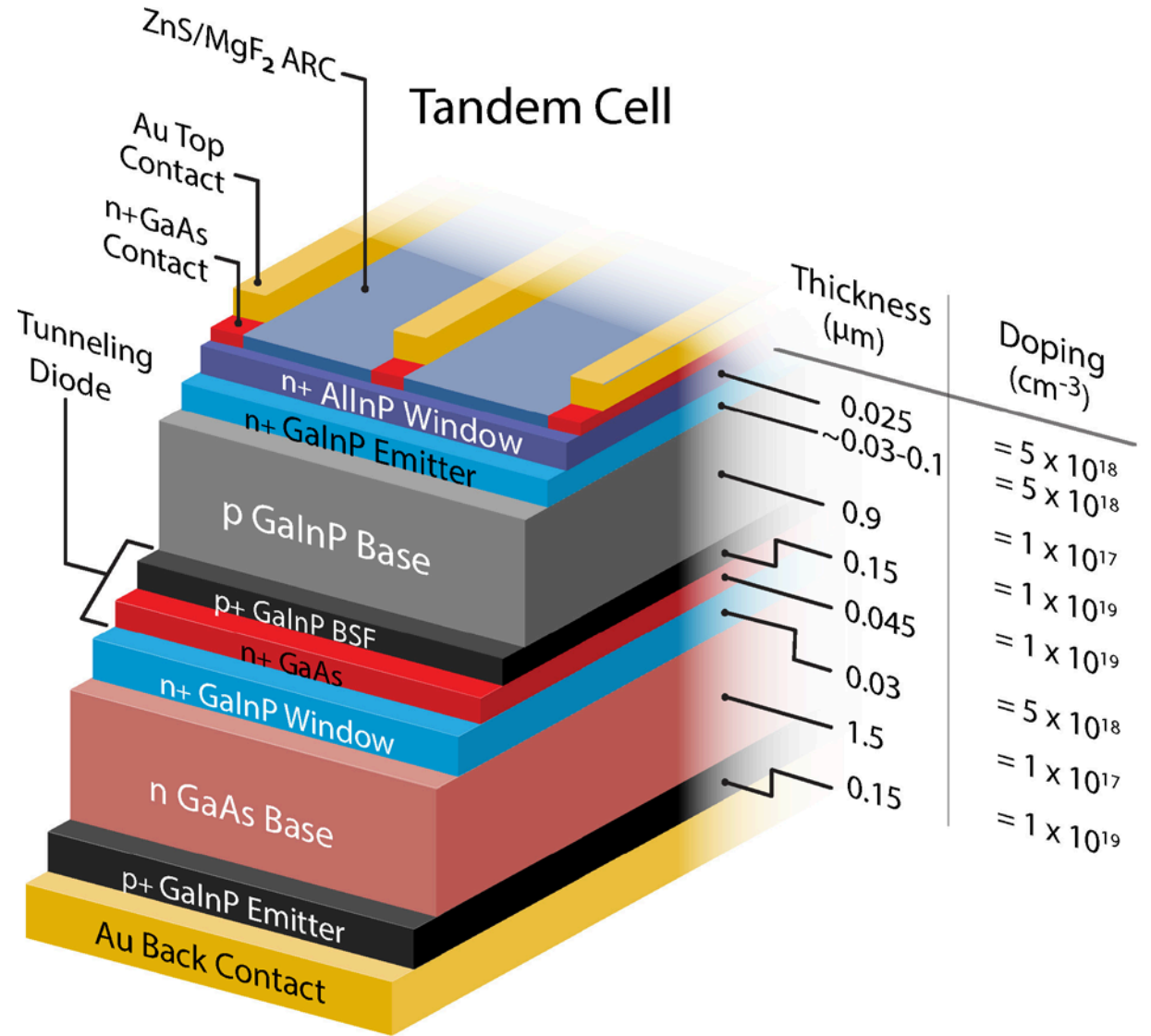
www.nrel.gov / jboyer@nrel.gov

NREL/PR-5900-82749

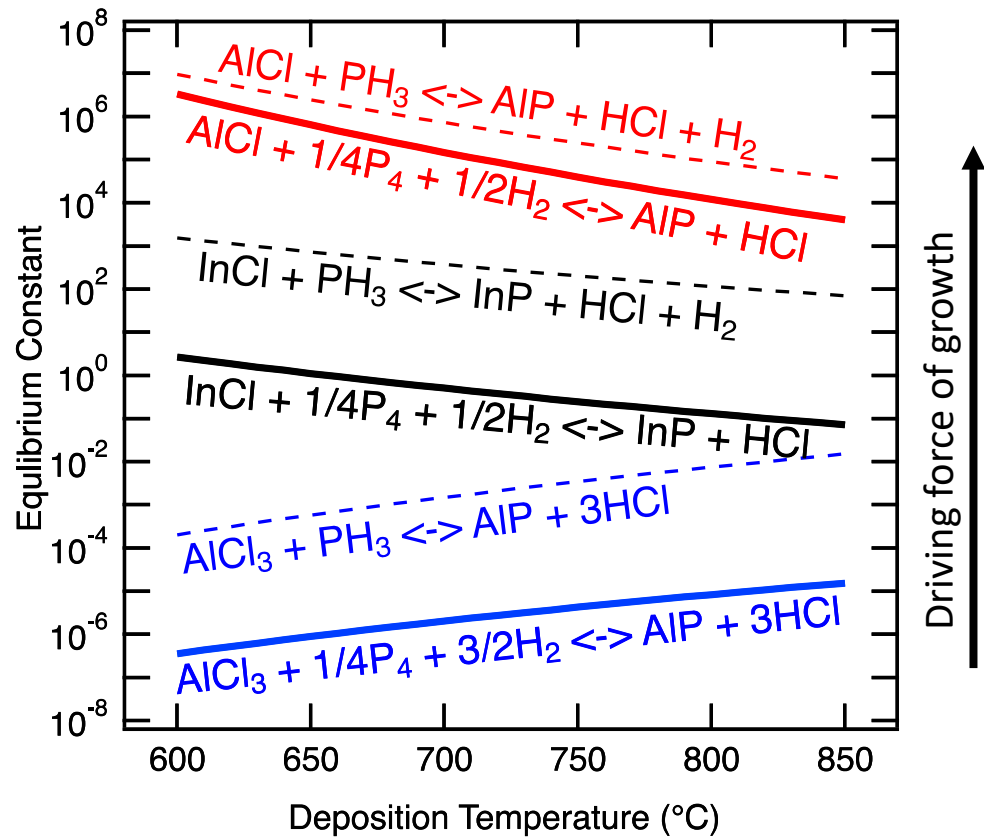
GaAs Cell



Tandem Cell

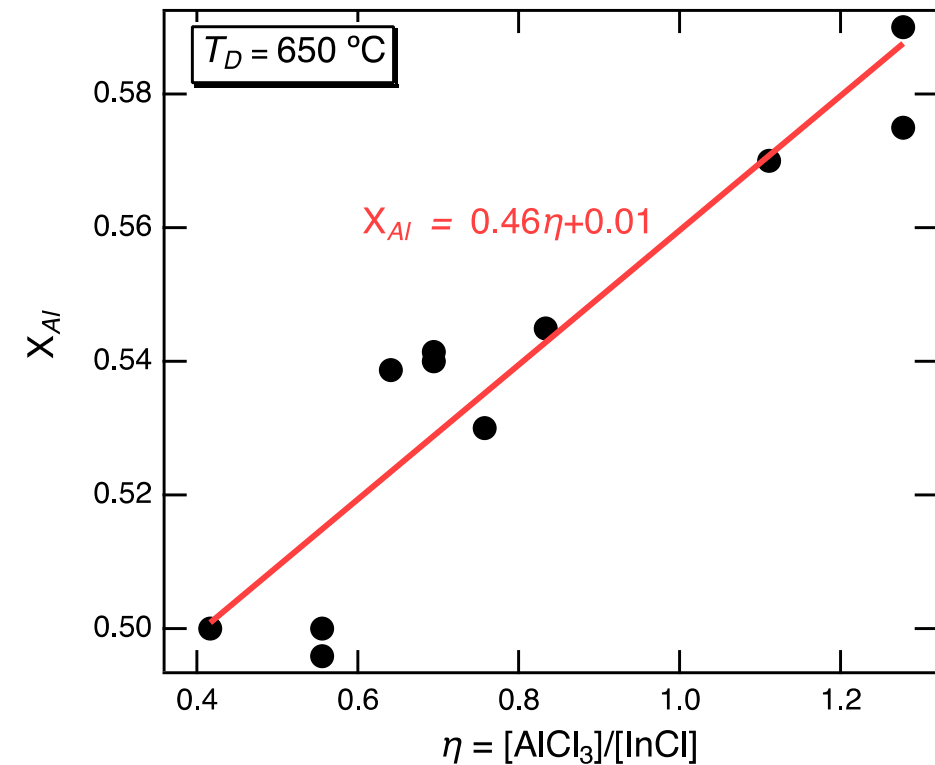


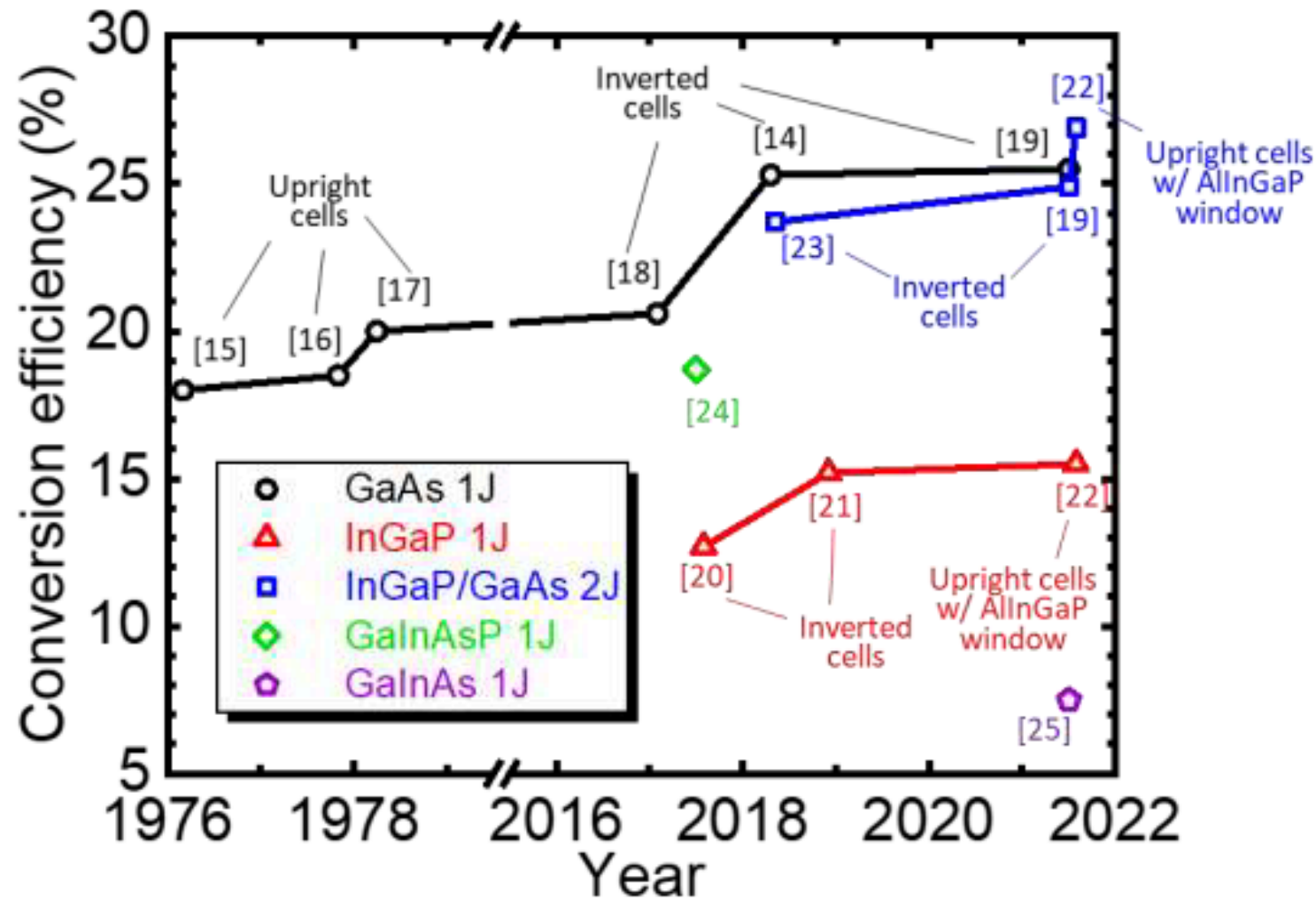
Using Uncracked Hydrides and AlCl₃ to Grow AlInP



- Uncracked PH₃ raises the thermodynamic driving force of growth, especially for AlCl₃
- Difference in growth from InCl vs. AlCl₃

- However, kinetics enable near unity [AlCl₃]/[InCl] to grow LM Al_{.53}In_{.47}P





Y. Shoji, et al., *Solar RRL*, p. 2100948, Dec. 2021

Learning curve of PV
grown in D-HVPE

- Many PV architectures demonstrated by HVPE

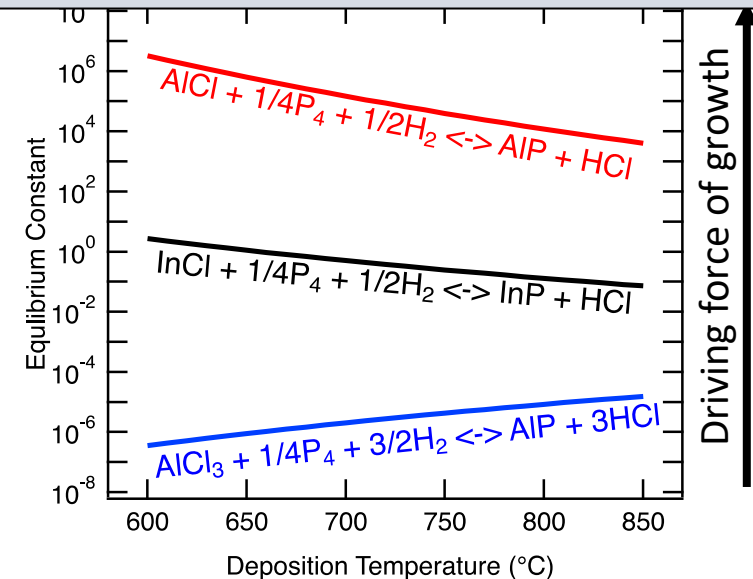
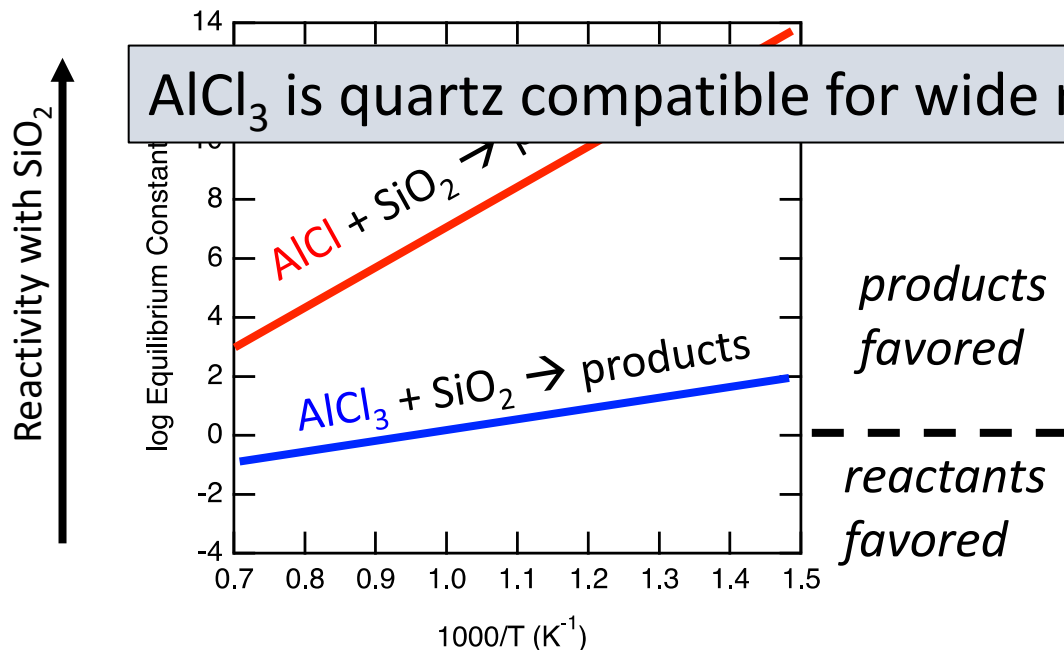
Challenges of Growing AlInP in HVPE

Al Precursor Reactivity with Quartz

- **AlCl** reacts strongly with quartz (SiO_2) reactor
- **AlCl₃** has low reactivity with quartz at typical growth temperatures

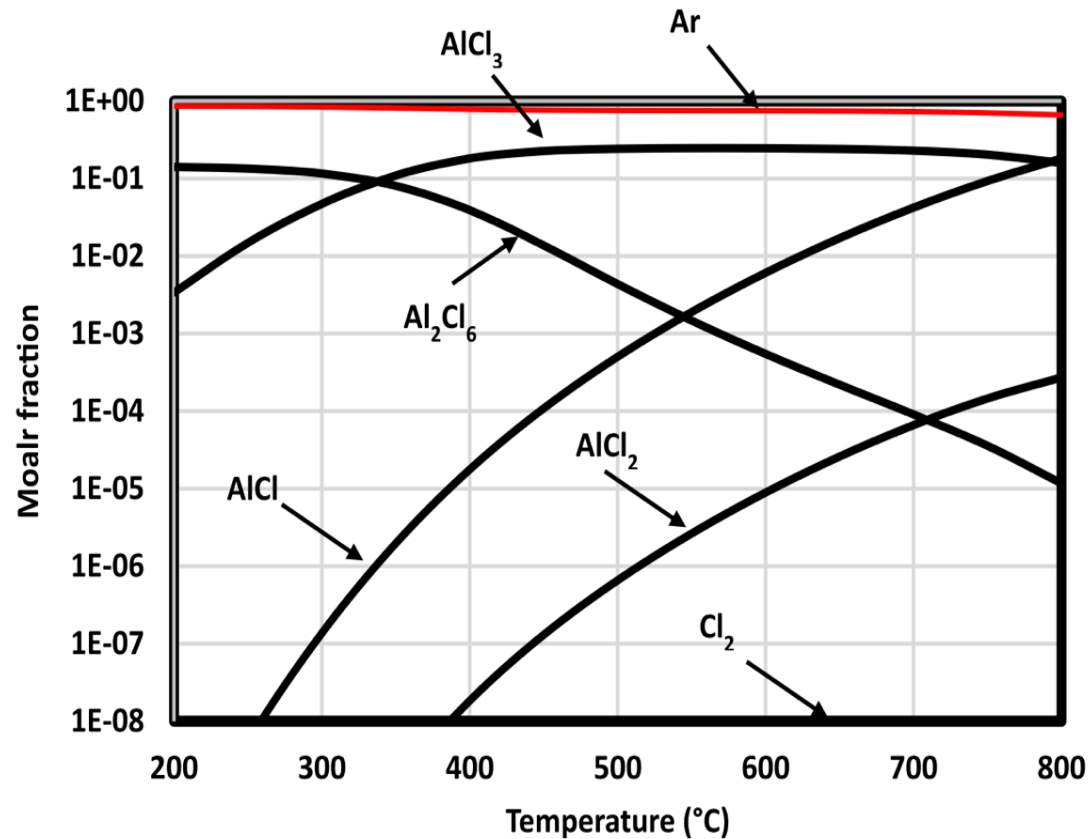
Precursor Growth Thermodynamics

- **AlCl**: large driving force for growth
→ **AIP predeposition**
- **AlCl₃**: small driving force for growth
→ **needs kinetic boost**
- **InCl**: far from either **AlCl** or **AlCl₃**
→ **theoretically impossible to grow AlInP**



Solution: Generate AlCl_3 without AlCl at lower temperature

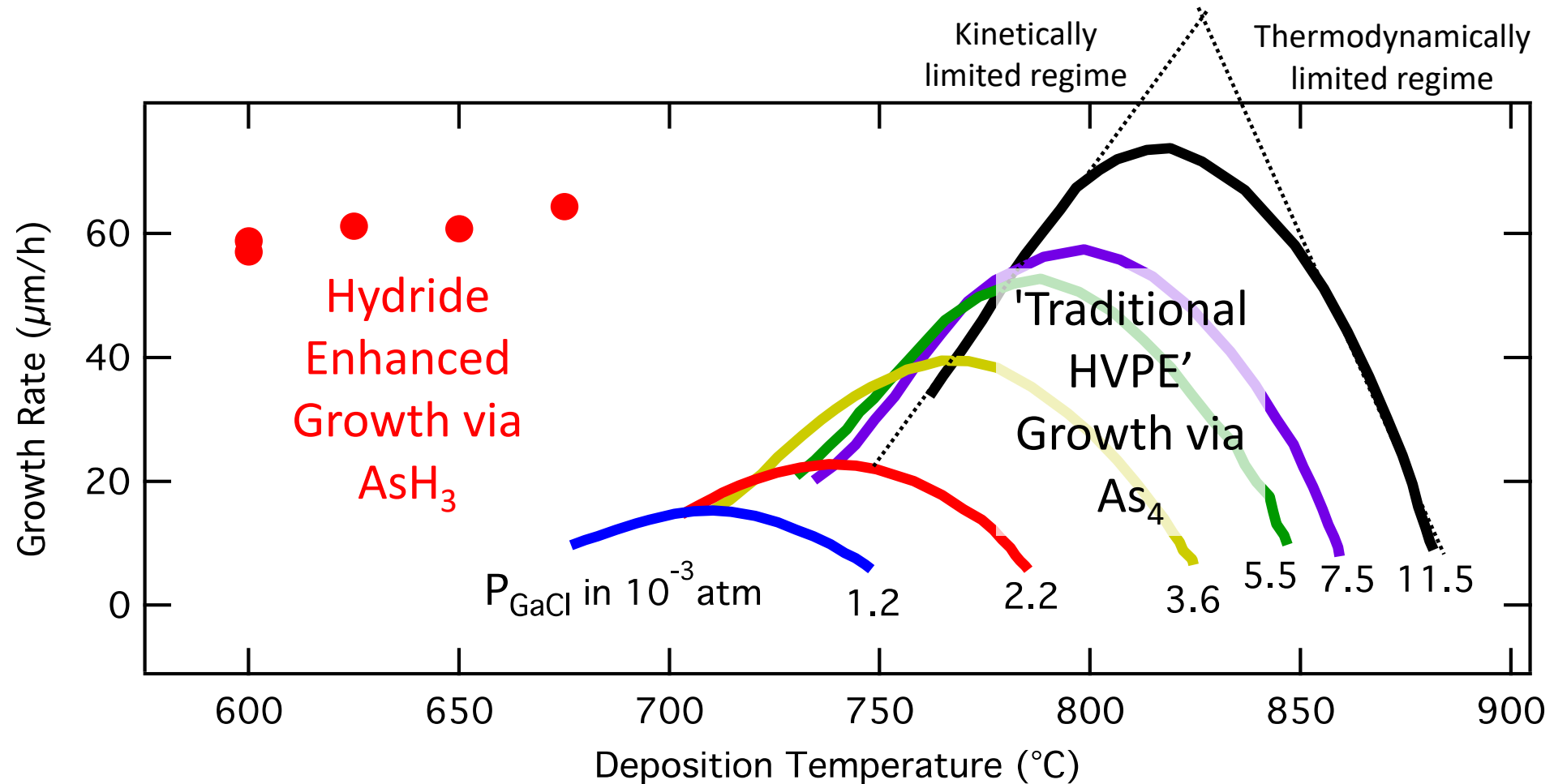
Molar fraction of Al-chlorides generated from HCl



Ex-Situ AlCl_3 Source

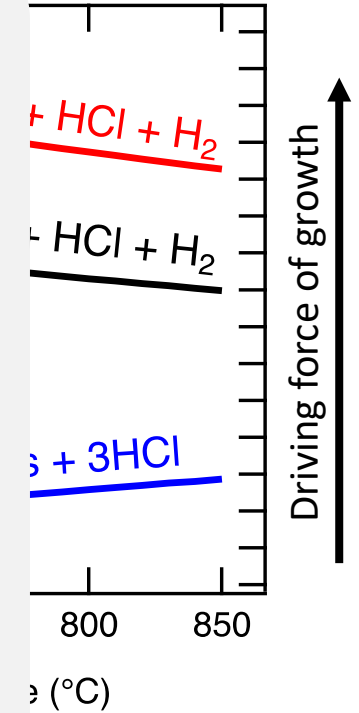
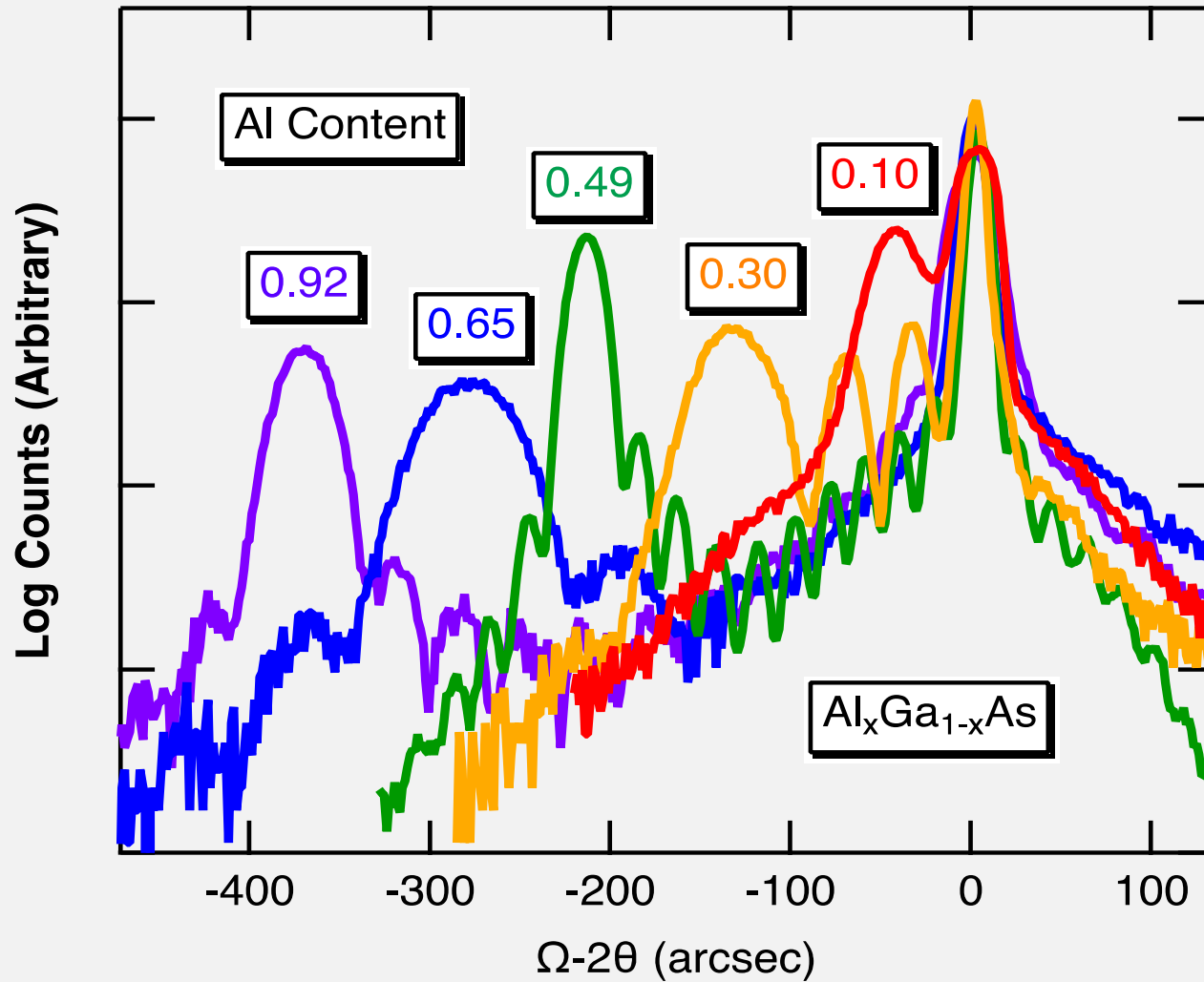
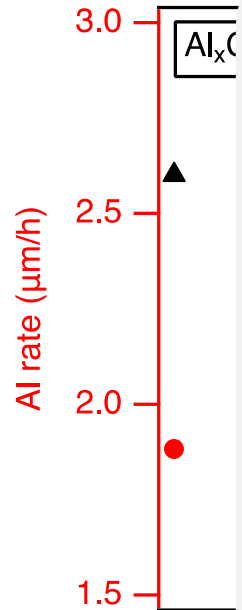
- Generate AlCl_3 just above reactor at colder temperature
- React Al and HCl @ 300 – 400°C to favor AlCl_3 generation
- 4 orders of magnitude less AlCl

Solution: Hydride Enhanced Growth to Enhance Kinetics



→ Apply hydride enhanced growth kinetics to growth of Al - materials!

Demonstrating Growth of AlGaAs via AlCl_3 & Uncracked AsH_3



- Al rate inc
- Ga rate de

dynamic
ning

