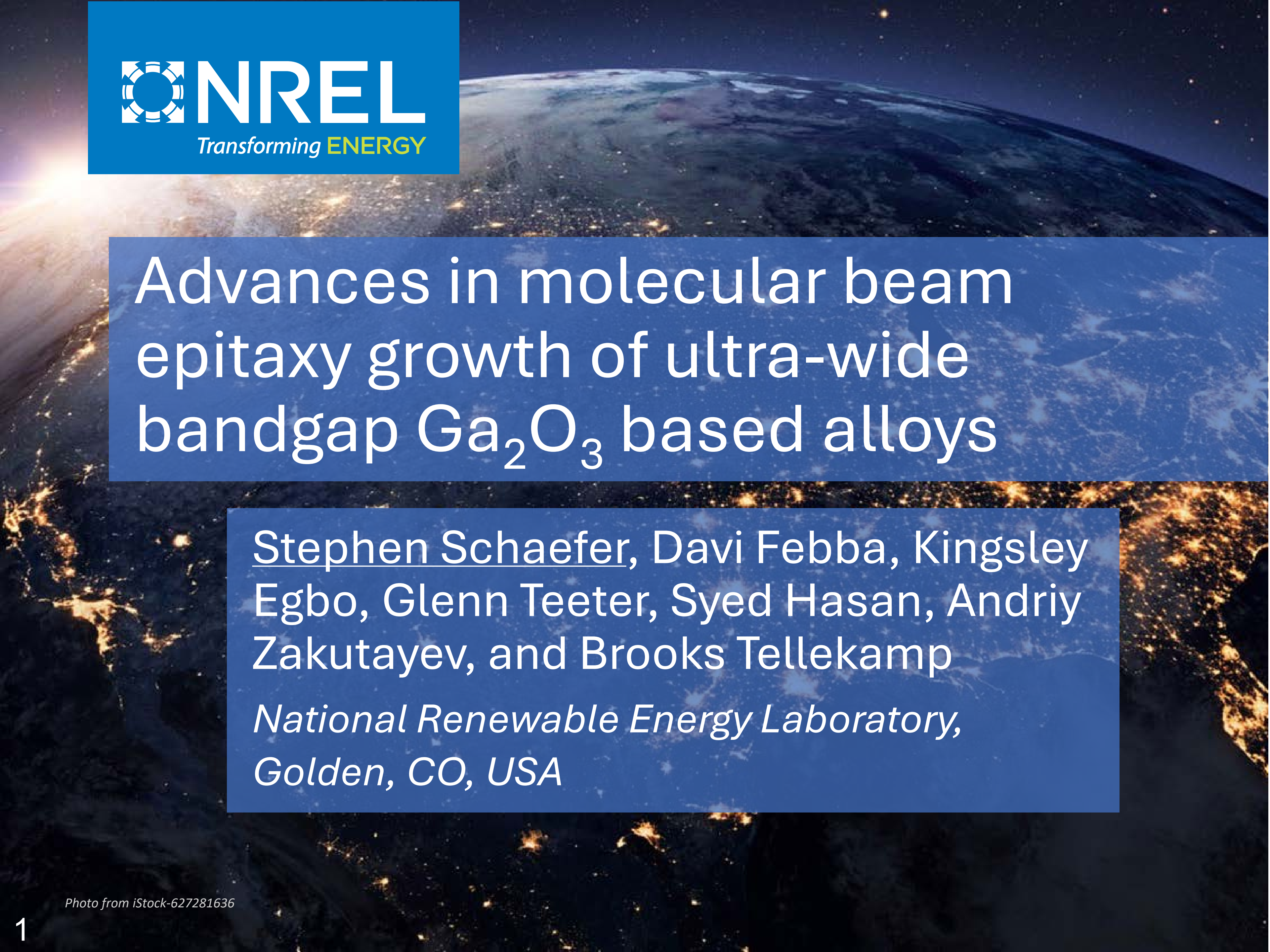

Advances in molecular beam epitaxy growth of ultra-wide bandgap Ga_2O_3 based alloys

Stephen Schaefer, Davi Febba, Kingsley Egbo, Glenn Teeter, Syed Hasan, Andriy Zakutayev, and Brooks Tellekamp

National Renewable Energy Laboratory, Golden, CO, USA

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Outline

- Ultrawide bandgap gallium oxide based alloys and PAMBE
- $(In_xGa_{1-x})_2O_3$ ternary alloys and high throughput MBE experimentation
- $(Al_xGa_{1-x-y}In_y)_2O_3$ quaternary alloys

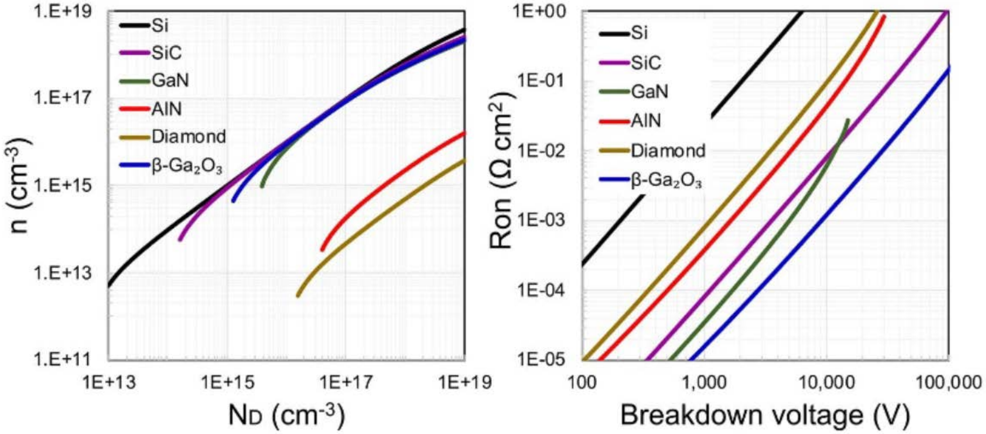
MBE

(noun) Acronym for Molecular Beam Epitaxy. Synonyms:
Mega Bucks Evaporator
Much Broken Equipment

Ultra wide bandgap (UWBG) materials for power electronics

Devices **Modules** **Applications**

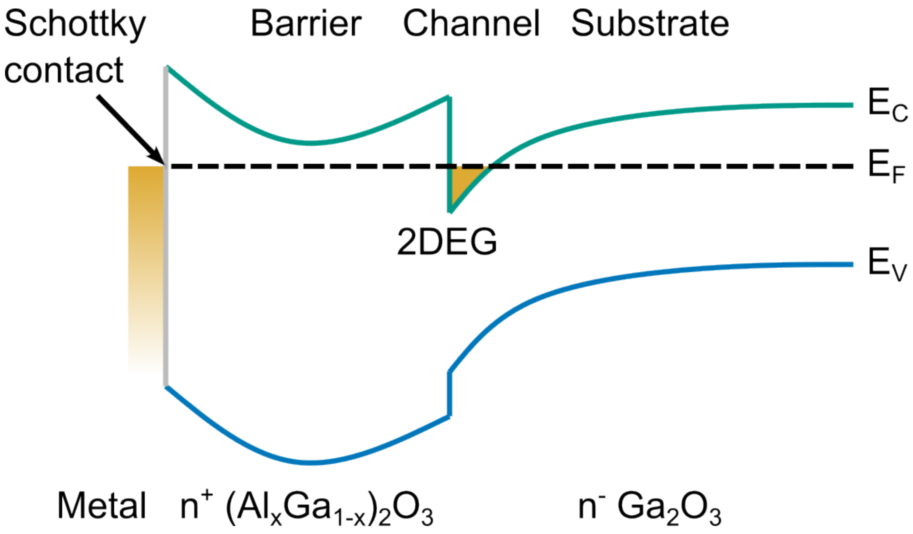
	Si	GaAs	4H-SiC	GaN	β-Ga_2O_3
Bandgap E_g (eV)	1.1	1.4	3.3	3.4	4.8-4.9
Electron mobility μ (cm_2/Vs)	1400	8000	1000	1200	300
Breakdown field E_b (MV/cm)	0.3	0.4	2.5	3.3	8
Rel. dielectric constant ε	11.8	12.9	9.7	9.0	10
Modified Baliga FOM $\frac{n}{N_{net}}\varepsilon\mu E_B^3$, 20 kV	1	15	320	1400	2335



Y. Zhang and J. S. Speck, Semicond. Sci. Technol. **35**, 125018 (2020).

Device applications for UWBG alloys

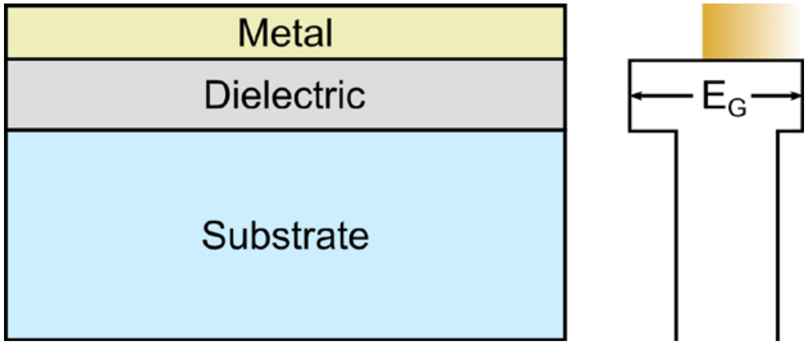
High electron mobility transistor (HEMT)



Needs:

- Sufficiently large conduction band offset between barrier & substrate
- Thickness of ~several tens of nm
- n-type dopable barrier
- High quality interface free of traps and defects

Dielectric layers for MOS



Needs:

- Dielectric layer bandgap energy larger than substrate (~10 k_BT or more)
- Variable thickness from ~1 to ~100 nm
- Highly insulating material with low unintentional doping concentration
- High quality interface free of traps and defects

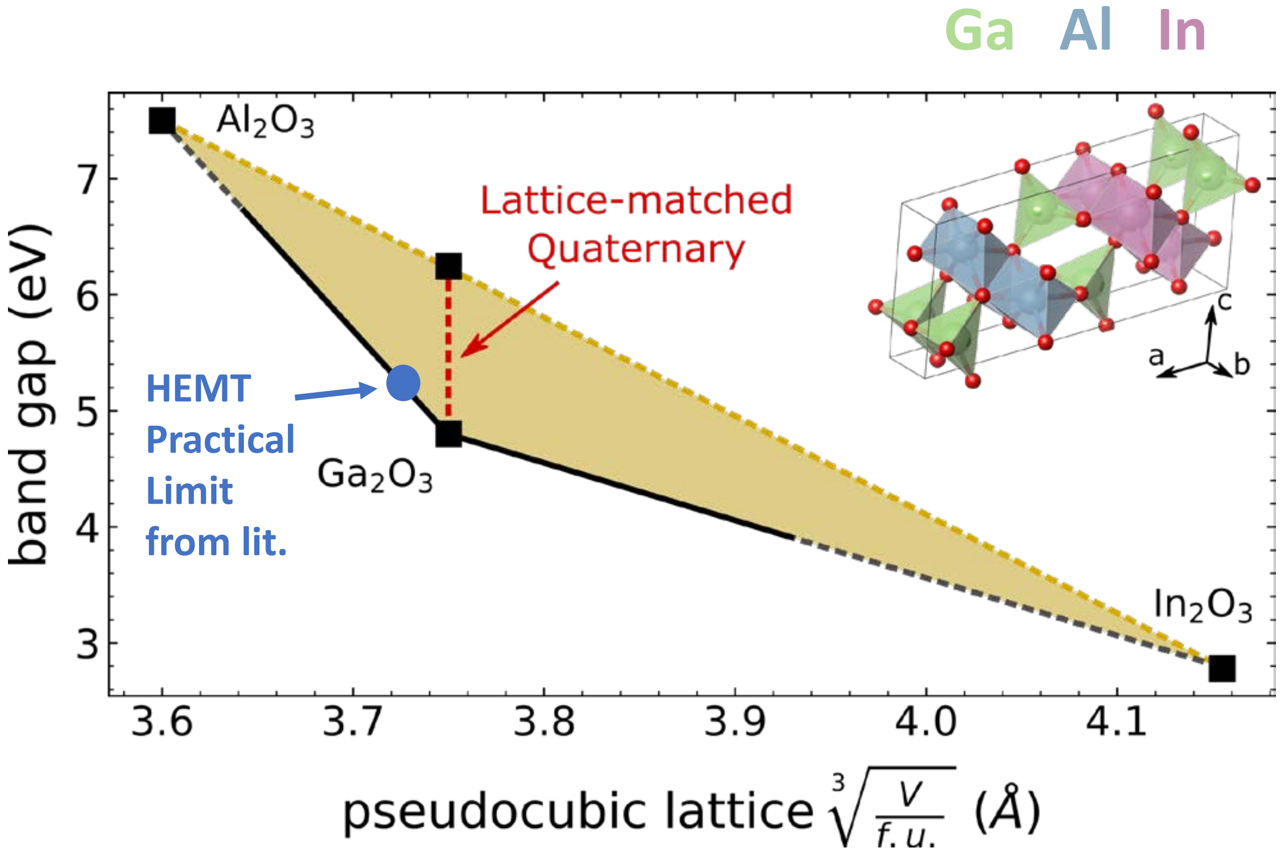
UWBG alloys can meet needs of both

Quaternary β-$(Al_xGa_{1-x-y}In_y)_2O_3$ alloys

Monoclinic phase	
Ga_2O_3	4.76 eV
Al_2O_3	7.2-7.5 eV
In_2O_3	2.7 eV

Overcome current limitations of phase stability through strain-balanced quaternary alloys

Alloy with Al to increase bandgap energy and alloy with In to counteract tensile strain

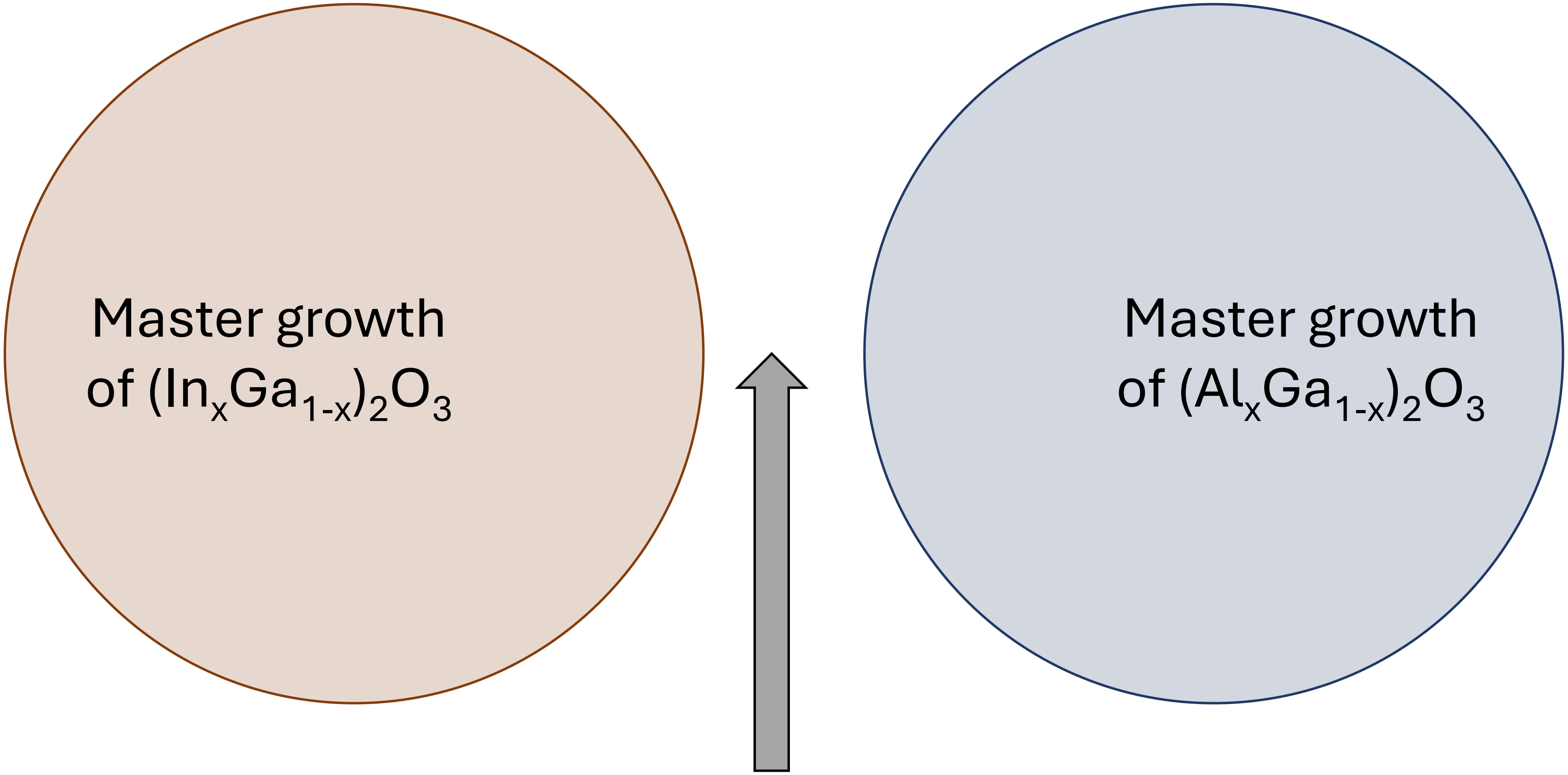


Lattice-matched $(Al_xGa_{1-x-y}In_y)_2O_3$ alloys span ~4.7 – 6.3 eV

Quaternary alloys enable independent adjustment of strain and bandgap energy

- ➢ Useful for band engineering without strain induced defects

Approach



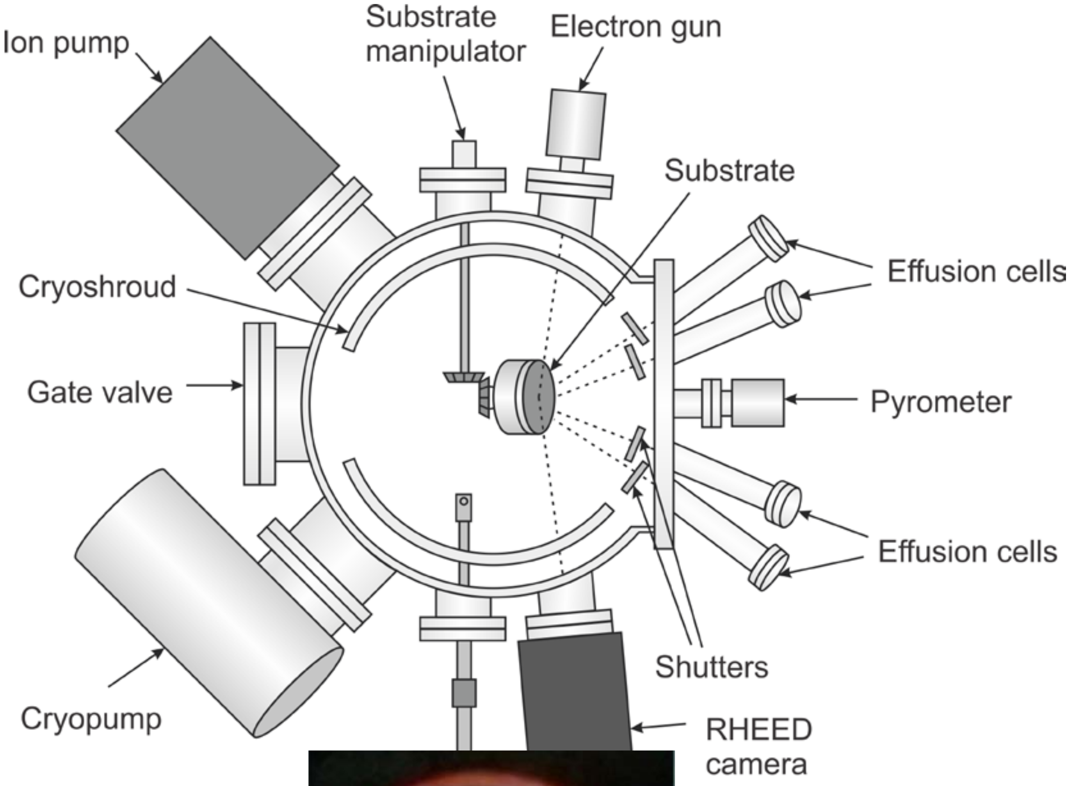
Master growth of $(In_xGa_{1-x})_2O_3$

Master growth of $(Al_xGa_{1-x})_2O_3$

Identify $(Al_xGa_{1-x-y}In_y)_2O_3$ growth window

Plasma-assisted molecular beam epitaxy (PAMBE)

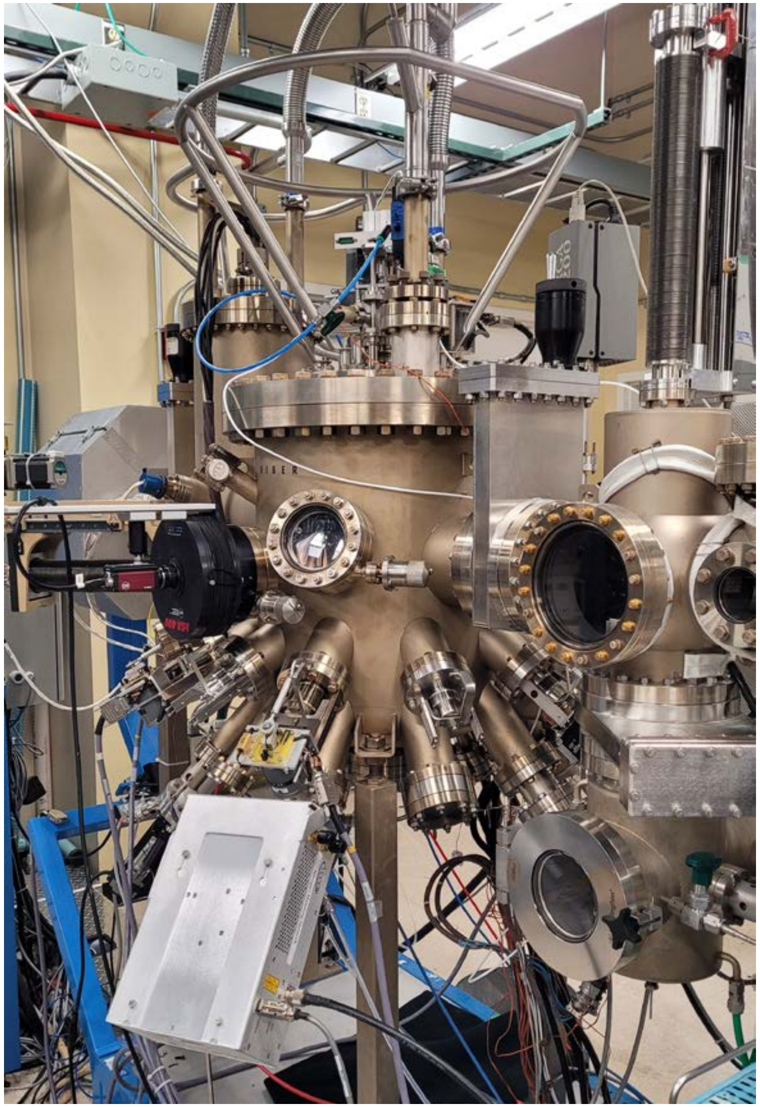
- Ultrahigh vacuum base pressure of 10^{-8} to 10^{-10} torr. Typical plasma operating pressure 10^{-5} torr
- Typical growth rate on the order of 1 Å/s = 6 nm/min = 0.36 µm/hr
- Low impurity concentrations on the order of 10^{13} cm^{-3} can be achieved
- Highly precise layer-by-layer control of growth

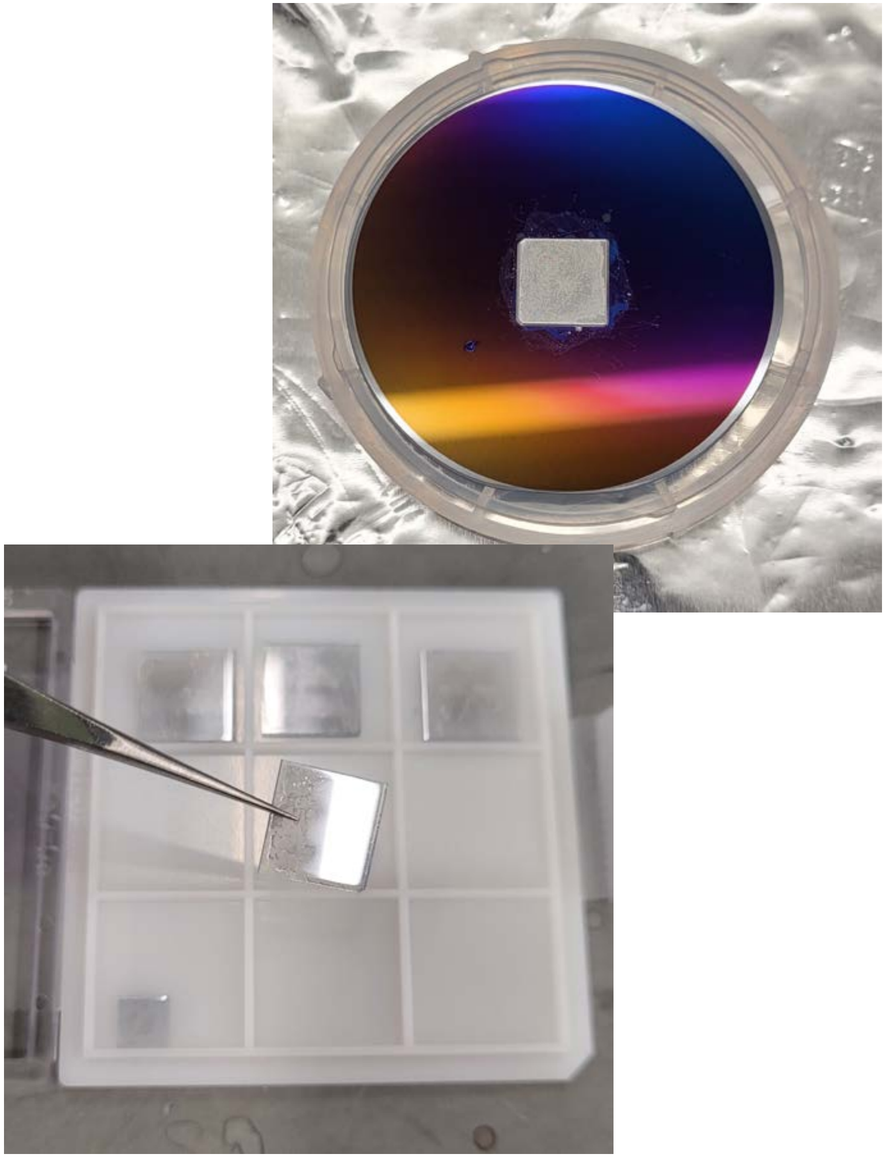


- Addition of an RF plasma source enables growth of inorganic oxide and nitride semiconductors
  - ➢ *Plasma splits inert molecular O_2 into reactive atomic O and O^+ ions*

https://vesconm.com/products/rf-plasma-sources/

Oxide MBE for UWBG alloys





Photos by Stephen Schaefer, NREL

Outline

- Ultrawide bandgap gallium oxide based alloys and MBE
- $(In_xGa_{1-x})_2O_3$ ternary alloys and high throughput MBE experimentation
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Can we speed up the MBE experimental process?

Traditional experimental paradigm is slow

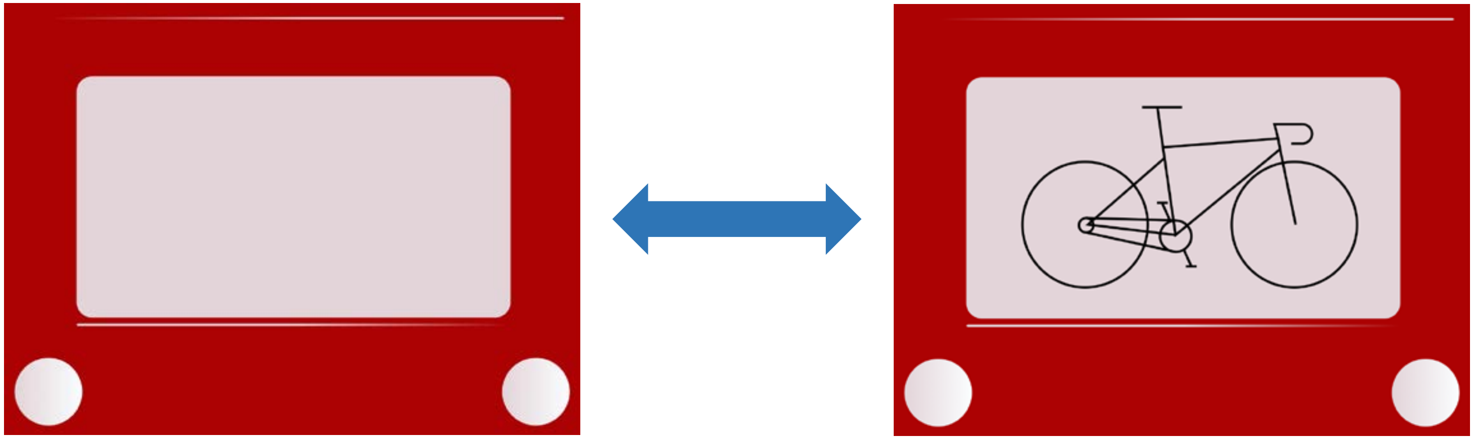
Plasma-assisted MBE growth of Ga_2O_3 has several advantages:

- Precise calibration of elemental Ga and In fluxes, wide temperature range
- Ultra high vacuum, low defect incorporation
- *In-situ* characterization techniques

But – MBE is slow!

We need a way to rapidly explore the available growth space:
Ga, In, and oxygen fluxes, growth temperature

What if we could restore our substrate back to its initial state, like an Etch-a-Sketch?



Cyclical Ga_2O_3 growth and etch-back

With gallium oxide, we can!

$4Ga(a) + Ga_2O_3(s) \rightarrow 3Ga_2O(a)$ [1]

Supplying only Ga flux results in *etching* of the Ga_2O_3 film

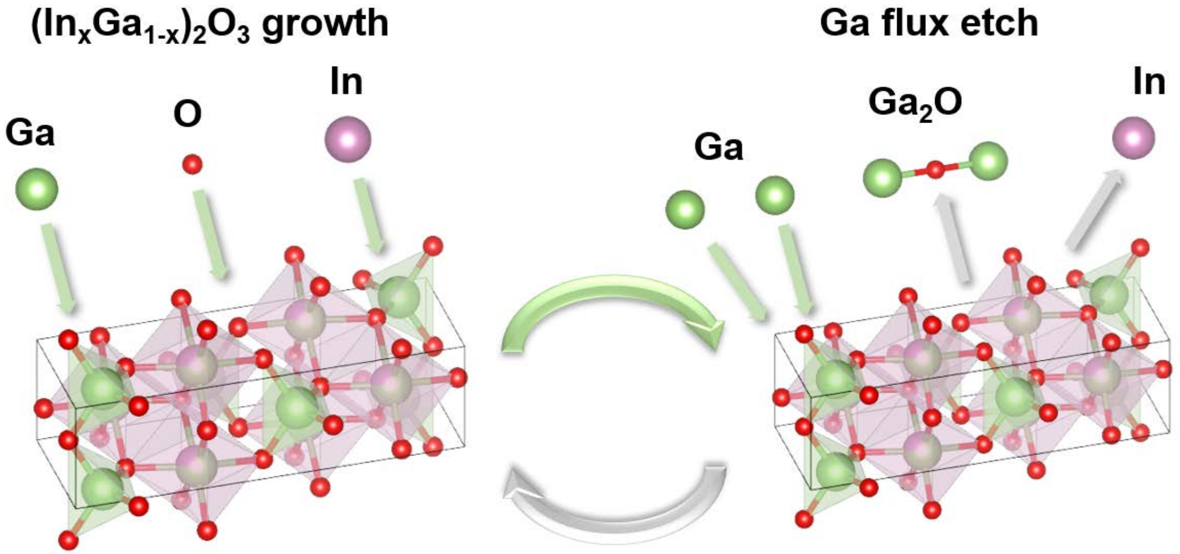
Ga_2O readily desorbs from surface

It also works for $(InGa)_2O_3$

$2(r_{Ga}-(1-x))Ga(a) + (In_xGa_{1-x})_2O_3(s) \rightarrow$
$2xIn(a) + Ga_2O_3(s) + 2(r_{Ga}-1)Ga(a)$

In desorbs at typical growth temps

Ga_2O_3 is then etched by excess Ga

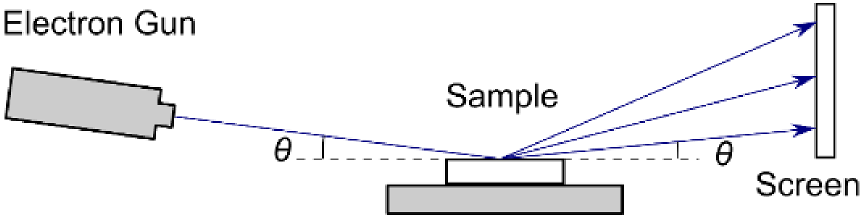


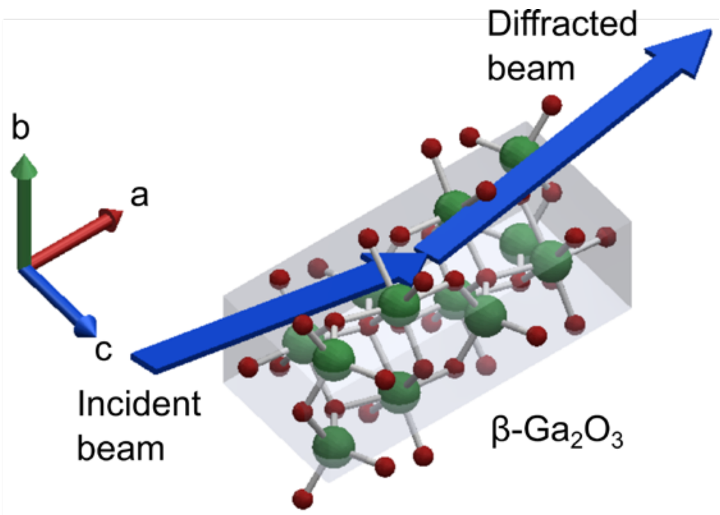
6× increase in experimental throughput

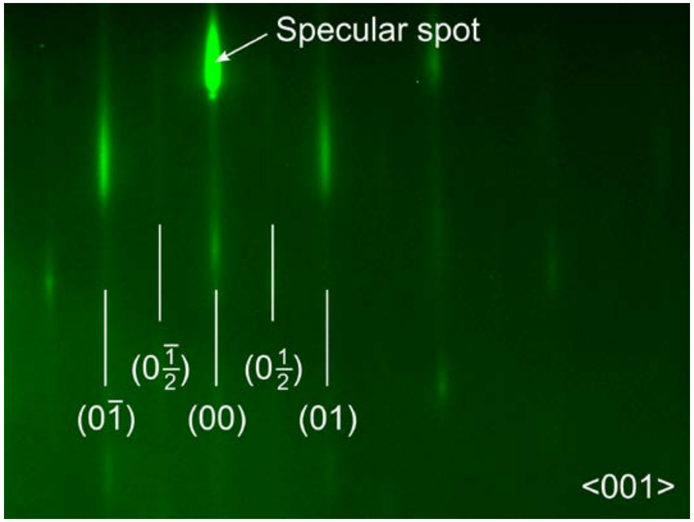
[1] P. Vogt and O. Bierwagen, "The competing oxide and sub-oxide formation in metal-oxide molecular beam epitaxy", Appl. Phys. Lett., 2015, 106, 081910.

Reflection high-energy electron diffraction (RHEED)

- For this to work, we need an *in-situ* characterization method
- RHEED is a highly surface-sensitive UHV compatible technique
- The pattern is (approximately) an image of the reciprocal lattice from the 2D growth surface



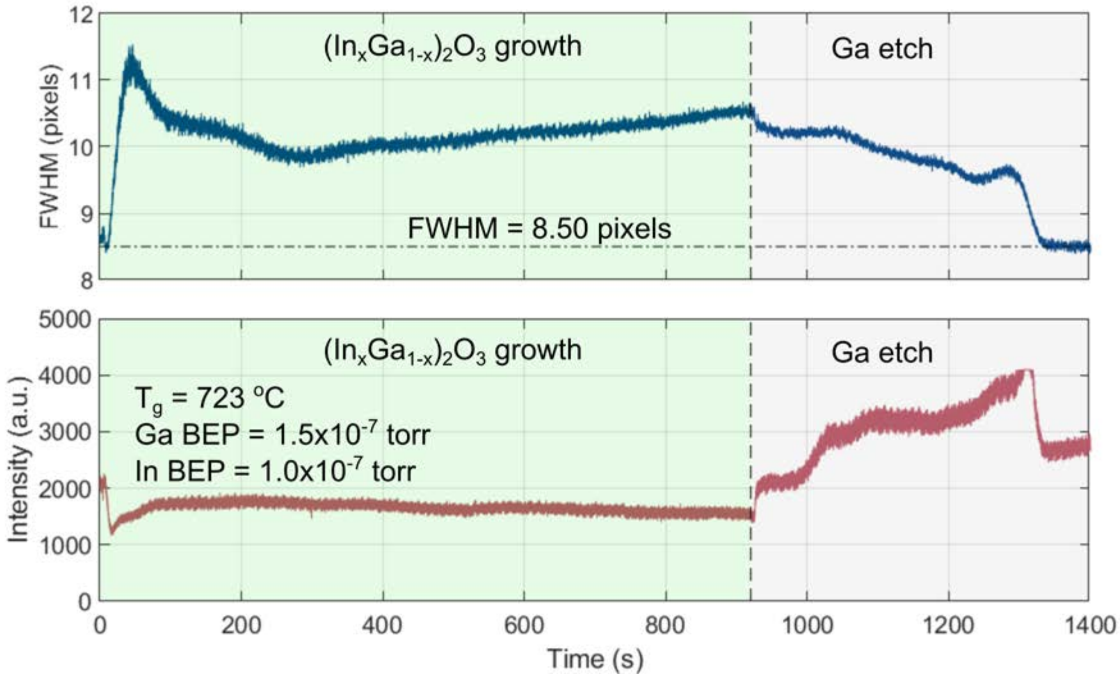




Cyclical growth/etch is highly repeatable

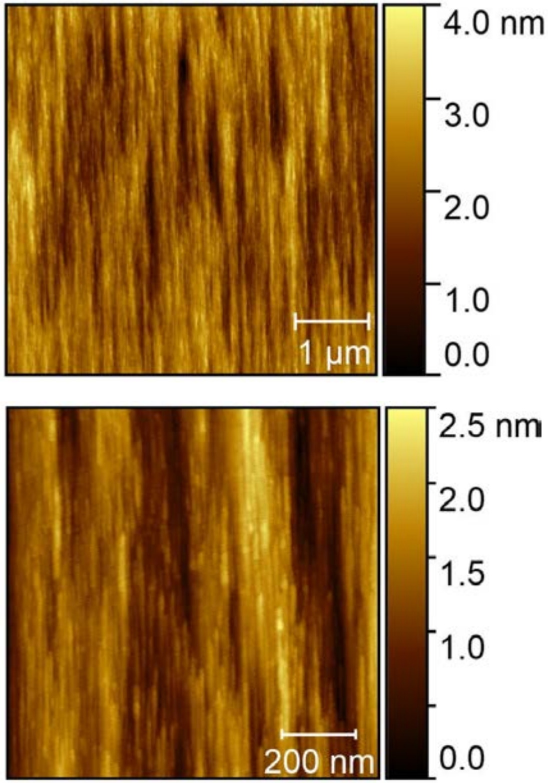
Track the FWHM and intensity of the specular (00) streak vs time

The FWHM returns to its initial value after the grown epilayer is completely removed



Limiting factor is the indium bonding process used to mount the Ga_2O_3 wafer!

6× increase in experimental iteration rate

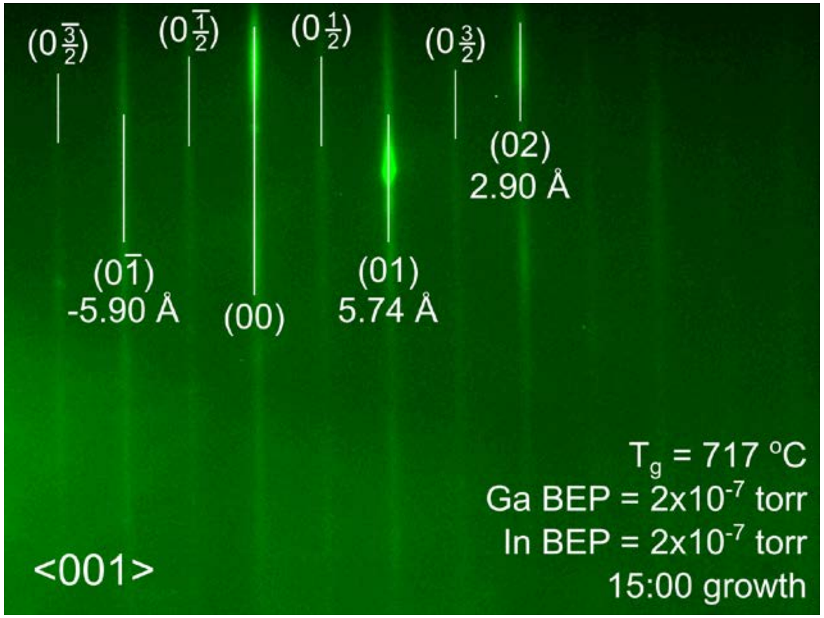


Sample was subjected to <u>46</u> growth/etch cycles

<1.6 nm RMS roughness over 5×5 µm

Two classes of RHEED patterns observed

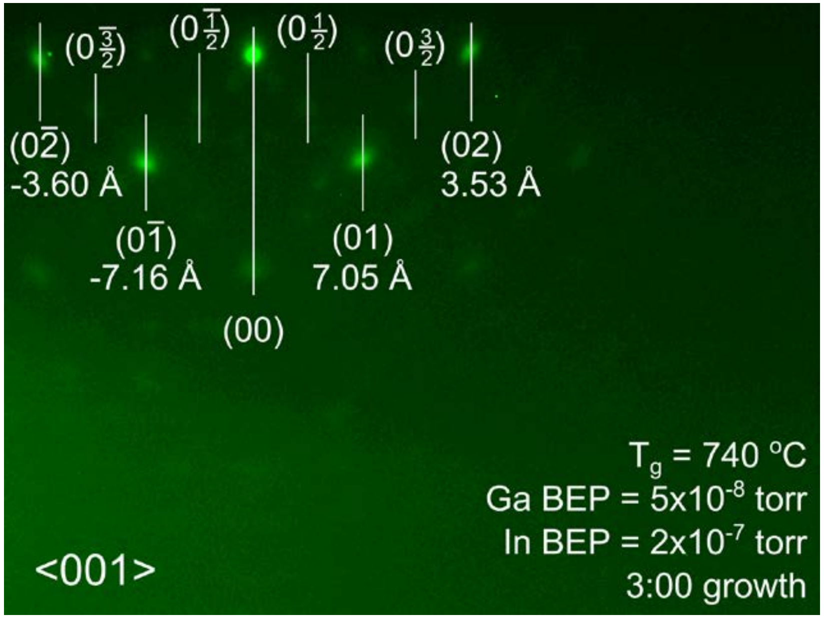
Streaky 2×



Typical of homoepitaxial β-Ga_2O_3 growth

Epilayer maintains monoclinic unit cell

Spotty/faceted



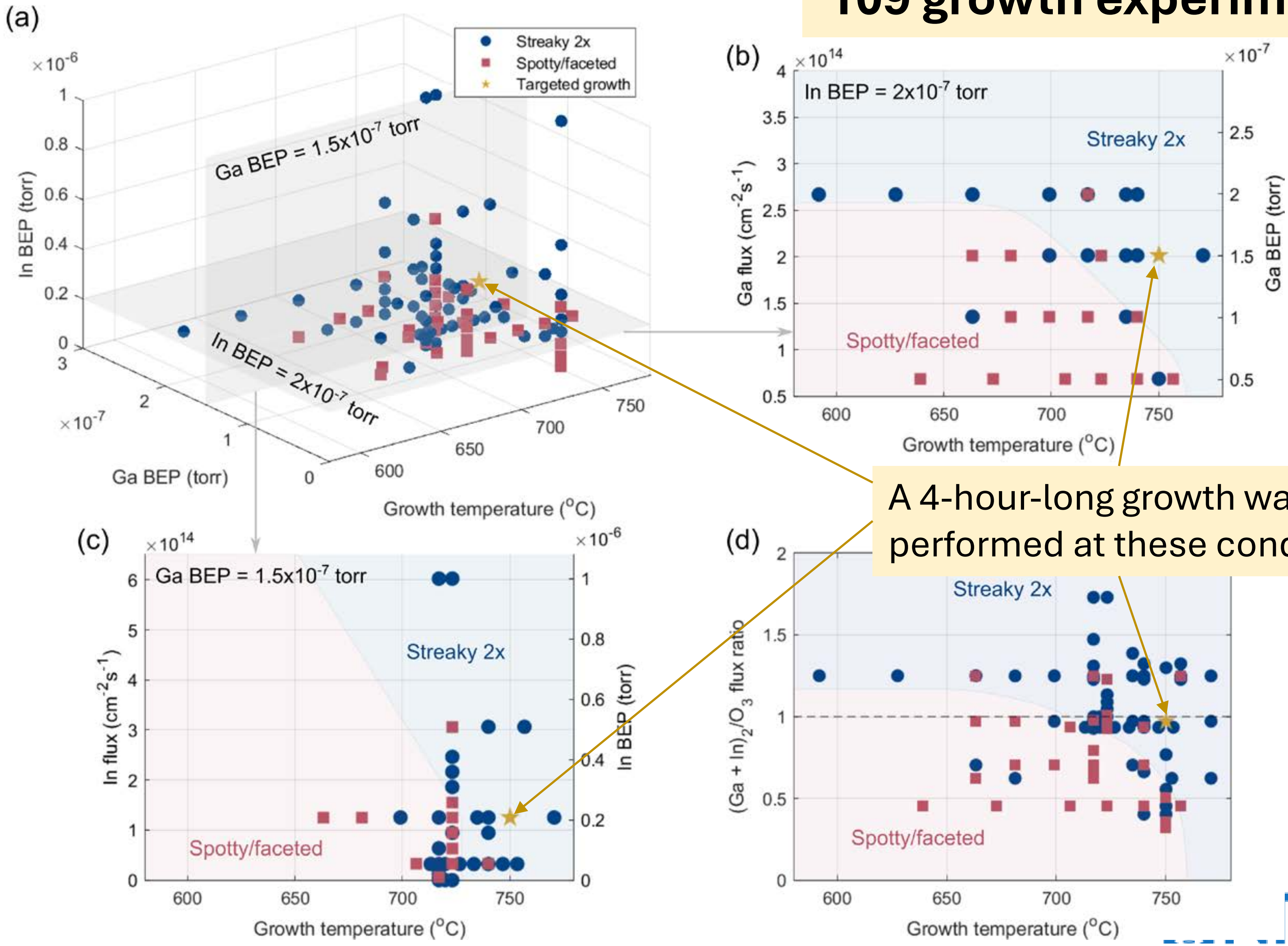
Typical of phase separated bixbyite In_2O_3 growth

Streak spacing is consistent with diffraction from In_2O_3 (110) plane

Patterns were classified using the Learned Perceptual Image Patch Similarity (LPIPS) metric, carried out using the PyTorch framework

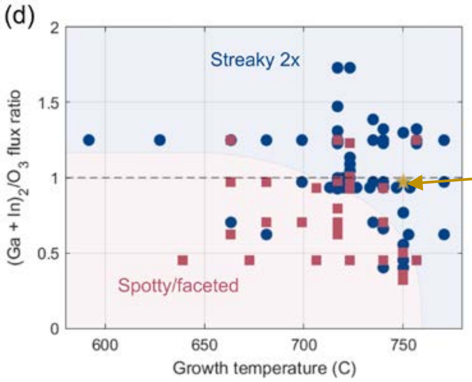
Rapid exploration of a 3-D growth space

109 growth experiments

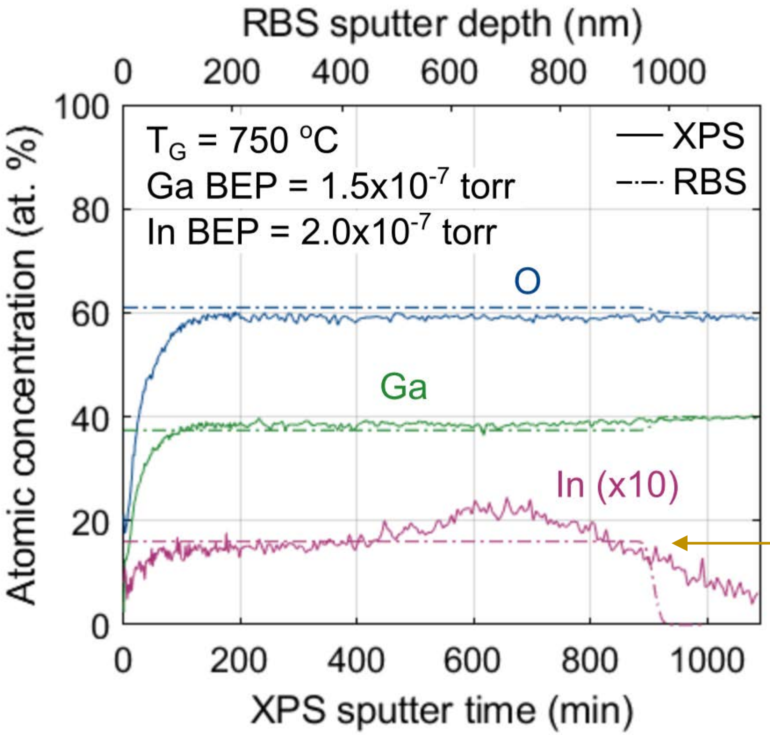


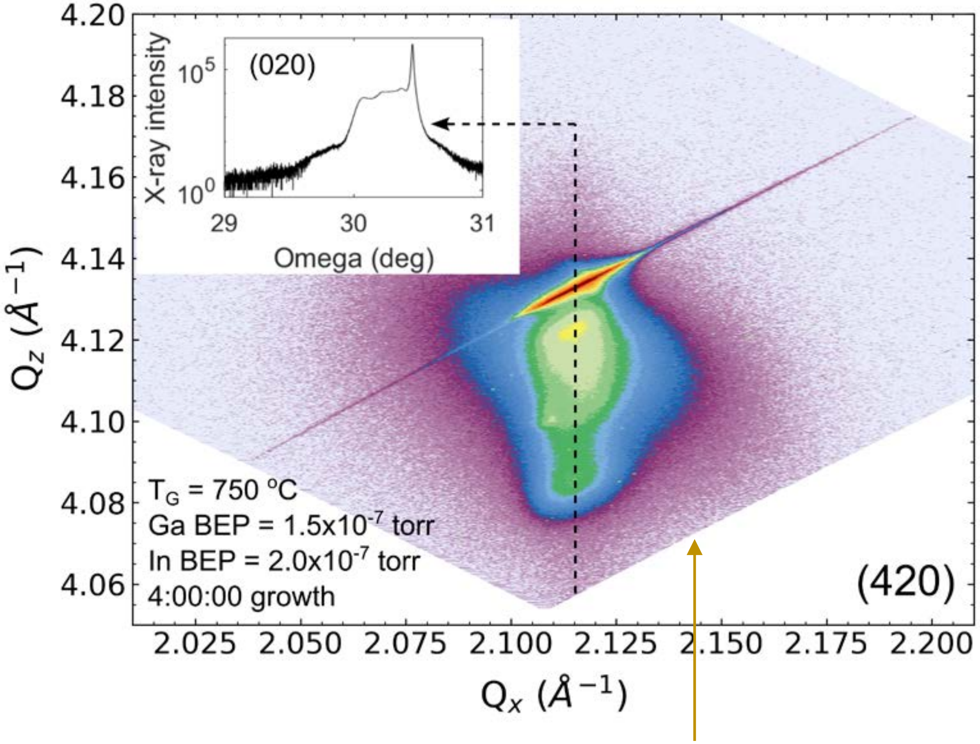
A 4-hour-long growth was performed at these conditions

Targeted thick $(In_xGa_{1-x})_2O_3$ growth



Growth conditions selected near boundary





X-ray diffraction indicates monoclinic crystal phase, non-uniform In incorporation

XPS and RBS confirm In incorporation with 5.6% peak In mole fraction (2.2 at. %)

~900 nm thick film

Outline

Ultrawide bandgap gallium oxide based alloys and MBE

$(In_xGa_{1-x})_2O_3$ ternary alloys and high throughput MBE experimentation

$(Al_xGa_{1-x-y}In_y)_2O_3$ quaternary alloys

Leveraging what we learned about $(In_xGa_{1-x})_2O_3$ to grow the first reported monoclinic $(Al_xGa_{1-x-y}In_y)_2O_3$ alloy

Al flux dependent growth series

$(AlGa)_2O_3$ growth:

- All aluminum flux incorporates
- Growth temperatures above ~700 °C

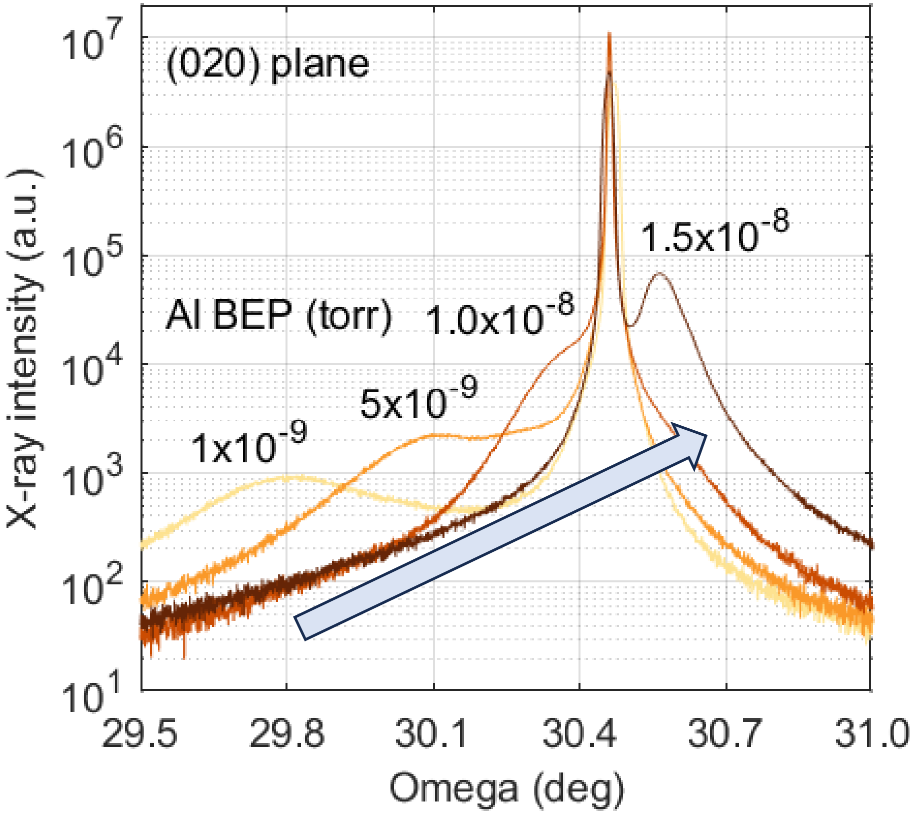
$(InGa)_2O_3$ growth:

- Low Ga/O flux ratio and high In flux
- Grow above ~725 °C

Choose growth conditions based on $(InGa)_2O_3$ study:

- Growth temp = 750 °C
- Ga BEP = 5×10^{-8} torr
- In BEP = 2×10^{-7} torr

Vary Al BEP from $1\times10^{-9} – 1.5\times10^{-8}$ torr

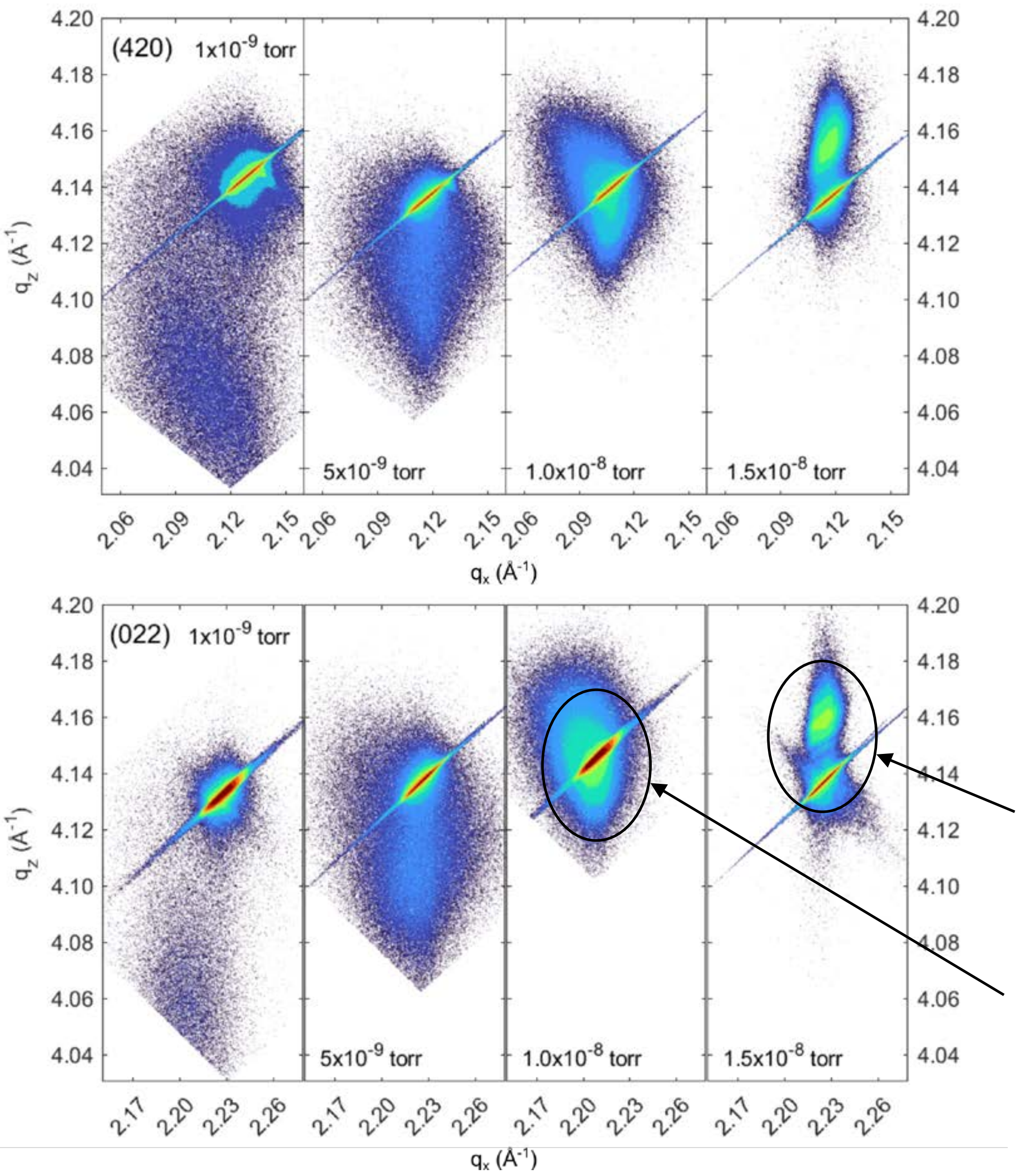


Monotonic shift with increasing Al flux

Al BEP (torr)	Mole fraction (%)		
	Al	Ga	In
1×10^{-9}	1.4	83.1	15.5
5×10^{-9}	8.5	81.7	9.8
1.0×10^{-8}	16.8	76.5	6.7
1.5×10^{-8}	24.4	72.5	3.1

Nearly lattice matched to β-Ga_2O_3

Reciprocal space maps



Films are coherently strained to the β-Ga_2O_3 substrate

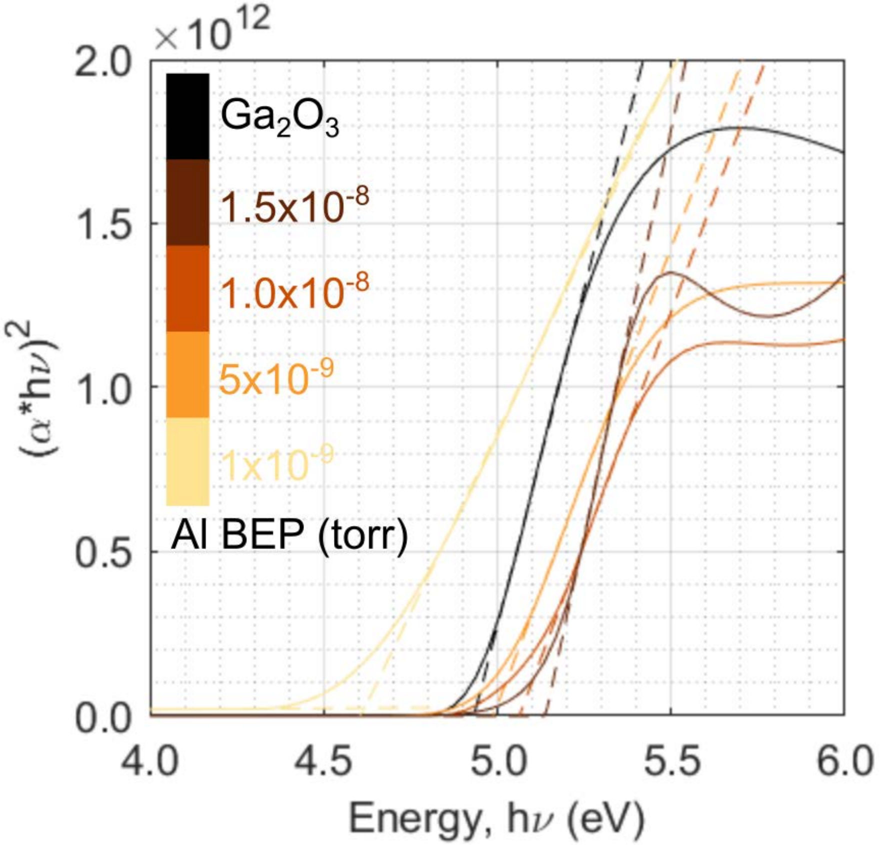
Identify strained lattice constants from reciprocal space maps of (420) and (022) planes

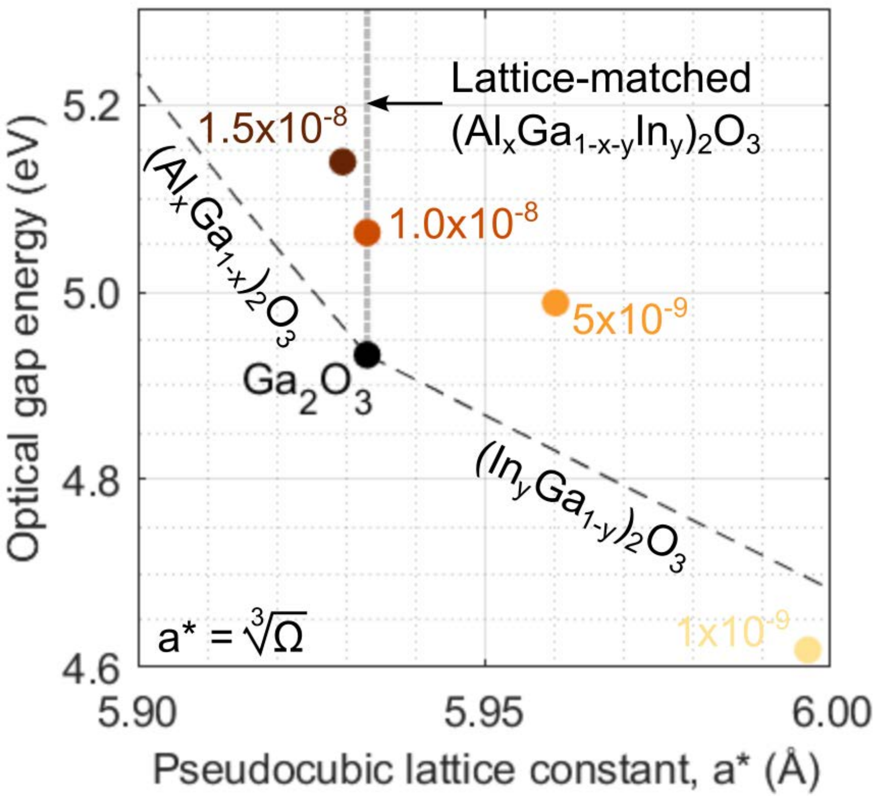
Al BEP (torr)	*a* (Å)	*b* (Å)	*c* (Å)
1×10^{-9}	12.366	3.088	5.888
5×10^{-9}	12.245	3.058	5.823
1×10^{-8}	12.214	3.037	5.798
1.5×10^{-8}	12.220	3.024	5.810
Reference β-Ga_2O_3	12.214	3.0371	5.7981

Pendellösung fringes indicate 130 nm film thickness for highest Al flux sample (1.5×10^{-8} torr)

$(Al_{0.17}Ga_{0.76}In_{0.07})_2O_3$ lattice matched to β-Ga_2O_3

Absorption onset shift with increasing Al





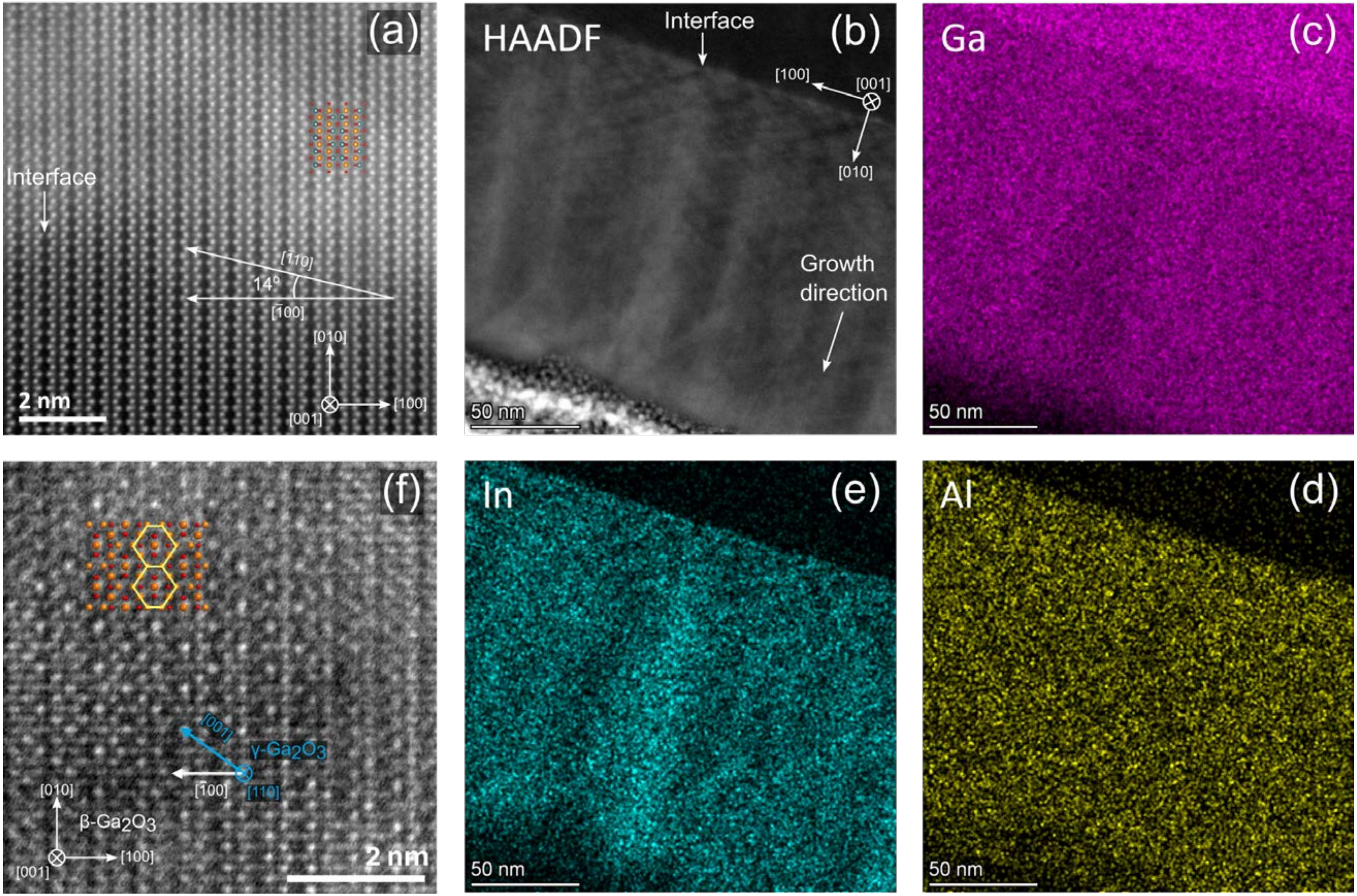
Spectroscopic ellipsometry measures absorption coefficient

Tauc plot fits show increase in absorption onset energy

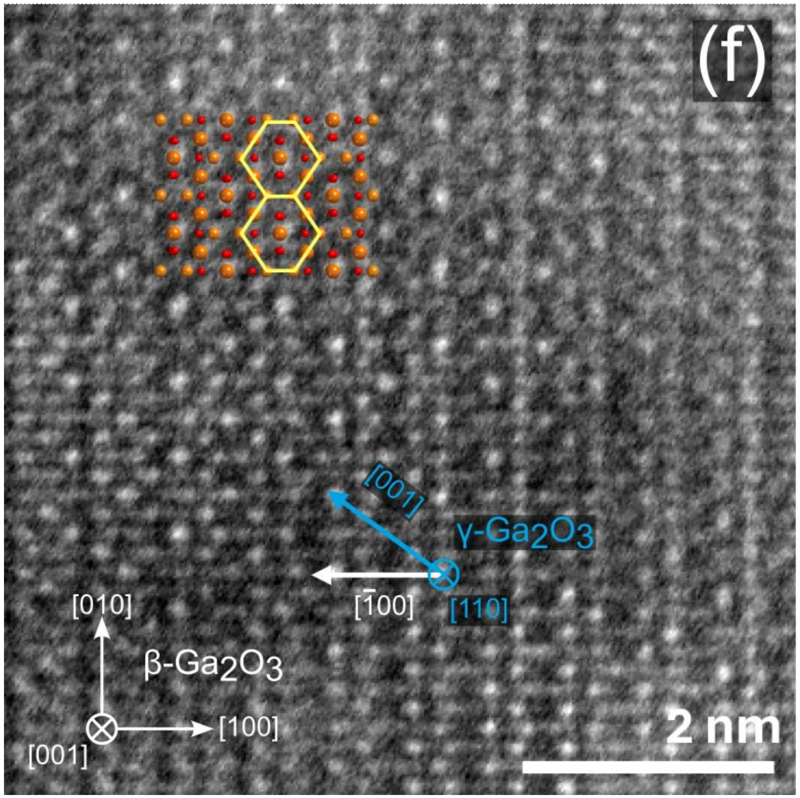
Lattice matched $(Al_{0.17}Ga_{0.76}In_{0.07})_2O_3$ exhibits 0.13 eV increase w.r.t. β-Ga_2O_3

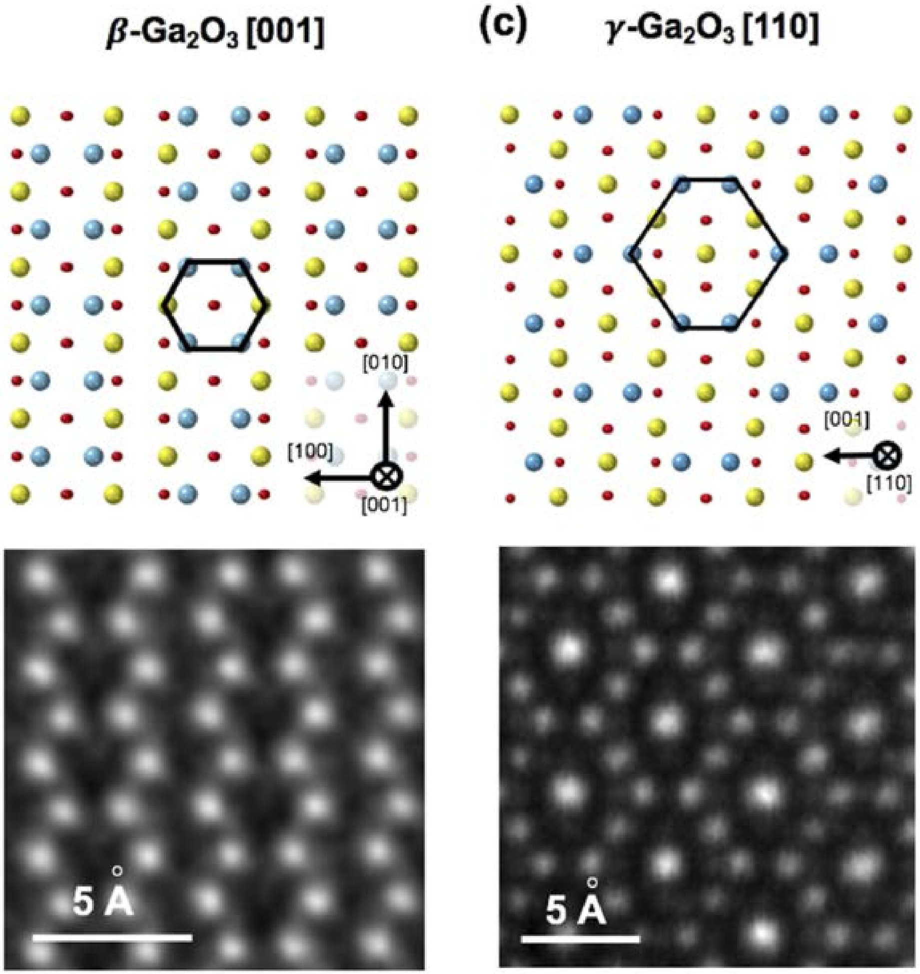
~0.12 eV conduction band offset assuming 89% band offset in CB

Transmission electron microscopy



γ-phase inclusions





C. S. Change *et al*, APL Mater. **9**, 051119 (2021). https://doi.org/10.1063/5.0038861

γ-Ga_2O_3 phase inclusions commonly observed for $(AlGa)_2O_3$ growth

Small clusters of γ -Ga_2O_3 phase not expected to strongly influence bulk properties

Conclusions and future work

- UWBG Ga_2O_3 based alloys are promising candidates for high voltage, high operating temperature power conversion devices
- Alloying with Al is easy, but alloying with In is challenging
- By mastering growth of the ternary alloys $(AlGa)_2O_3$ and $(InGa)_2O_3$ separately, we have demonstrated the first synthesis of monoclinic quaternary $(AlGaIn)_2O_3$
- The unique suboxide kinetics of gallium oxide growth were leveraged to develop a “high throughput MBE” experimental methodology
- Quantitative RHEED measurements and image analysis could be deployed in future work to optimize composition and microstructure for $(AlGaIn)_2O_3$
- The cyclical MBE growth/etch methodology can be used to examine other emerging oxide semiconductors, such as GeO_2

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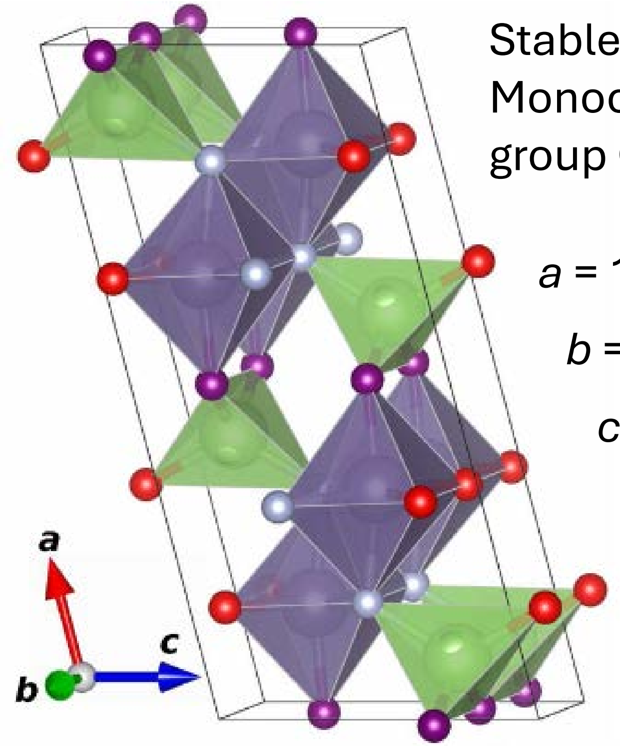
Transforming ENERGY

Extra slides

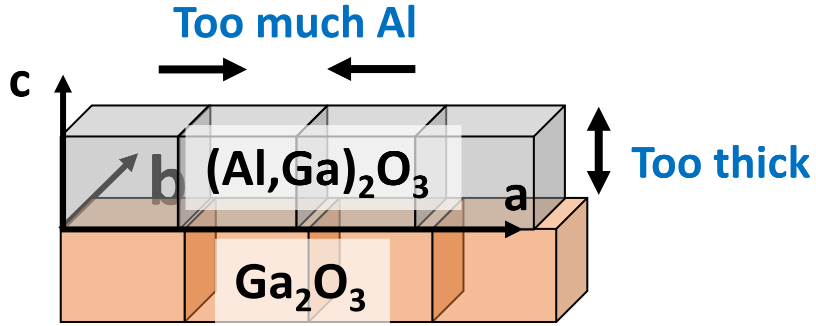
Ultra wide bandgap β-Ga_2O_3 alloys



Stable phase at STP
Monoclinic, space group C2/m

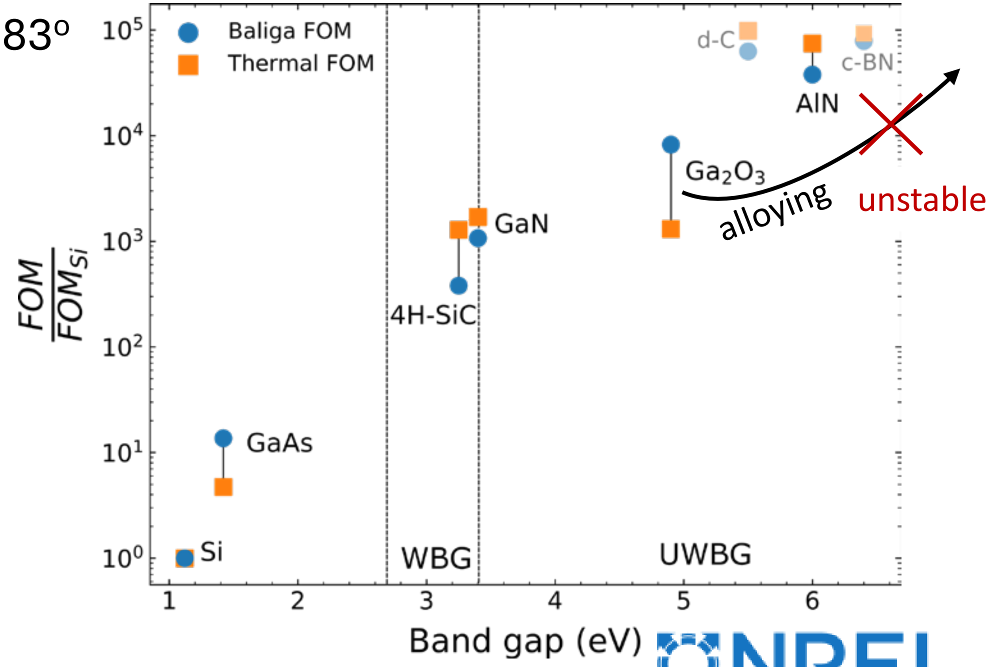
a = 12.214 Å
b = 3.0371 Å
c = 5.7981 Å
β = 103.83°

H. Peealaers and C. G. Van de Walle, Phys. Status Solidi B **252**, No. 4 (2015)



Increasing thickness and/or Al-content can result in phase separation

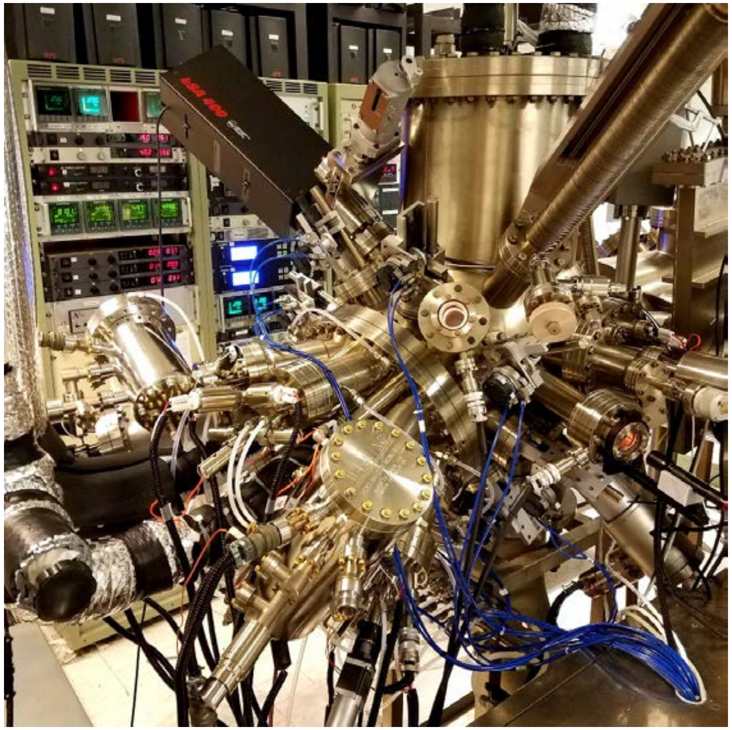
Large bandgap and high breakdown field make β-Ga_2O_3 ideally suited for high temperature, high voltage devices

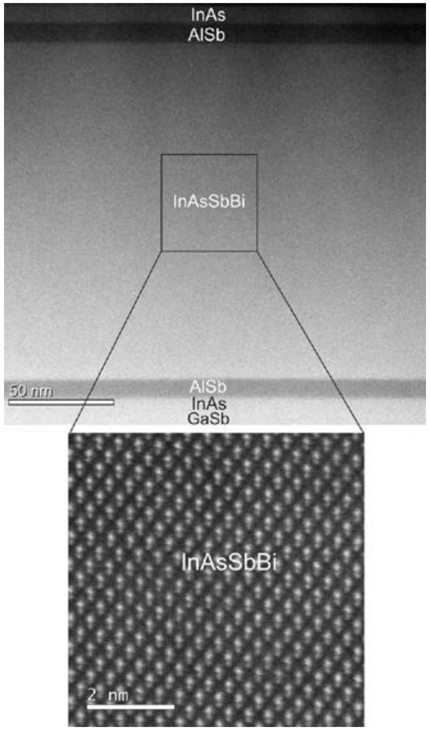


Isovalent alloying with Al increases bandgap energy and FOM

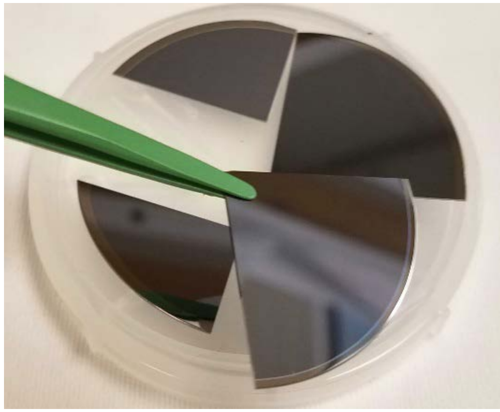
Characteristics of MBE

- Ultrahigh vacuum of 10^{-8} to 10^{-10} torr yields mean free path of dozens (or hundreds!) of meters
  - *Ballistic transport regime for gas molecules*
- Typical growth rate on the order of 1 Å/s = 6 nm/min = 0.36 μm/hr
- Low impurity concentrations on the order of 10^{13} cm^{-3} can be achieved
- Highly precise layer-by-layer control of growth
  - *Ideally suited for low-dimensional or quantum-confined structures*



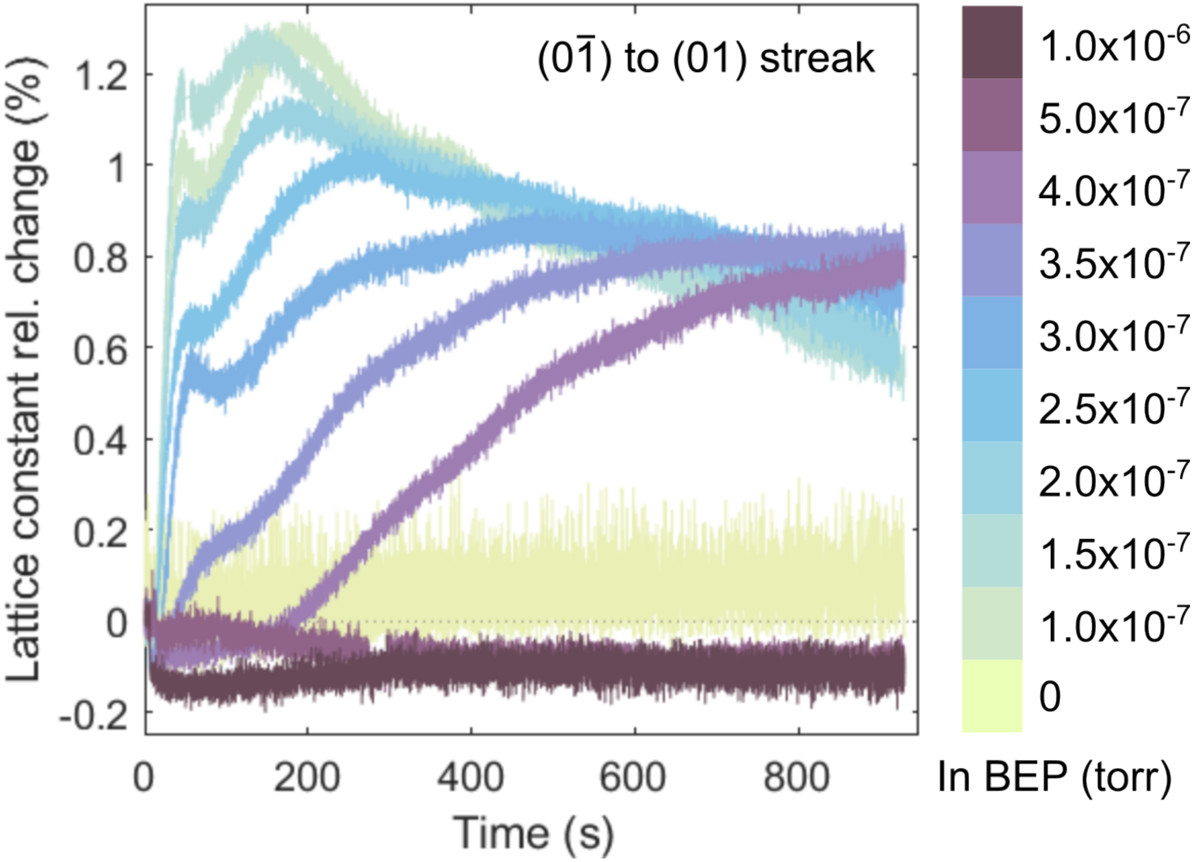


Left: III-V MBE chamber at Arizona State University
Center: TEM image of InAsSbBi grown by MBE
Right: InAsSbBi sample grown on InAs wafer by MBE



Photos by Stephen Schaefer, NREL

Increase in *d*-spacing with In incorporation



Track the spacing between RHEED pattern streaks vs time

Expansion in *d*-spacing associated with larger unit cell → In incorporation

At very high In fluxes, no expansion is observed – no growth, or only In-catalyzed Ga_2O_3

Decrease in *d*-spacing vs time suggests In incorporation falls off

$$\frac{2d - c}{c} \times 100\%$$

Approximately 10% In mole fraction for d-spacing increase of 1%

Al and In mole fractions in $(Al_xGa_{1-x-y}In_y)_2O_3$

X-ray photoelectron spectroscopy (XPS) provides depth profiles of Ga, Al and In concentrations

Al mole fraction $x = 1.4 – 24.4\%$

In mole fraction $y = 3.1 – 15.5\%$

Can use Vegard's Law and elastic strain equations to self-consistently calculate Ga, Al, and In mole fractions from RSM lattice constants

Linear increase in Al concentration with Al BEP – full incorporation of incident Al flux

In incorporation reduces non-linearly with Al BEP