# An Investigation into the Role of Energy and Symmetry at Epitaxial Interfaces

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McMaster University

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# Outline


1 Introduction

2 Background
- Theoretical
- Experimental

3 Symmetry Breaking at Interfaces
- Twins and Epitaxy on Vicinal (Offcut) (001) Silicon
- Tilted Epitaxy on (211) Silicon

4 Unusal Bond Energies at Interfaces
- CdTe on Sapphire Epitaxy and Liftoff

5 Conclusions


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# Introduction

- Epitaxy from the greek *epi* (above) and *taxis* (in an ordered manner) is the process of growing one crystal on another
- Prior work in epitaxy has concentrated on systems with:
  - Identical crystal structure
  - Nearly lattice matched spacings (unit cells of the same or commensurable size)
  - Chemically similar properties (metal-metal, semiconductor-semiconductor)
- This work examines some examples of epitaxy where:
  - Symmetry is broken across the epitaxial interface
  - Substrates have low symmetry
  - Bond energy (chemistry) is very different across the interface
- By investigating these cases, we hope to improve overall epitaxy of mismatched material systems

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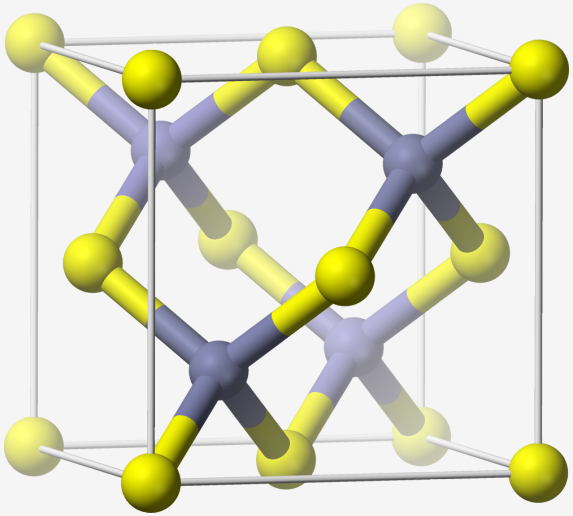

Wikipedia: Zincblende

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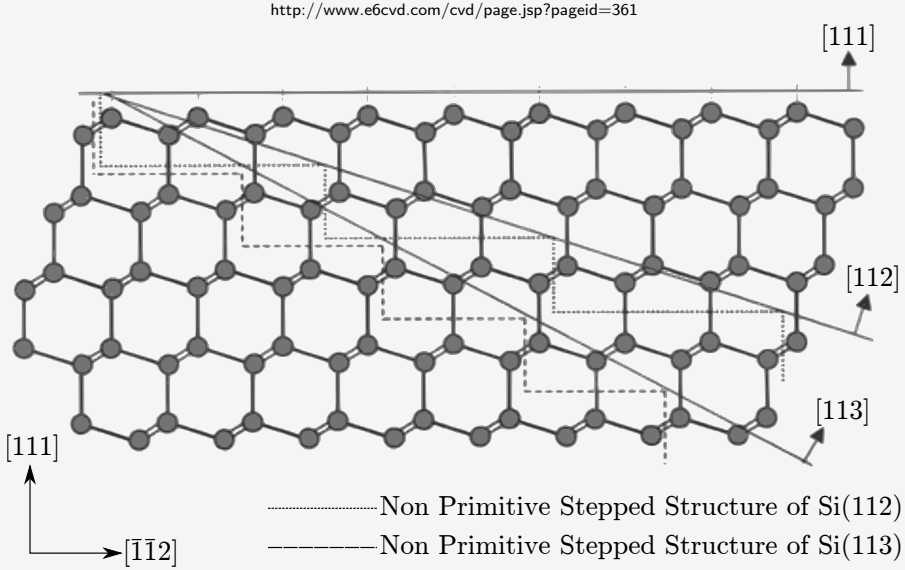


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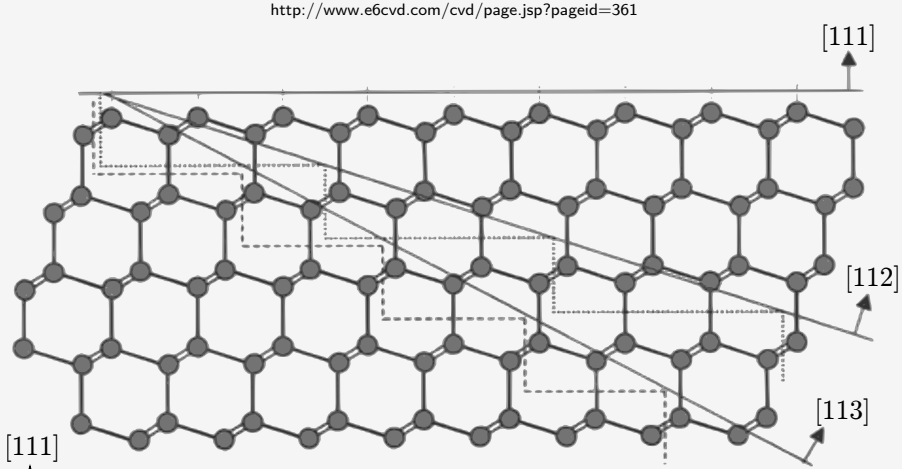


Non Primitive Stepped Structure of Si(112)

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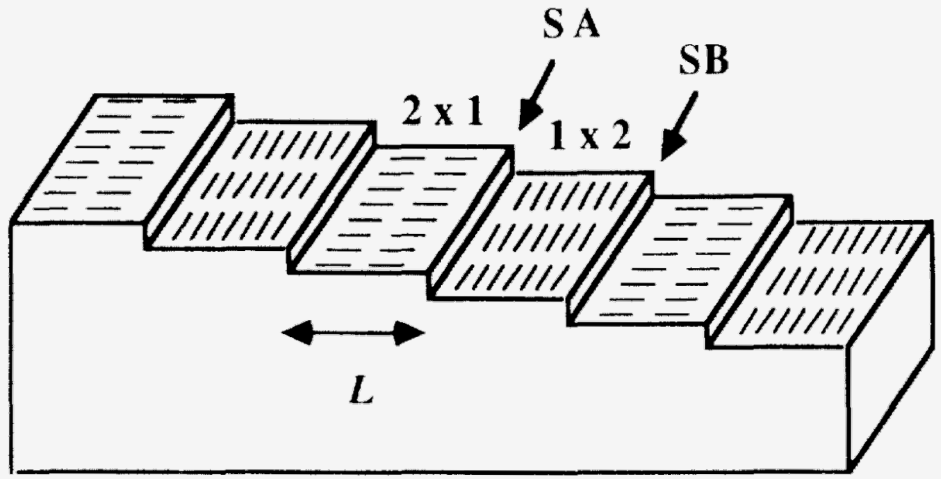


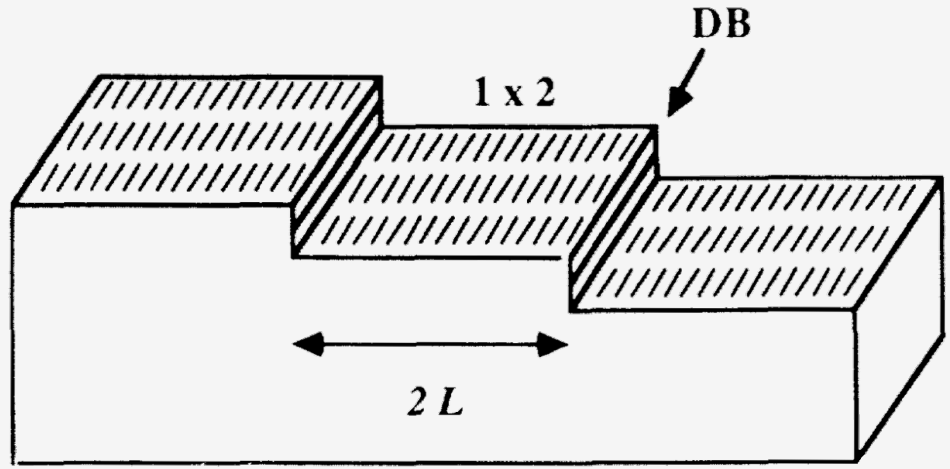


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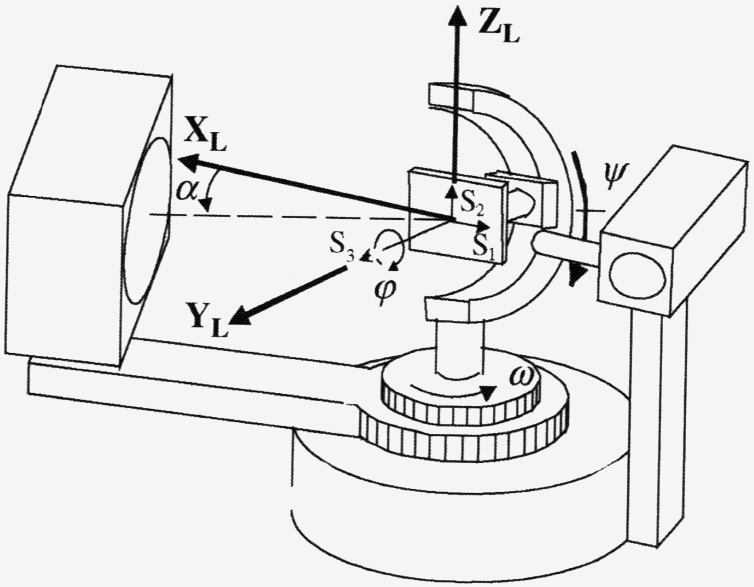
# 2D X-Ray Diffraction and Pole Figures

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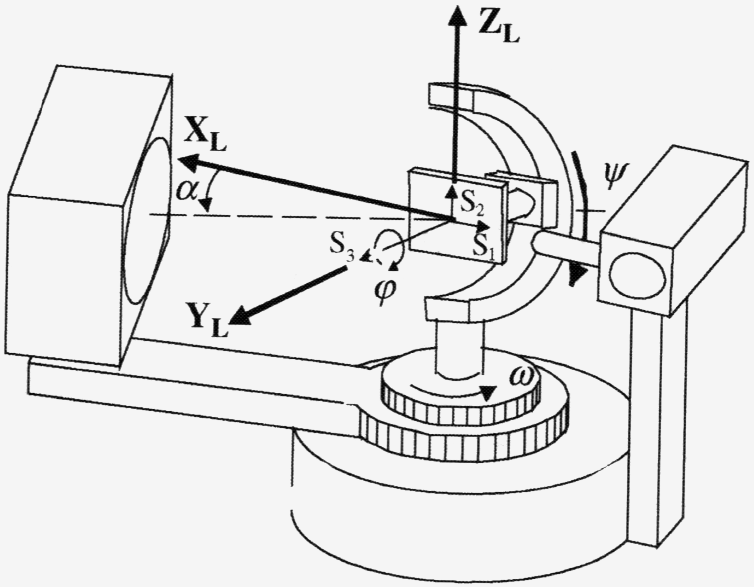


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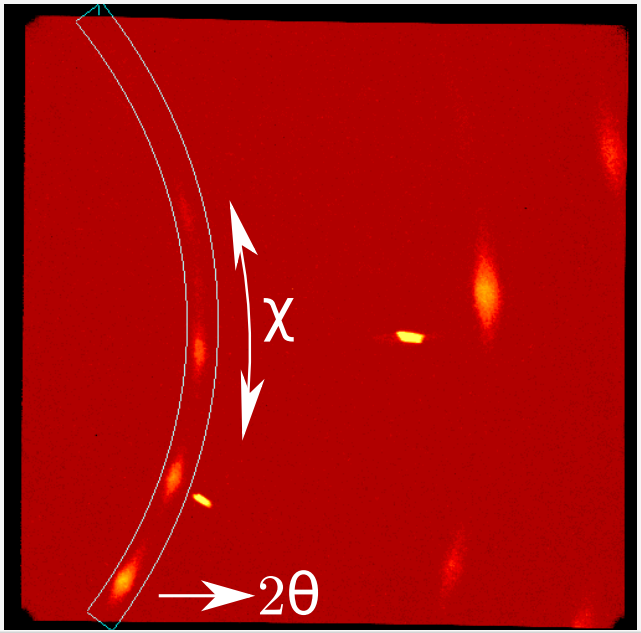


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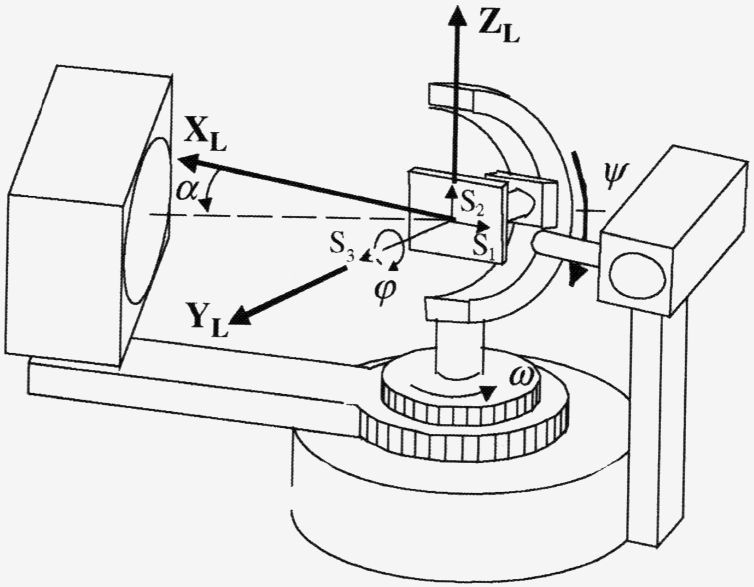


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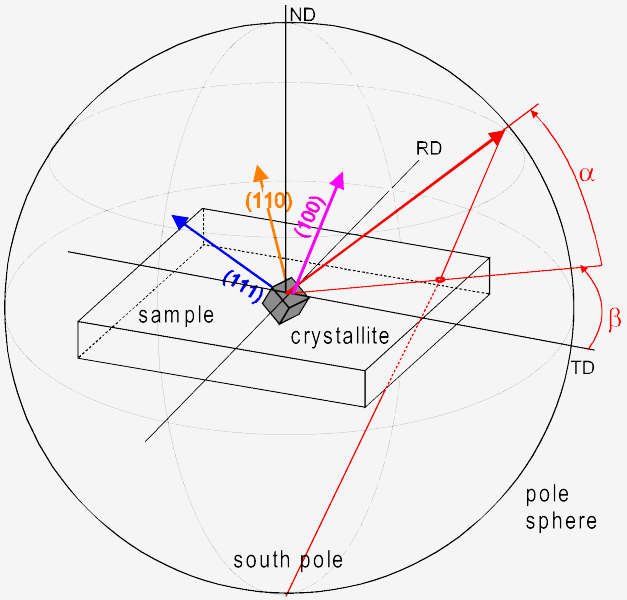


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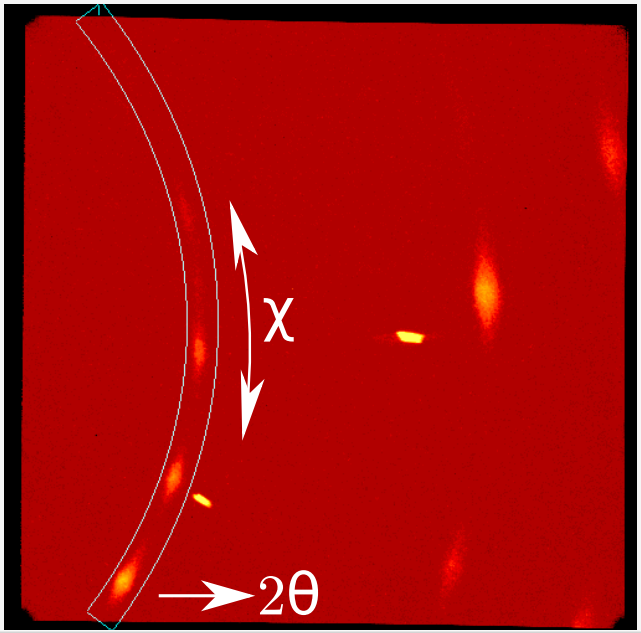


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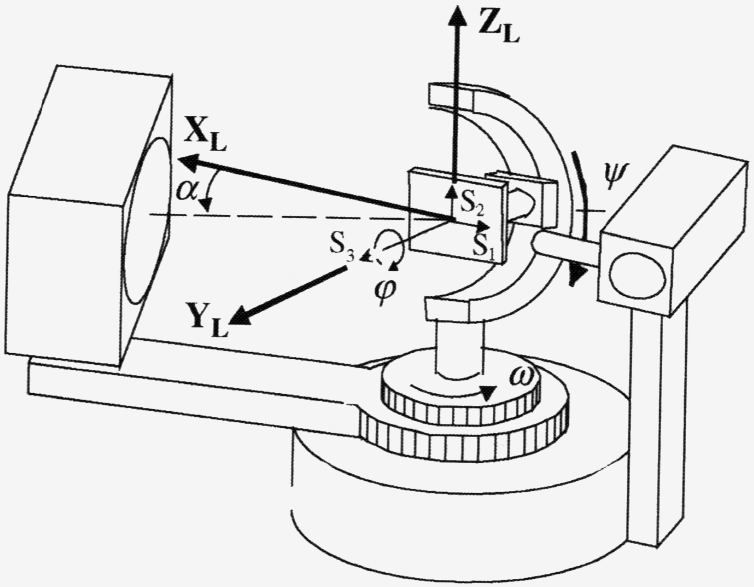


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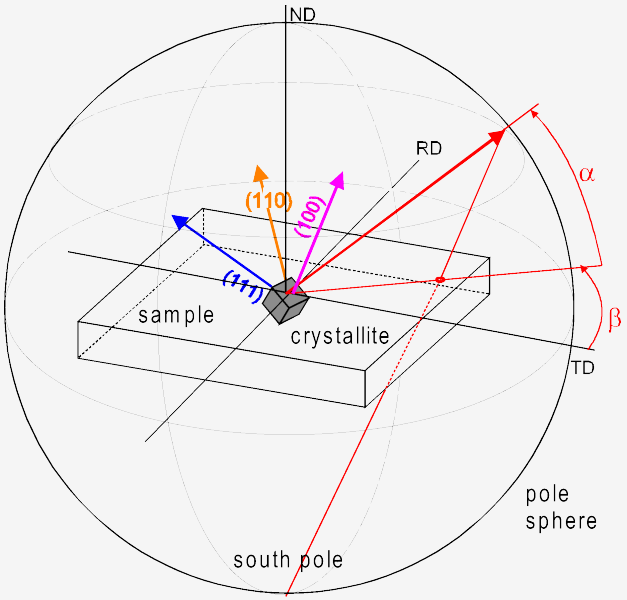


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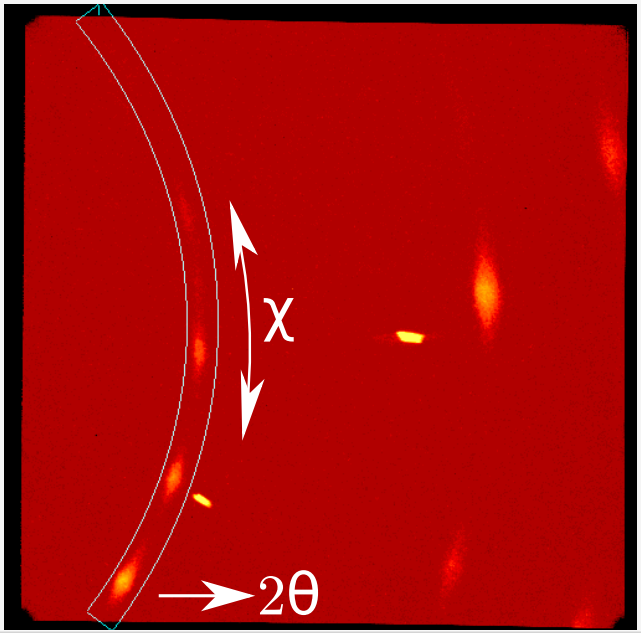


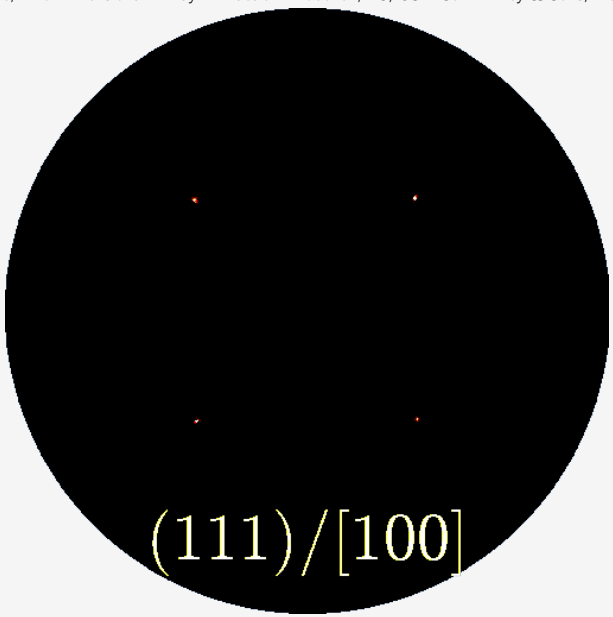


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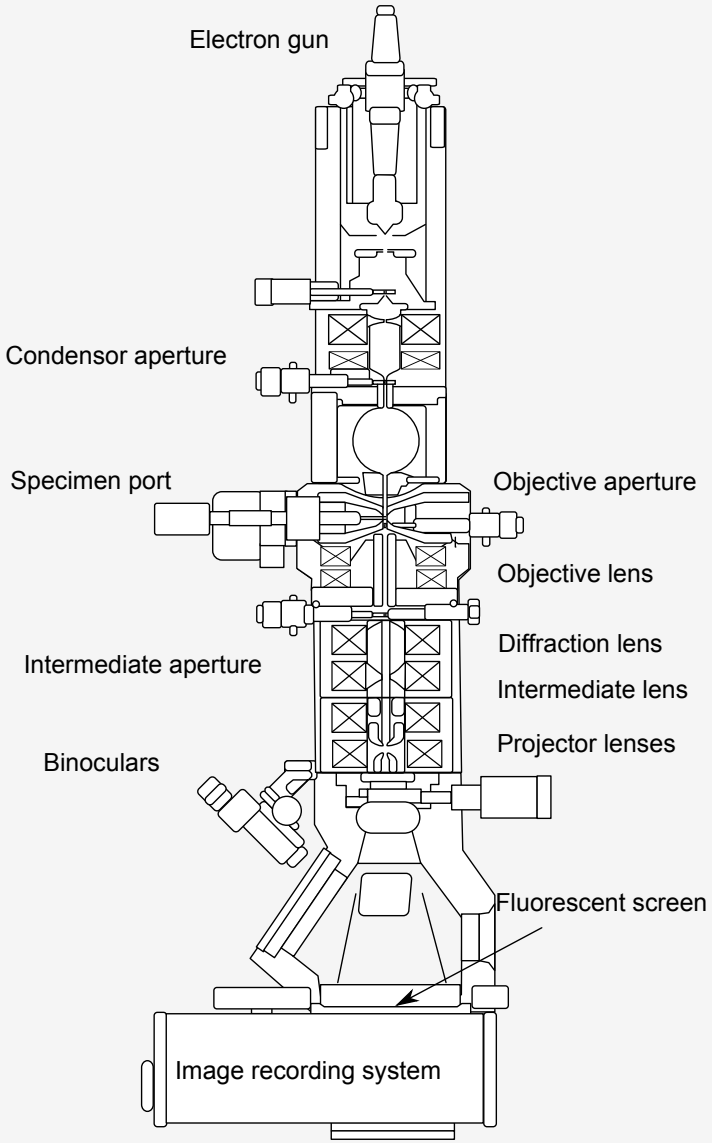
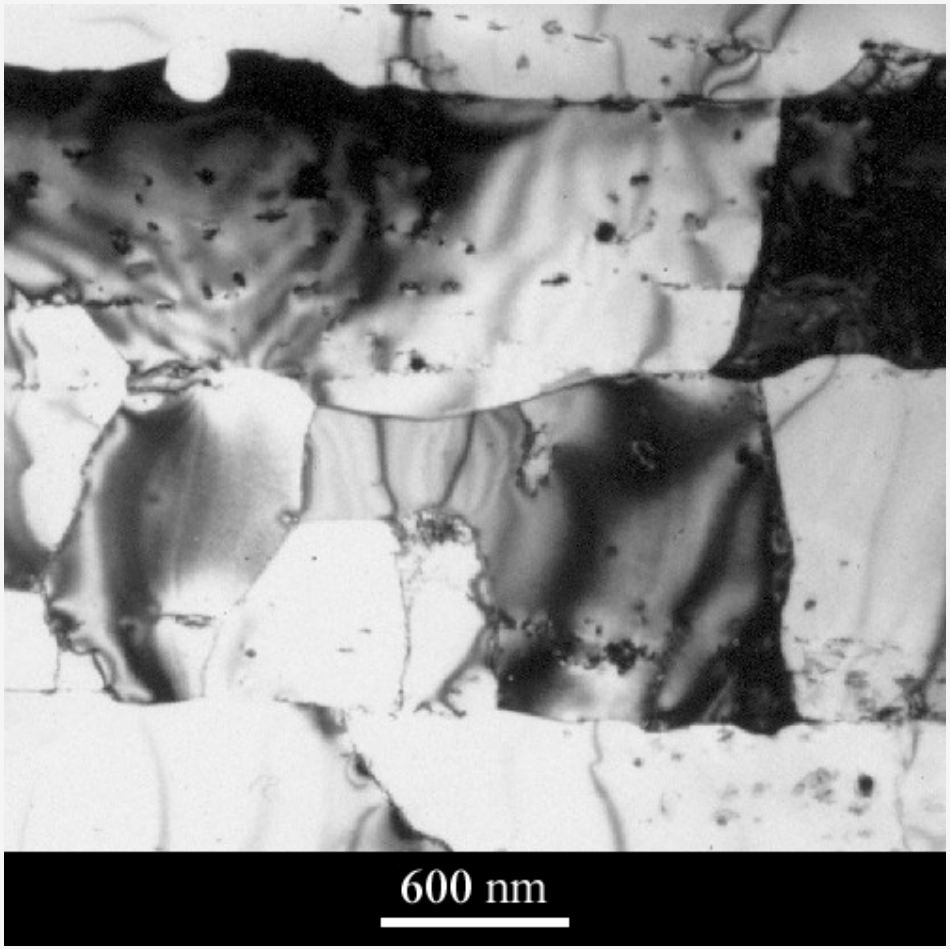
# Transmission Electron Microscopy




Wikipedia: TEM

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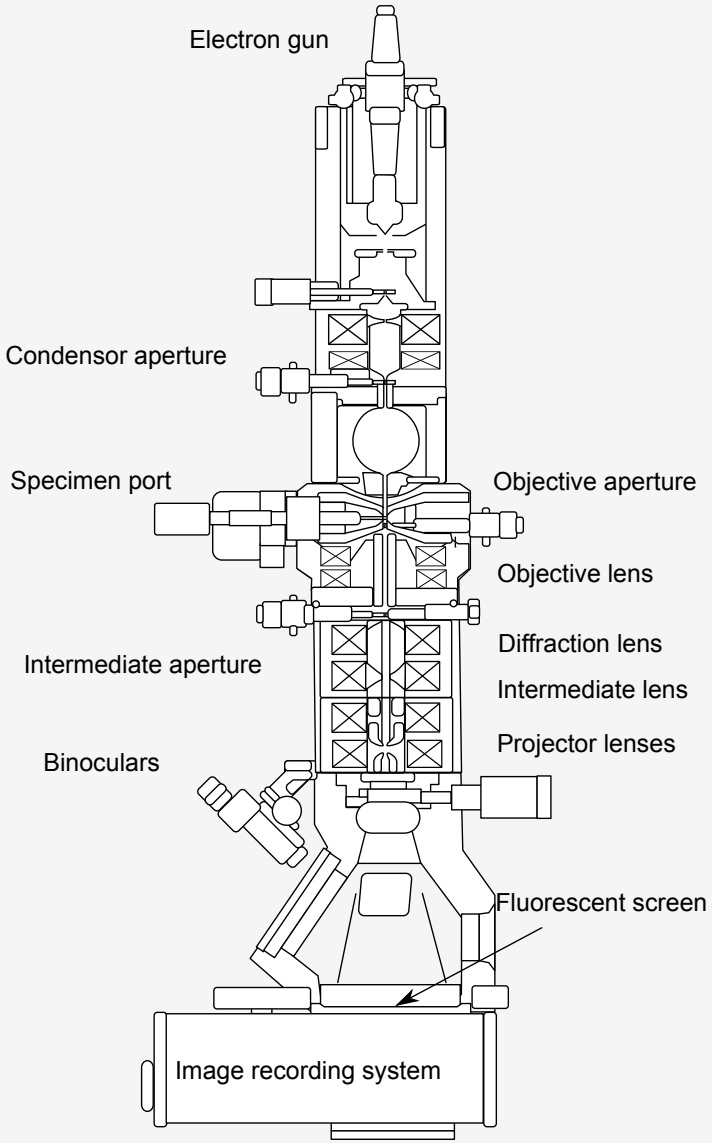
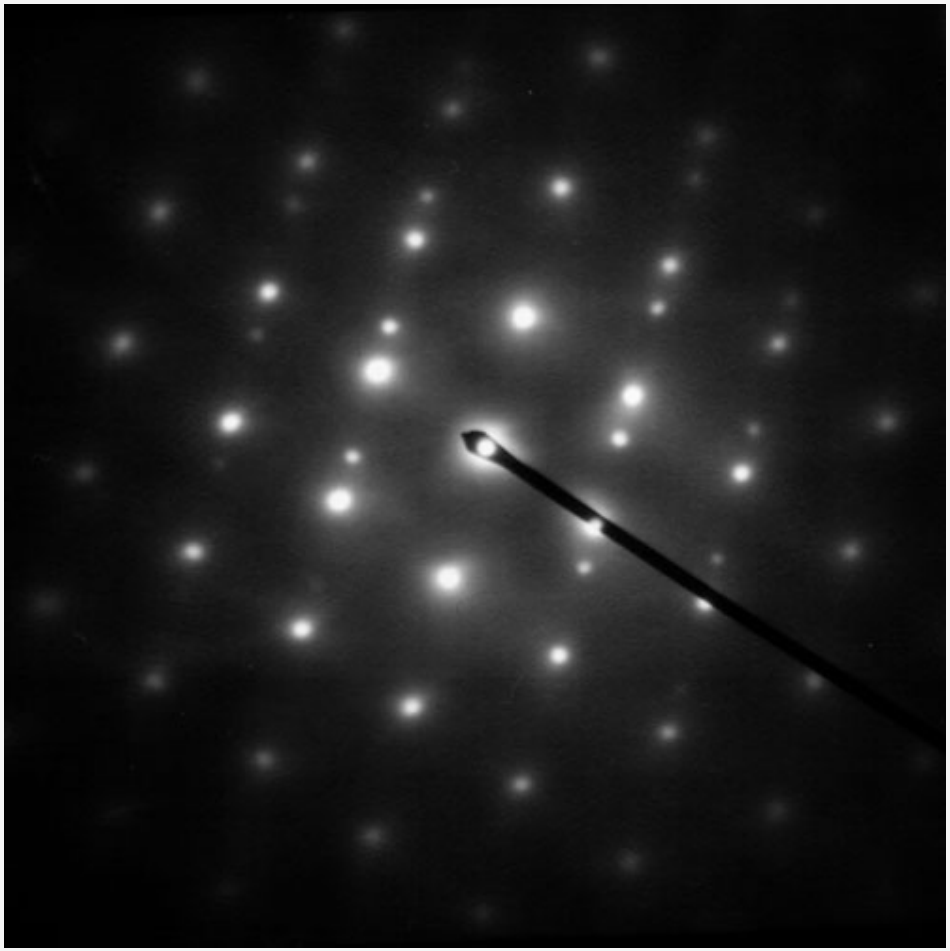



Wikipedia: TEM



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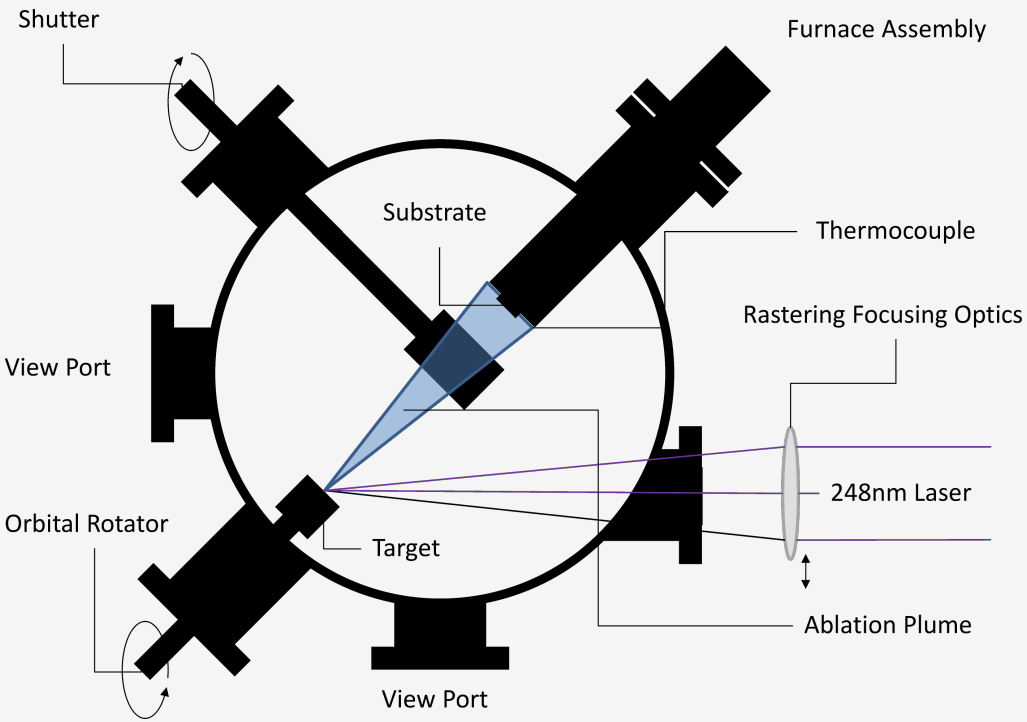
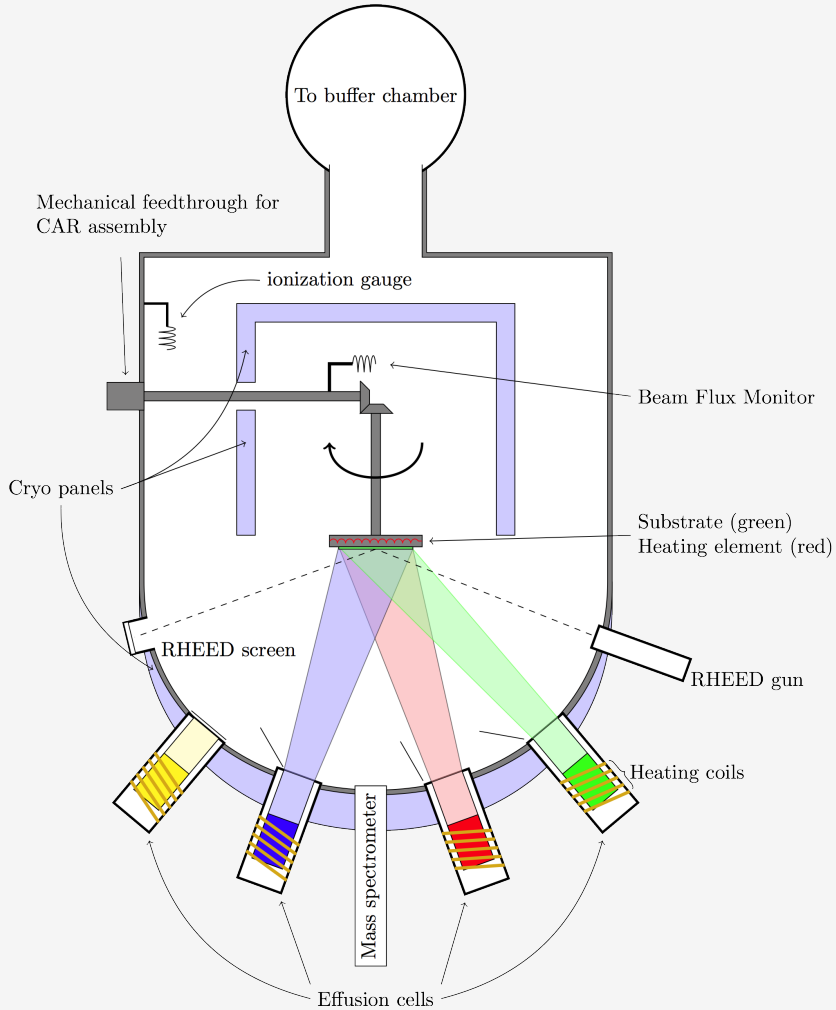
# Growth




Pulsed Laser Deposition (PLD)




Molecular Beam Epitaxy (MBE)

Wikipedia: MBE

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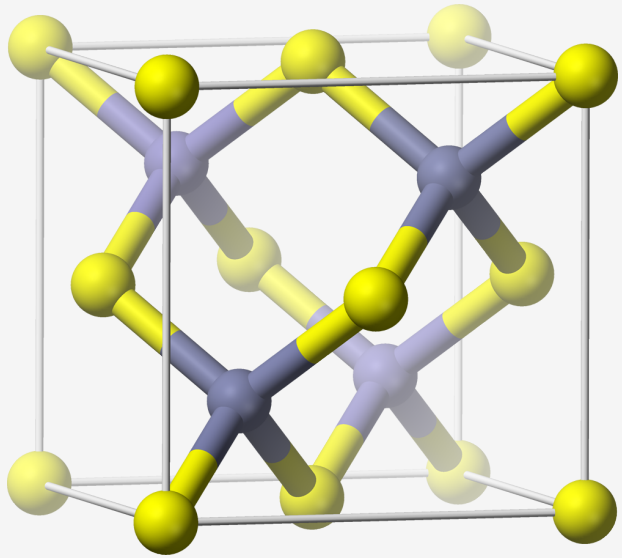
- Semiconductors are most commonly the zincblende crystal structure
- Twins (stacking faults on <111> planes) are common low energy defects
- Investigations into III-V epitaxy showed a relationship between vicinal (offcut) substrates and twinning



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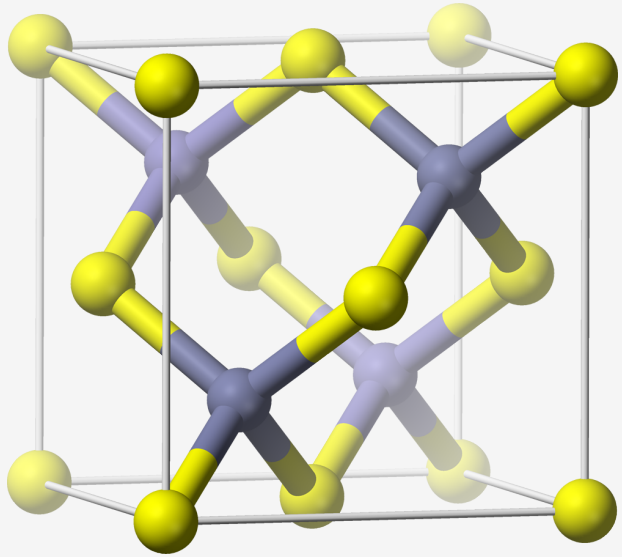

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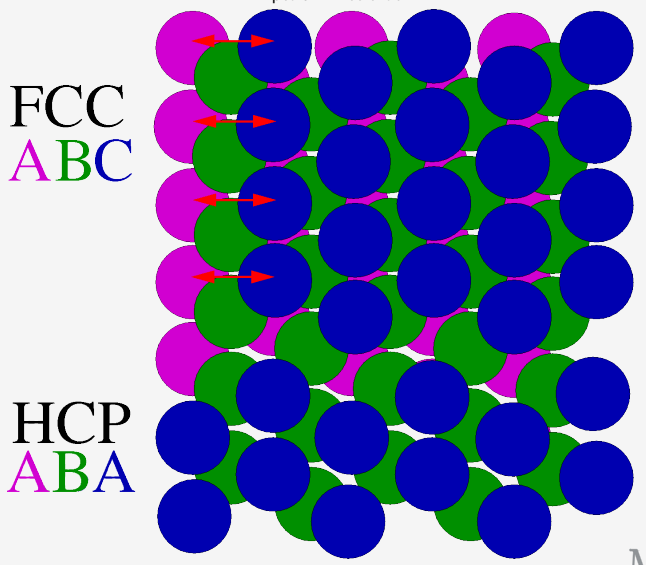


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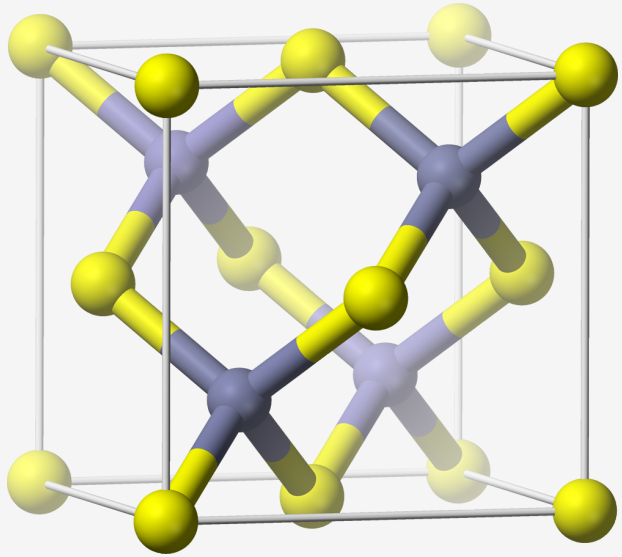

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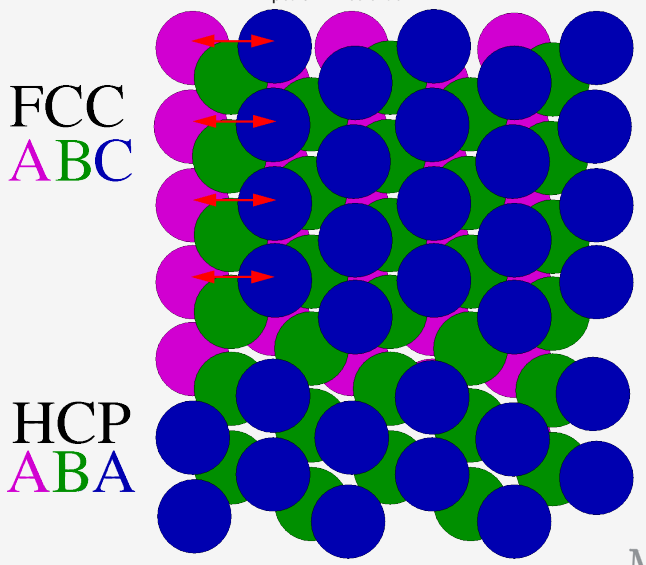


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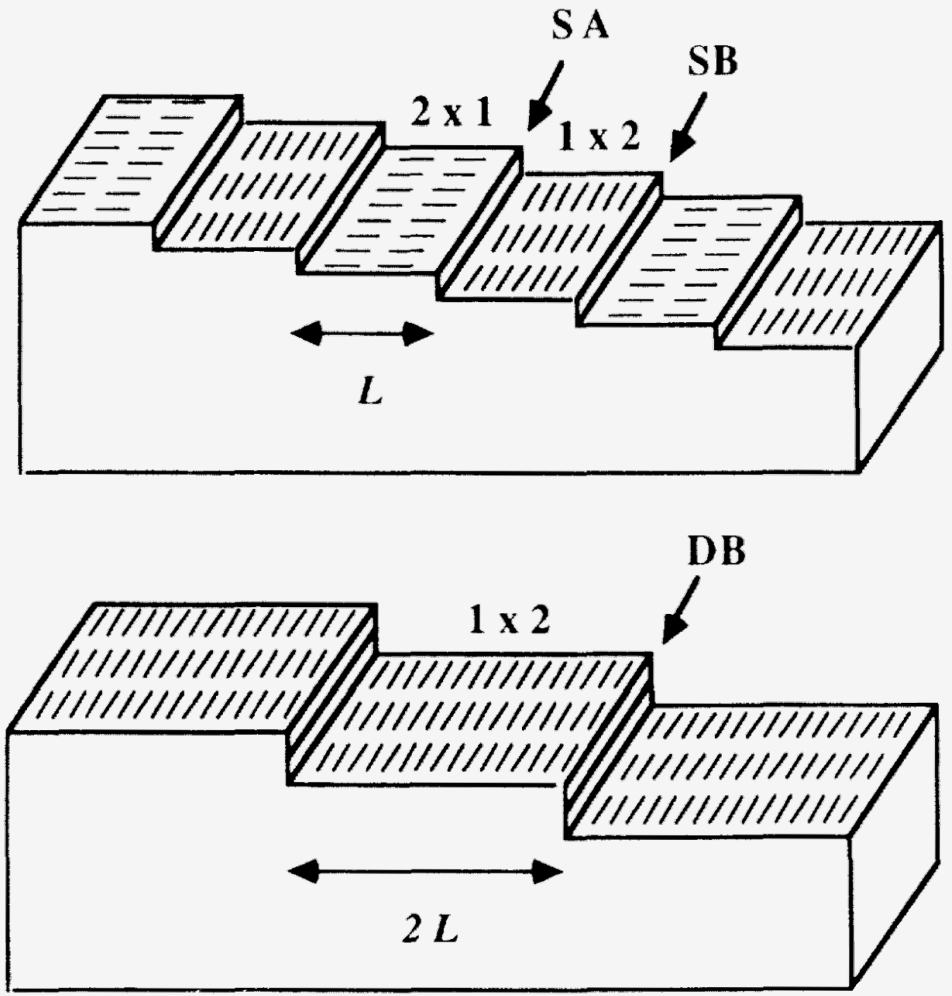
- Nominal (flat) and vicinal (off-cut) silicon (001) substrates
- Initially investigated due to their ability to control anti-phase boundaries in III-V epitaxy via step formation
- Substrates were reconstructed *in-situ* in the MBE via thermal treatment
- 500 nm films of GaAs, InP, GaSb, and AlSb were deposited, covering a lattice mismatch of 4–13%

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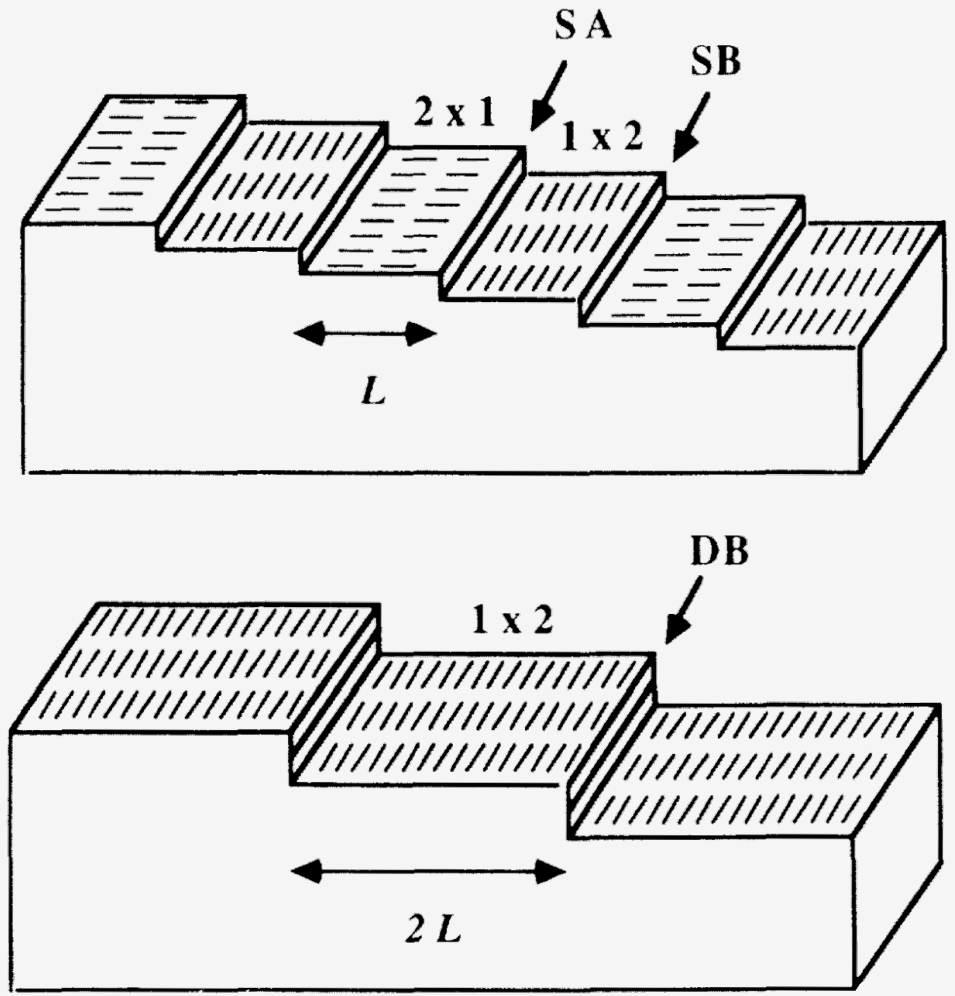


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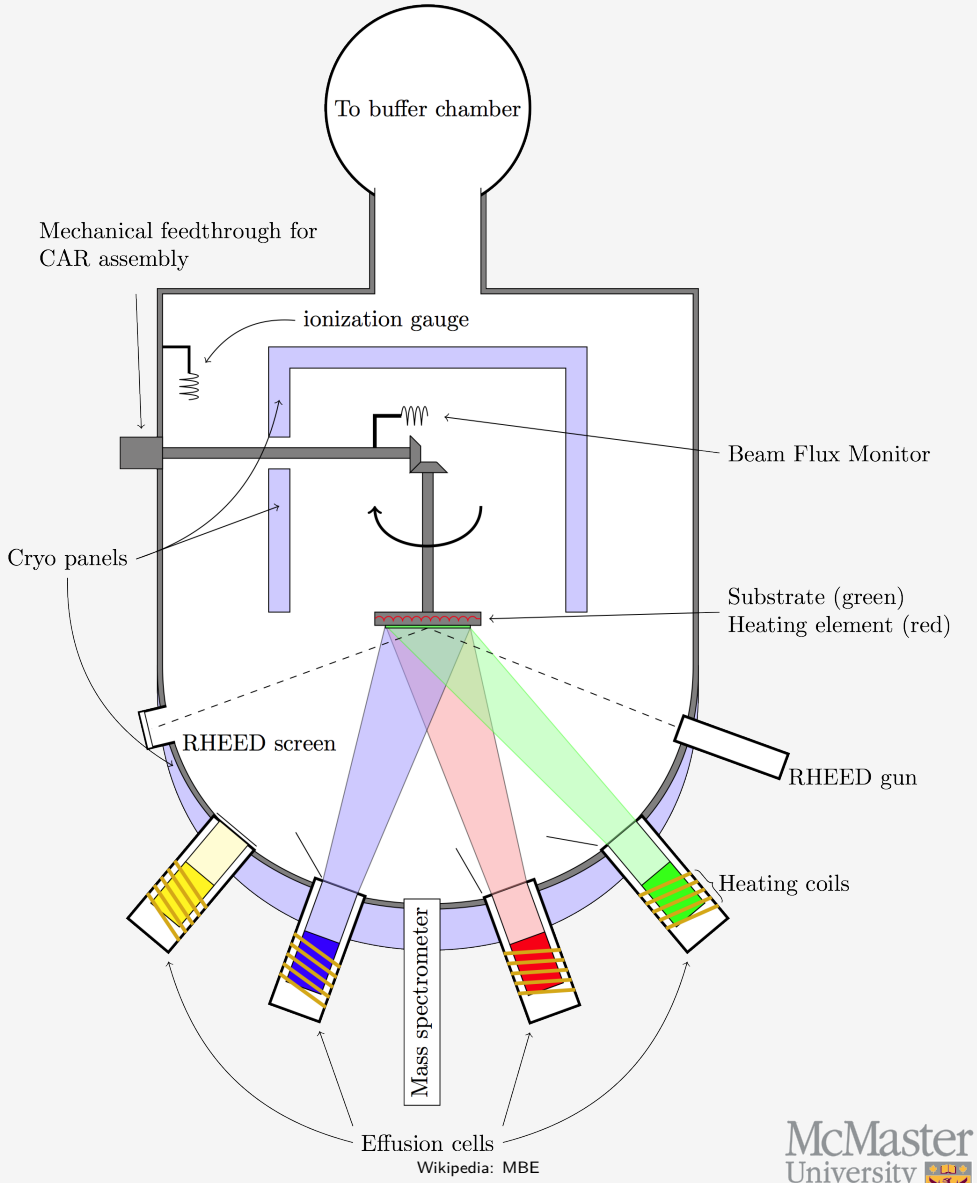


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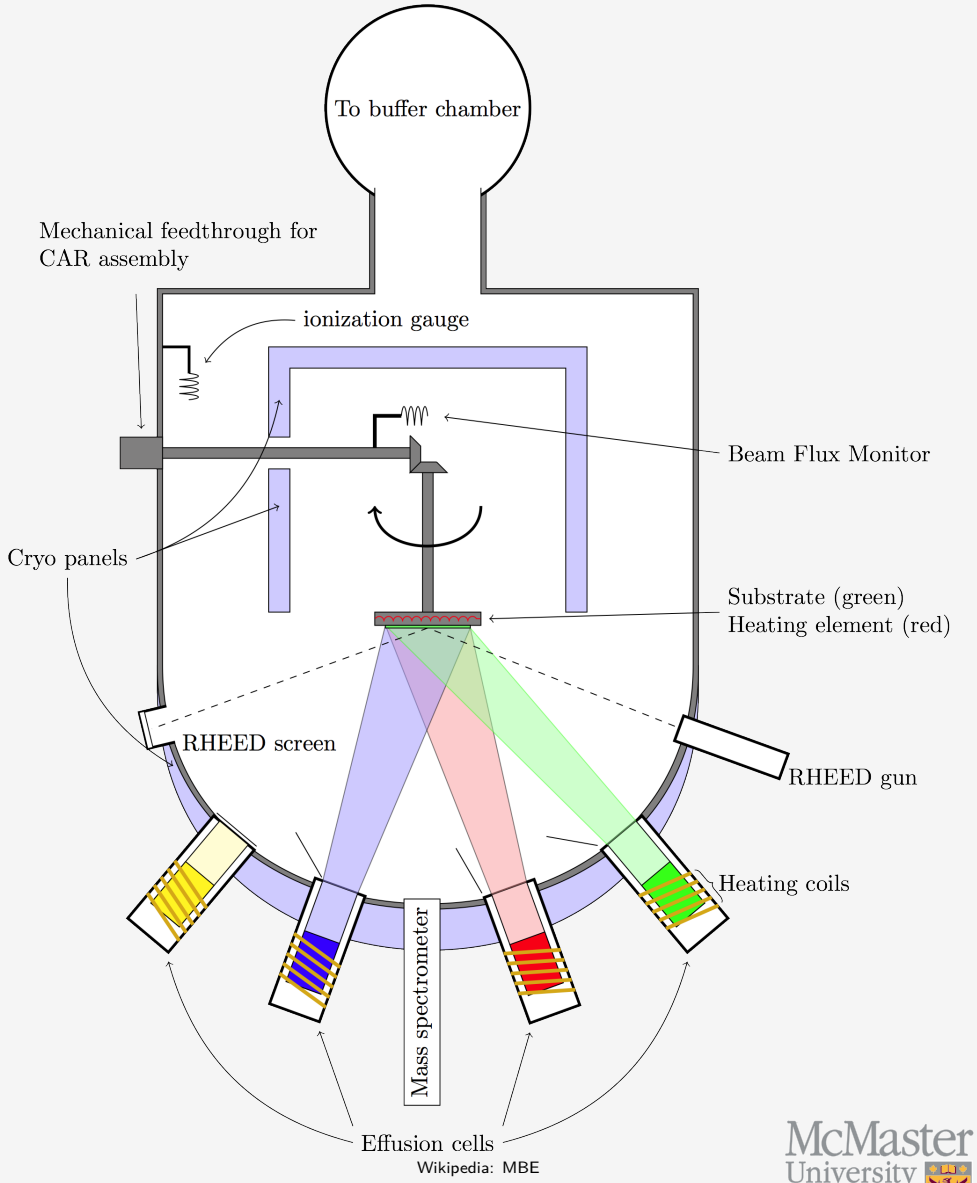


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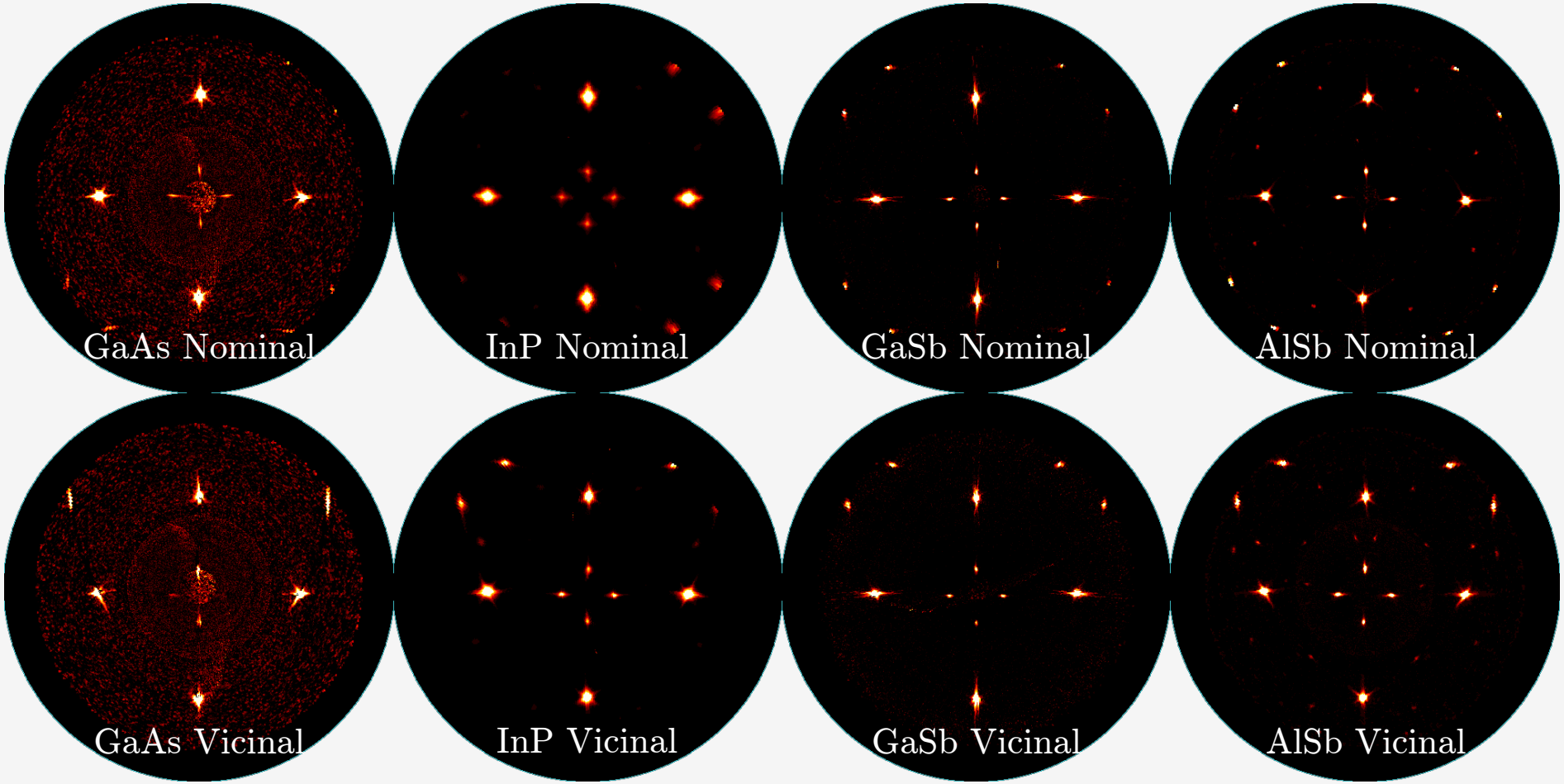
# (111) 2DXRD Pole Figures

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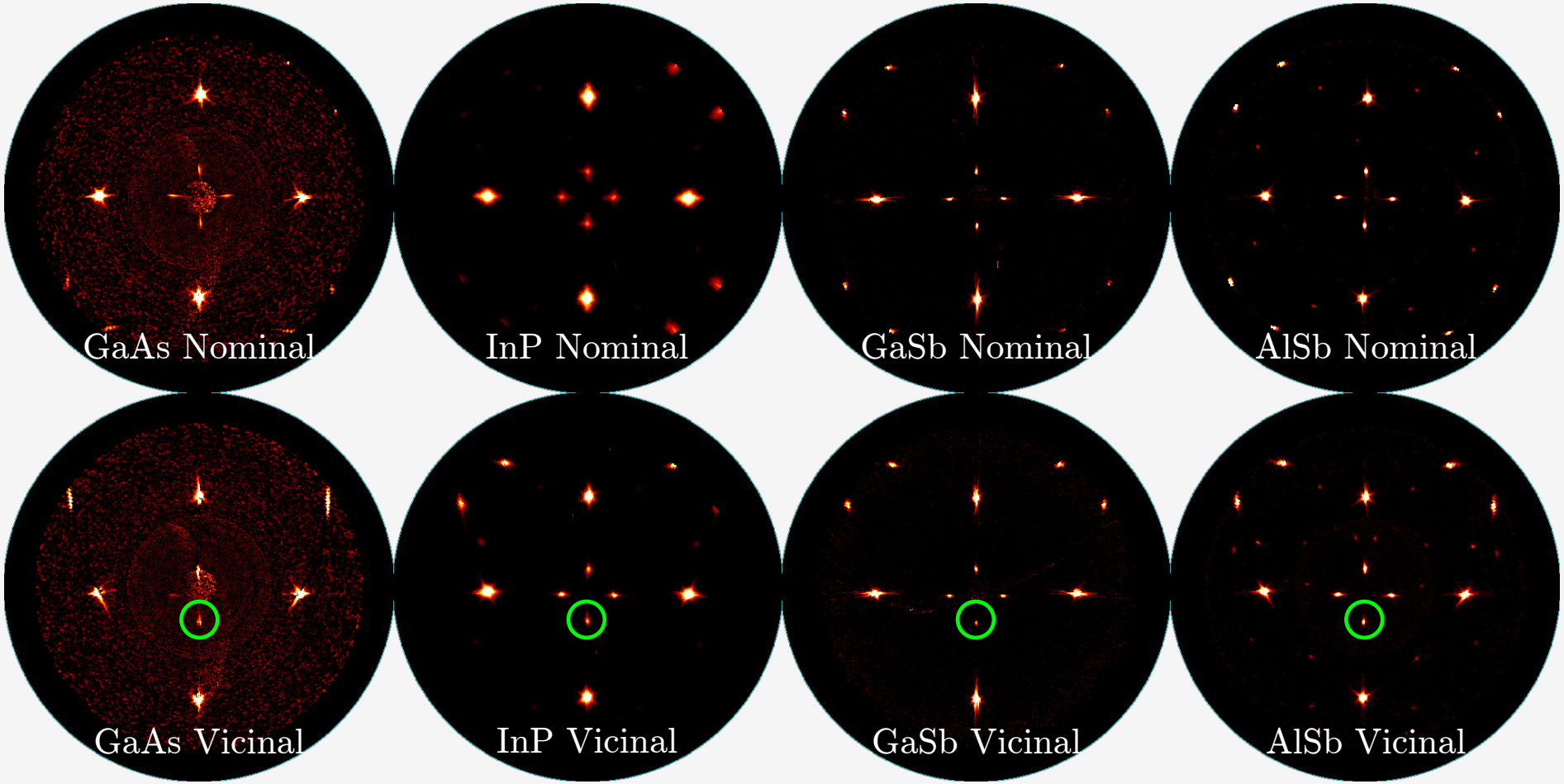


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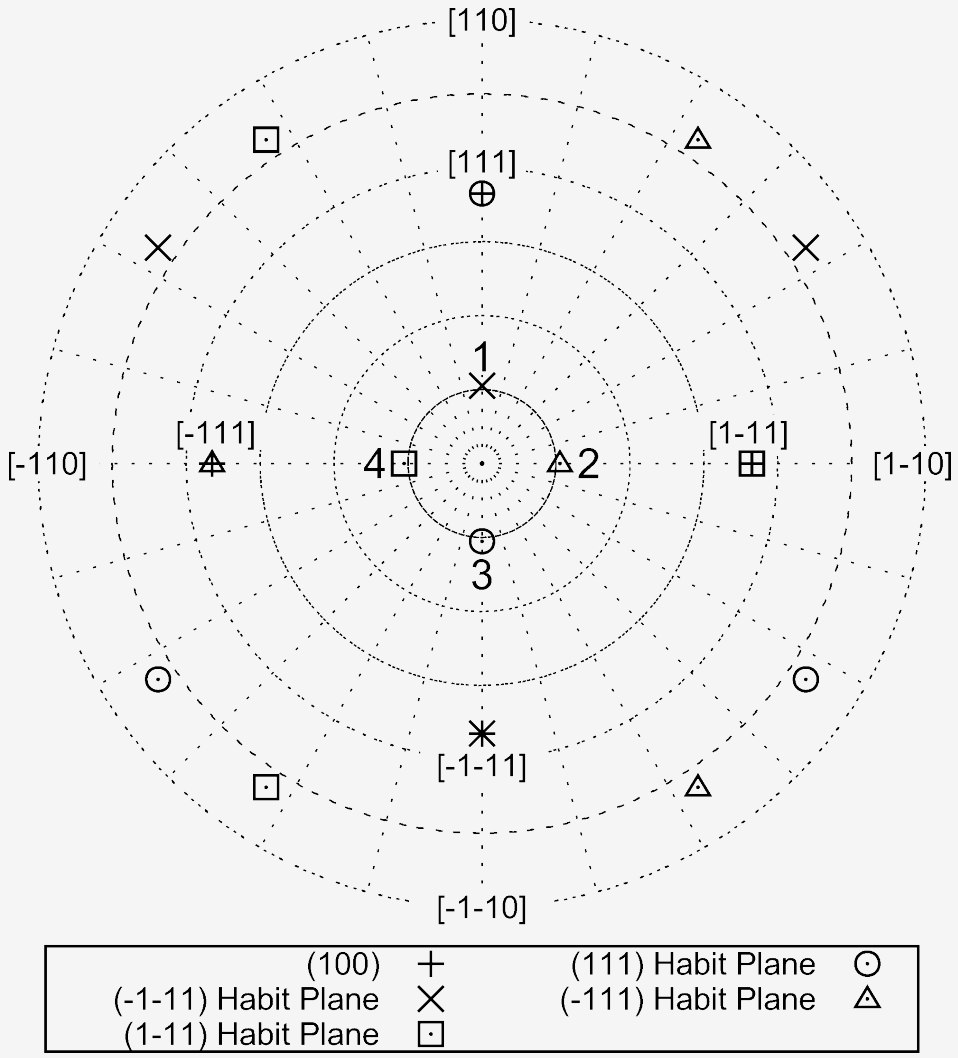
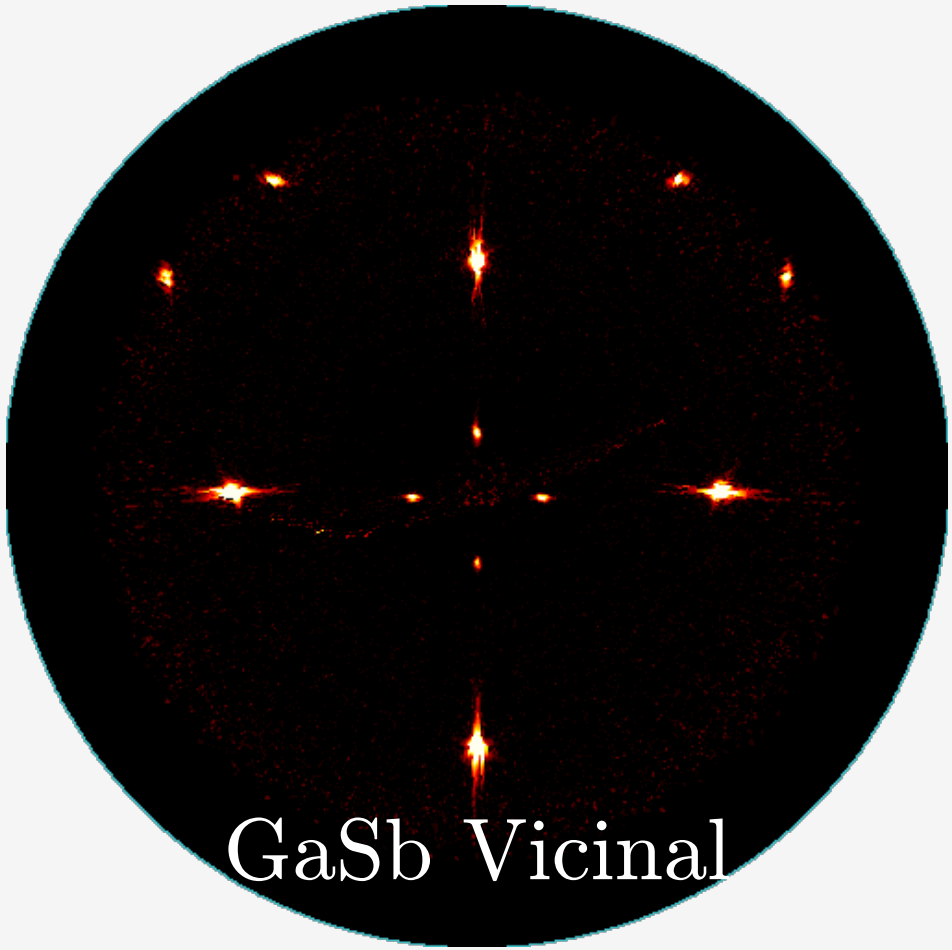
# (111) Pole Figure Modelling and Intensity



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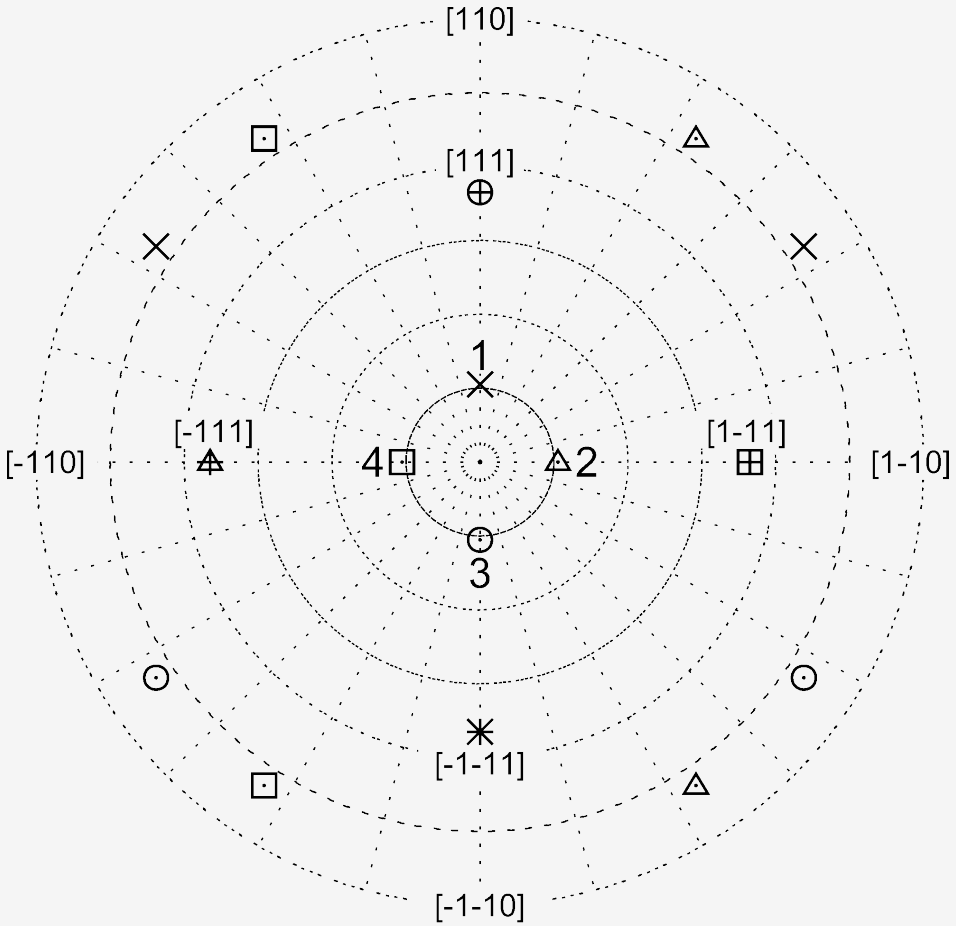
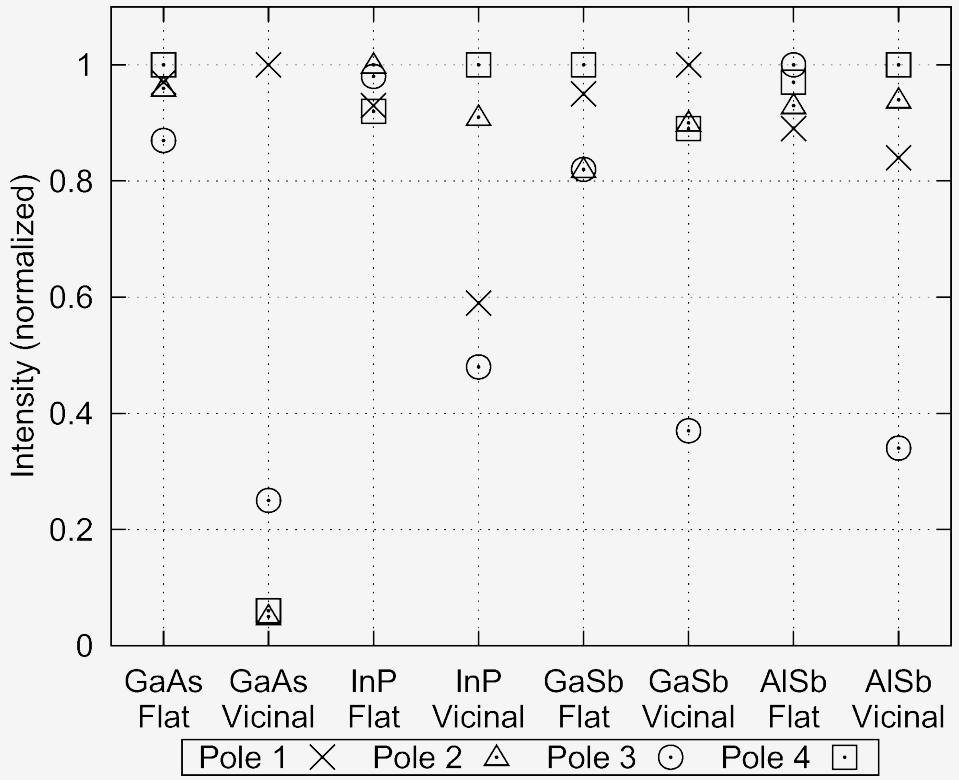
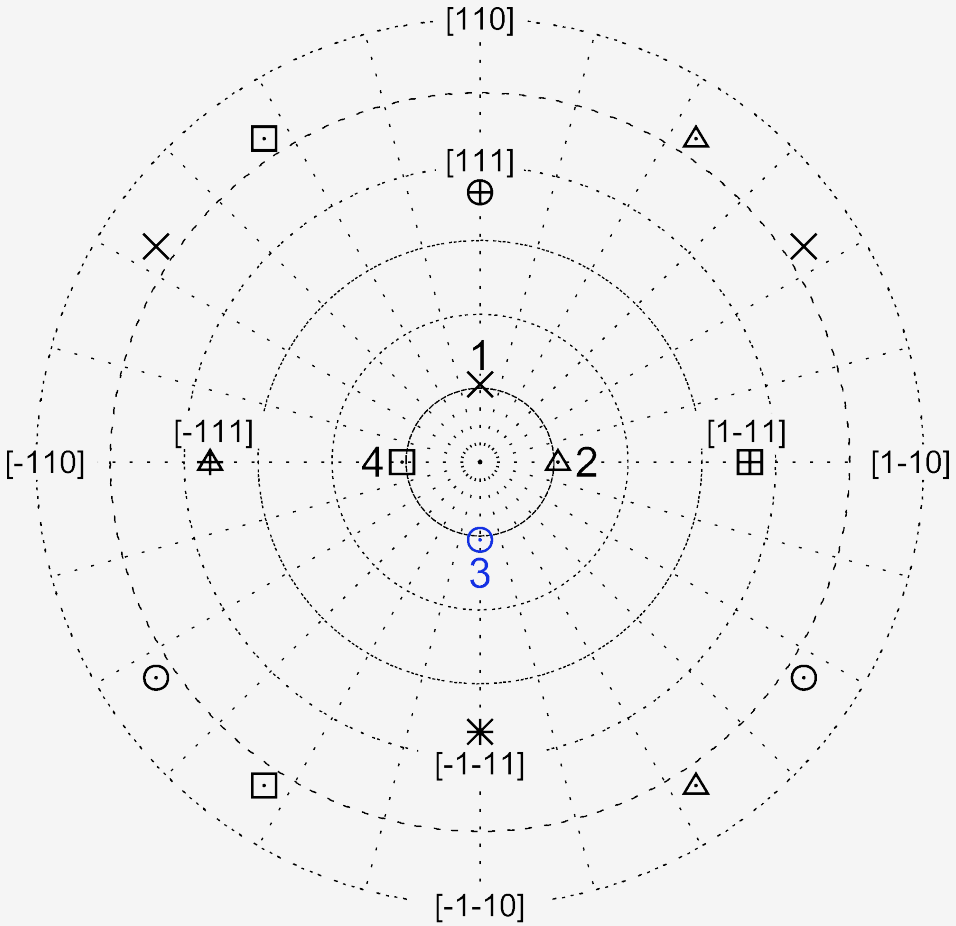
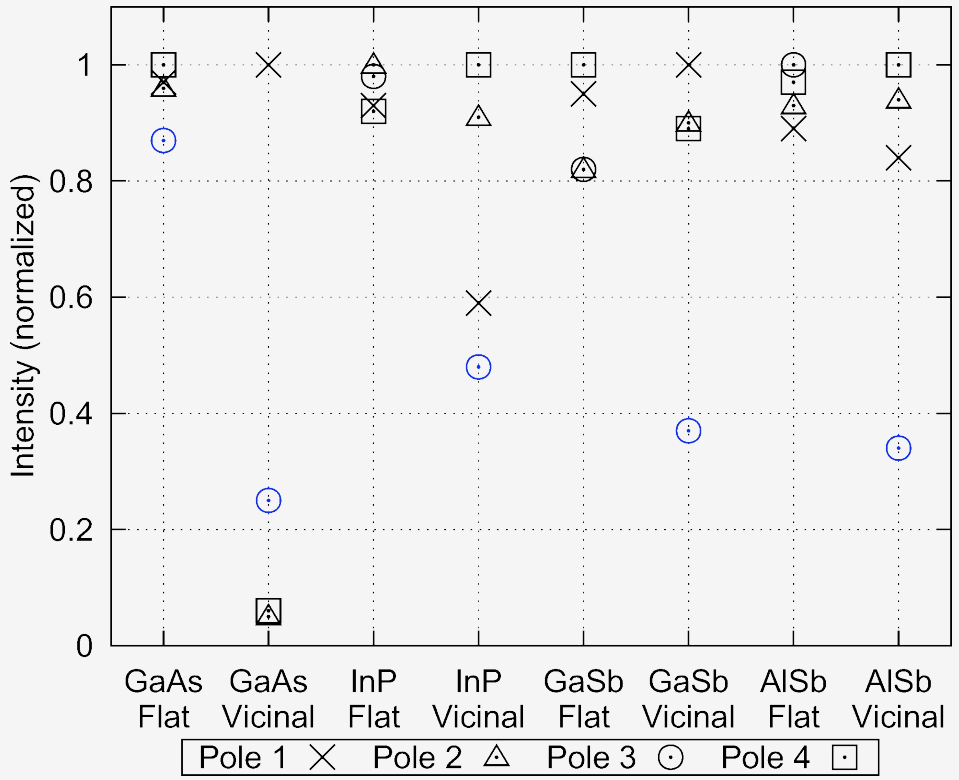


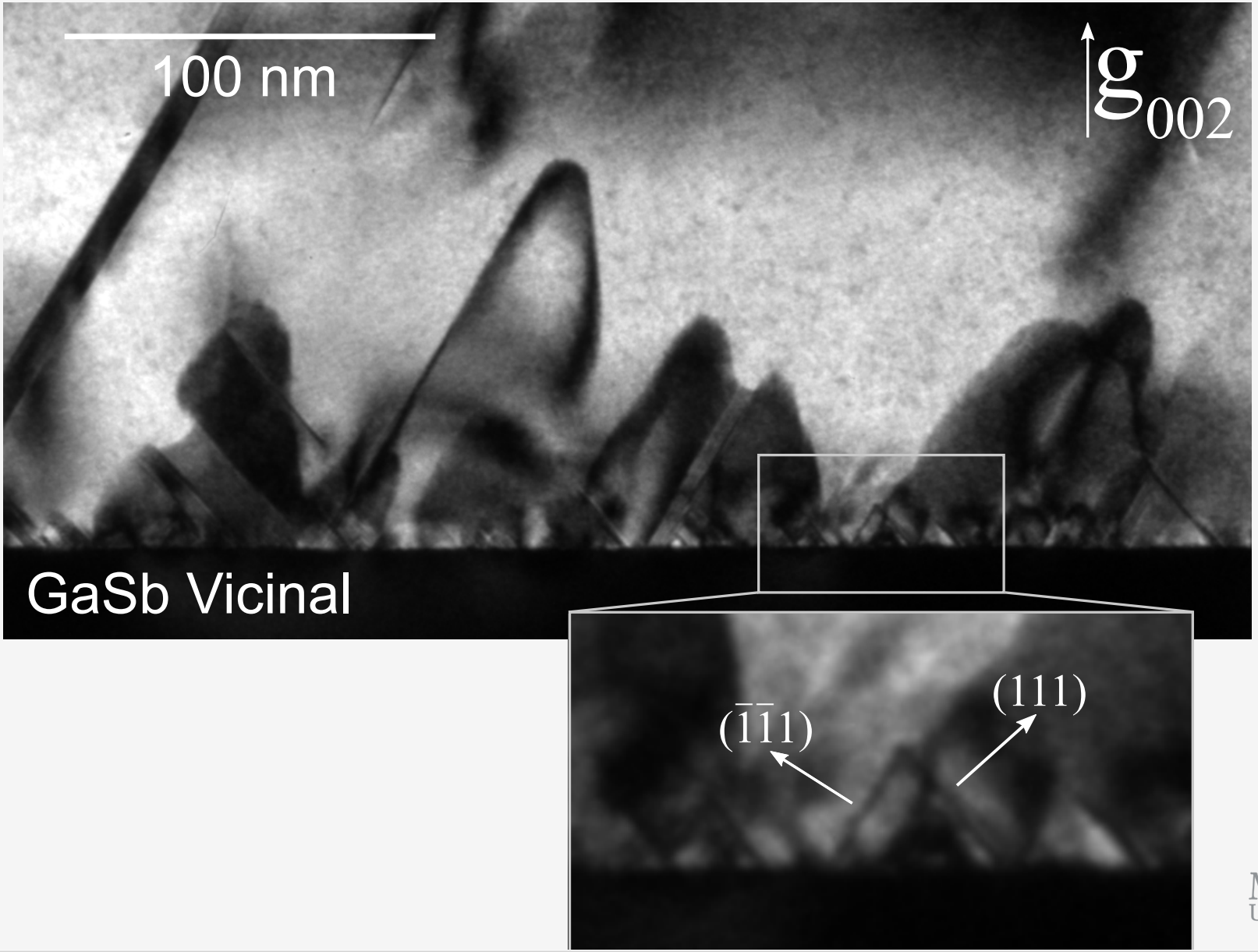
# (111) Pole Figure Modelling and Intensity



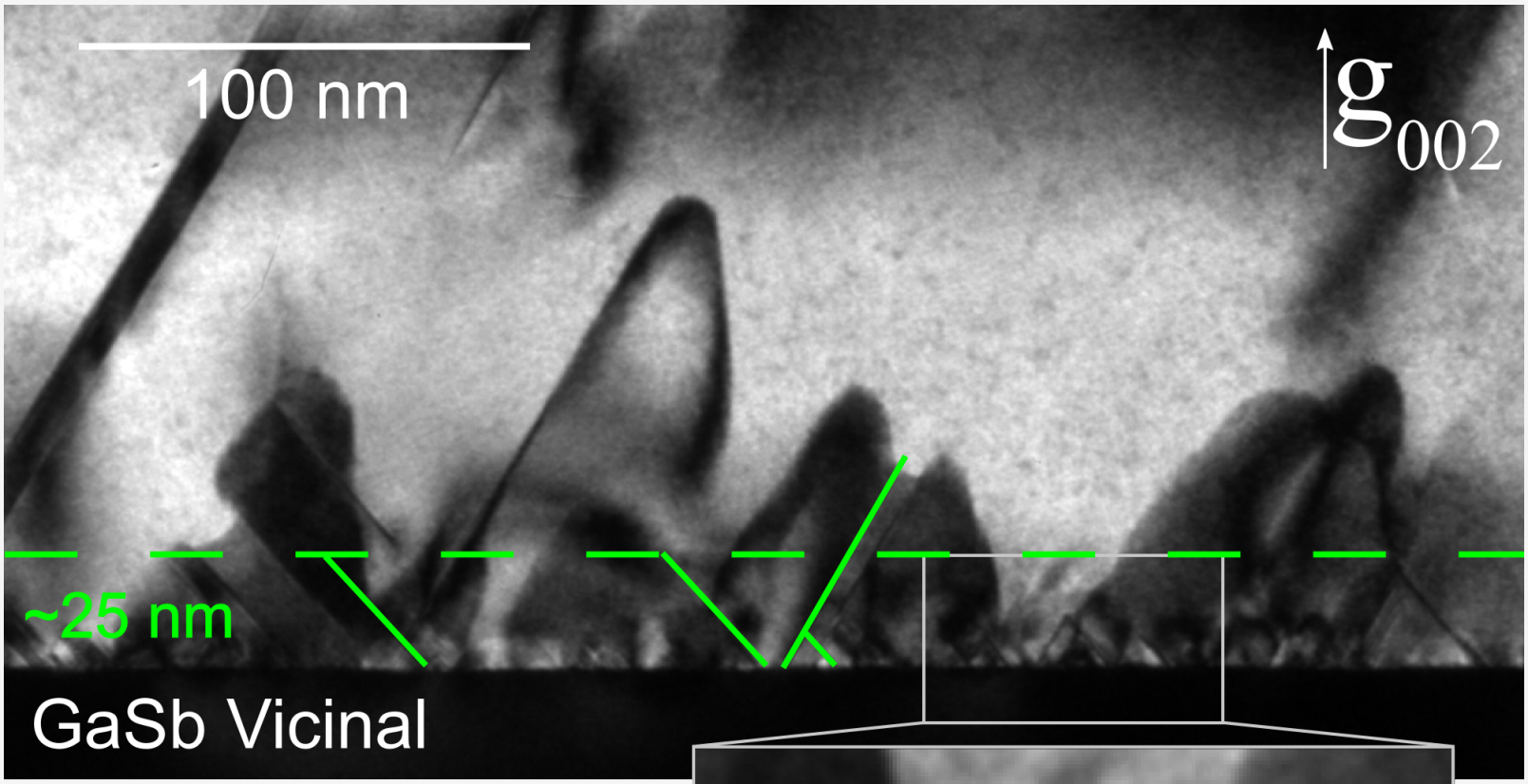

| | | | |
|---|---|---|---|
| (100) | + | (111) Habit Plane | ⊙ |
| (-1-11) Habit Plane | × | (-111) Habit Plane | △ |
| (1-11) Habit Plane | ⊡ | | |

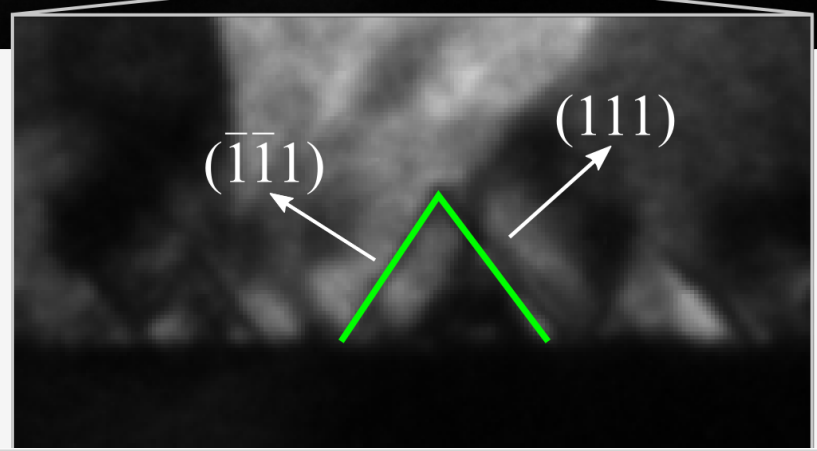


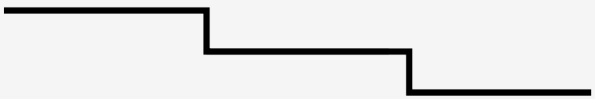
# (110) TEM



# (110) TEM



Step Direction

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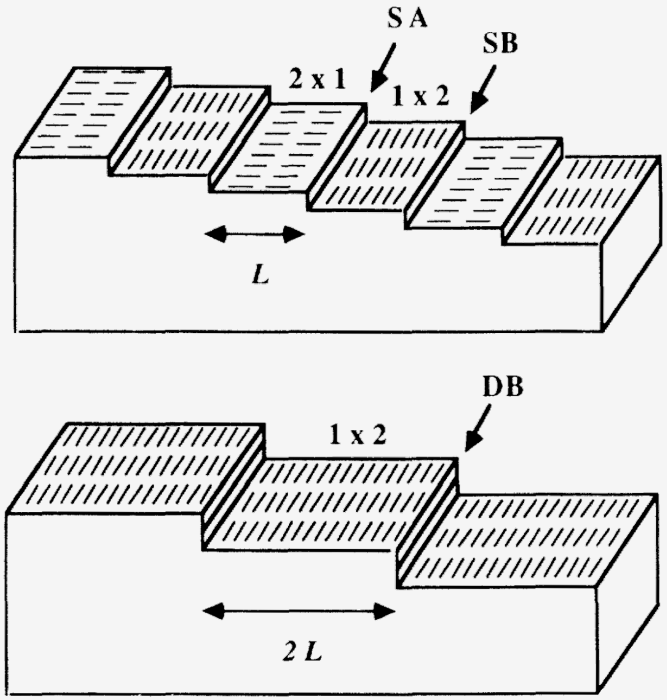
# Twins Epitaxy on Vicinal (001) Silicon

## Conclusions

- Twins form on all <111> surfaces
- Vicinal substrates cause asymmetric step formation in (001) silicon substrates
- Steps on the surface enhances the growth rate away from step edges
- Asymmetric growth rate overgrows twins limiting to a thin layer at the interface




O. Alerhand, et. al., Phys. Rev. Lett., vol. 64, no. 20, pp. 2406–2409, May 1990.

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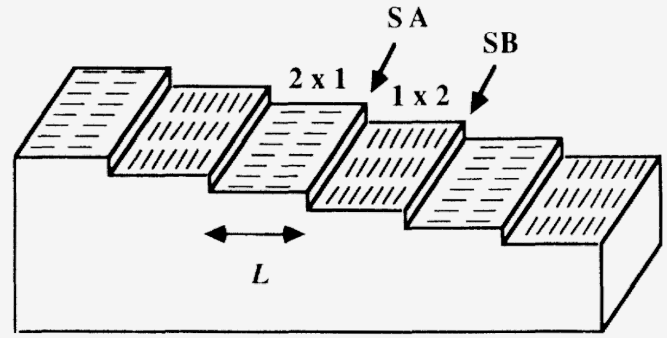


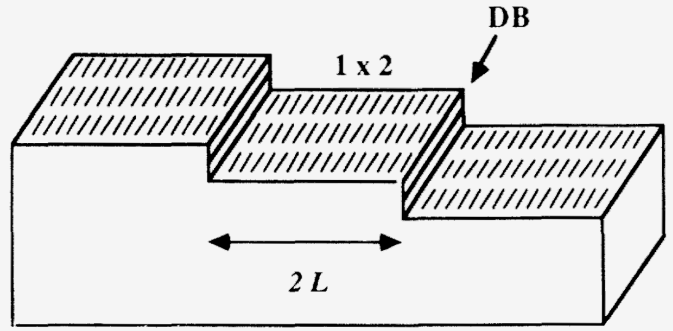


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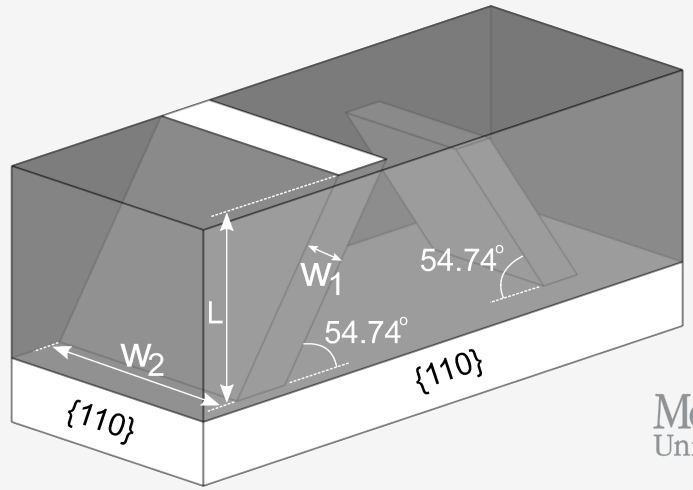


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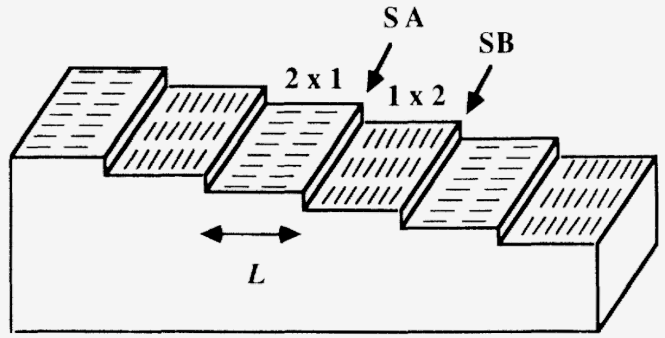


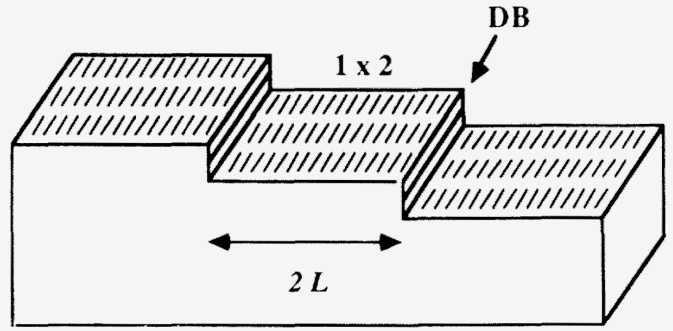


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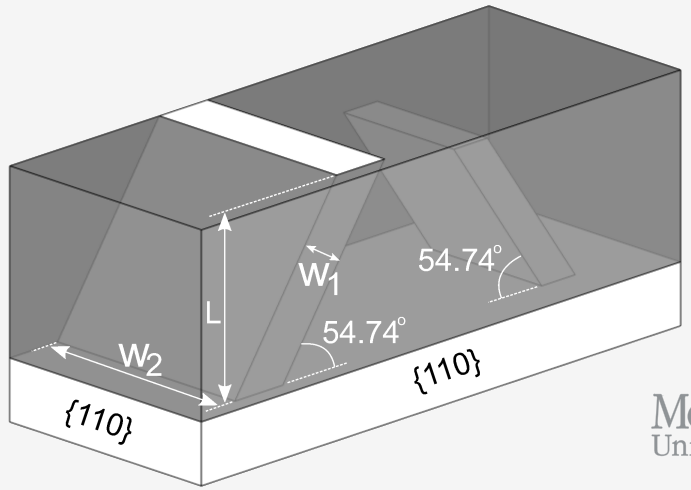


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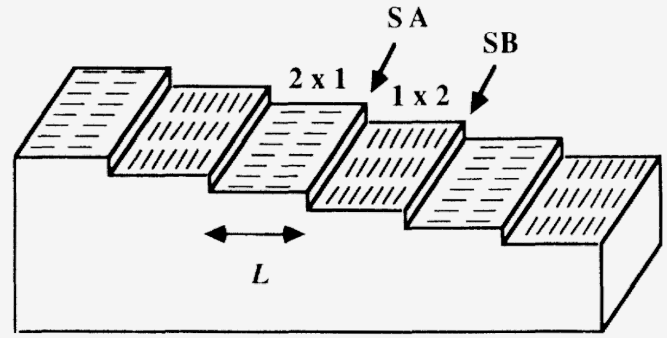


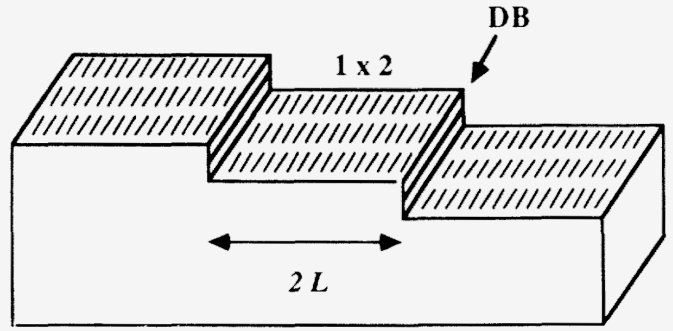


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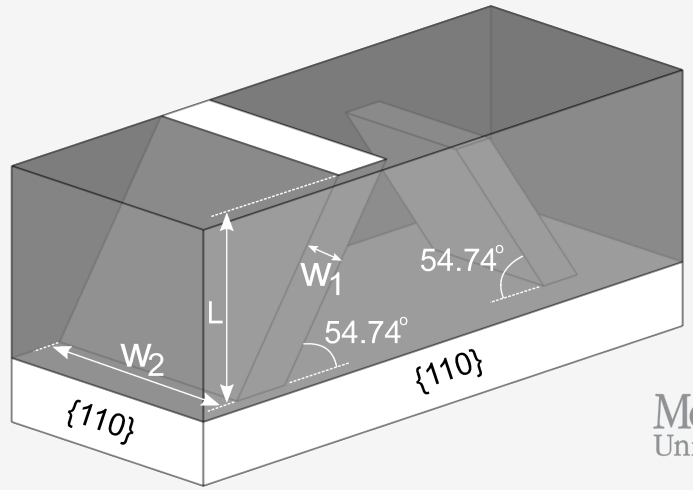


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# Outline

1 Introduction

2 Background
- Theoretical
- Experimental

3 Symmetry Breaking at Interfaces
- Twins and Epitaxy on Vicinal (Offcut) (001) Silicon
- Tilted Epitaxy on (211) Silicon

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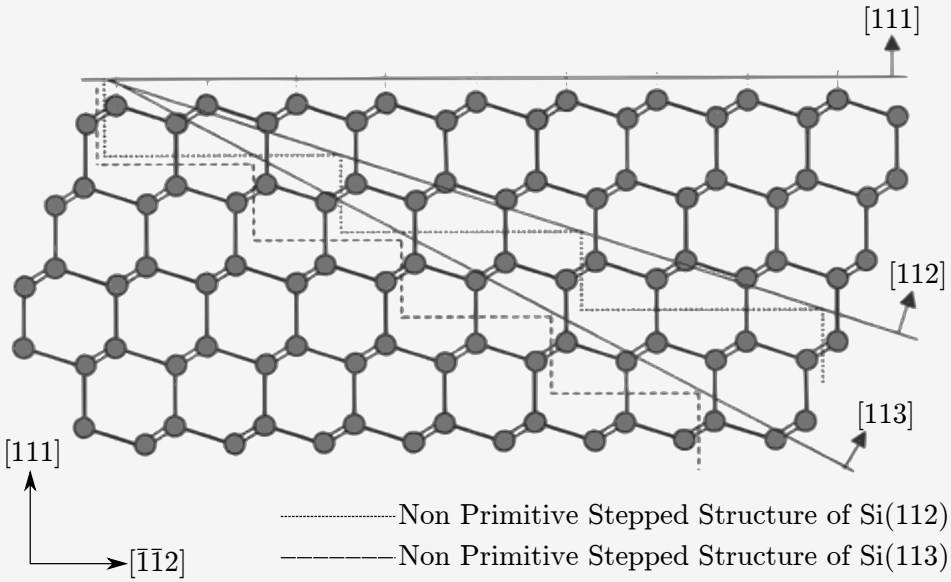
# Tilted Epitaxy on (211) Silicon

## Introduction

- The (211) surface of cubic diamond crystals are asymmetric, exhibiting atomic stepping
- (211) surfaces also have two non-equivalent lattice sites for zincblende semiconductor nucleation
- (211) substrates were initially investigated to solve the polar on non-polar problem of binary growth on silicon




G. Brill, et. al., J. Electron. Mater. 32, 717–722 (2003).

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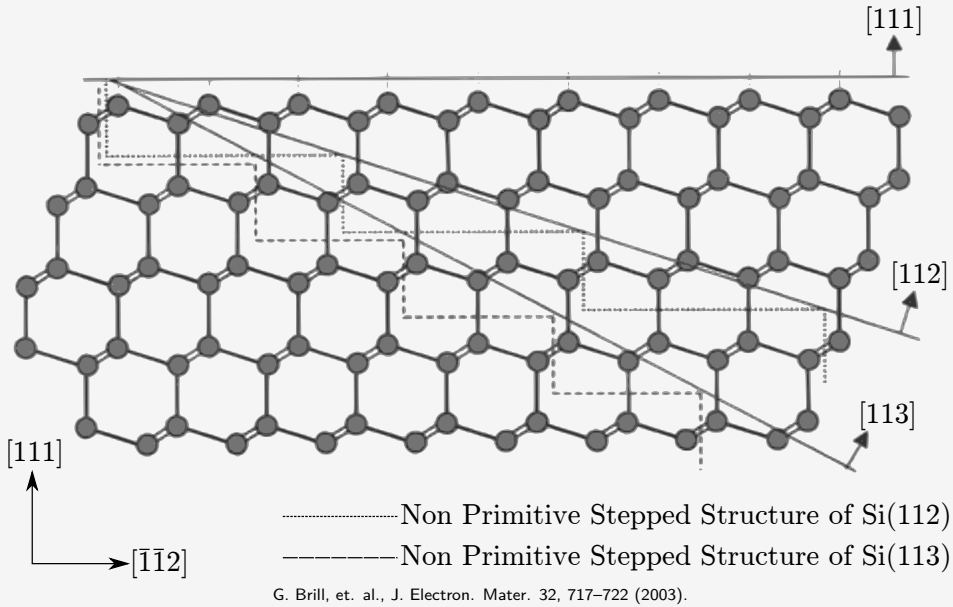


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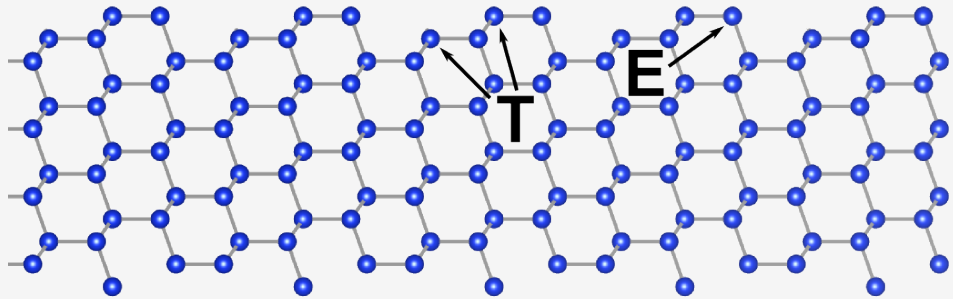


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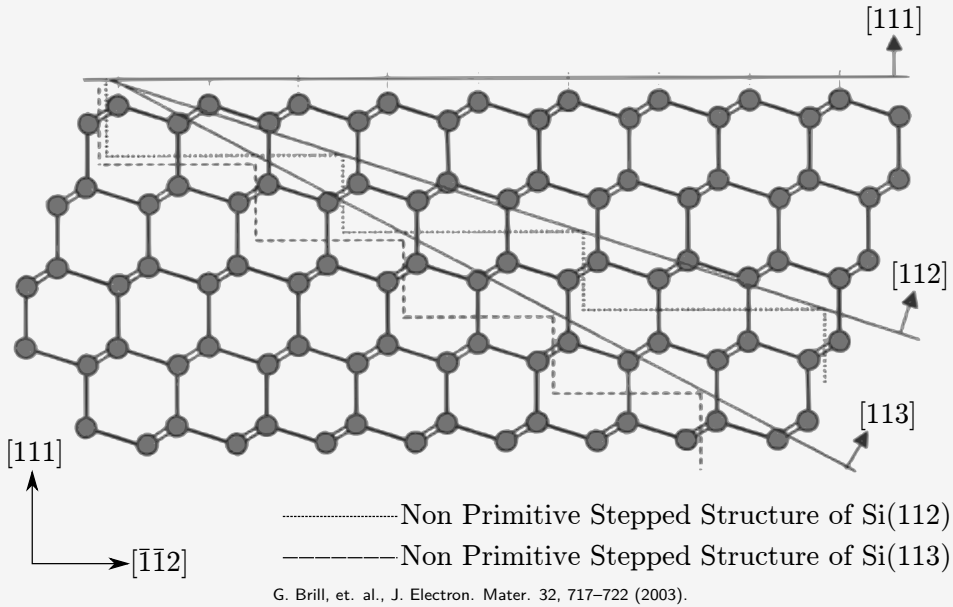


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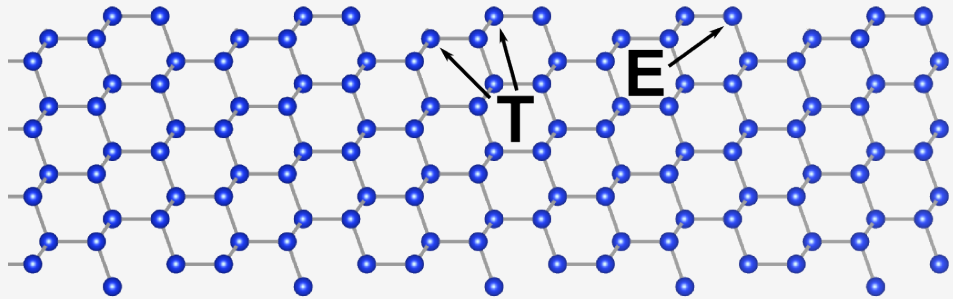


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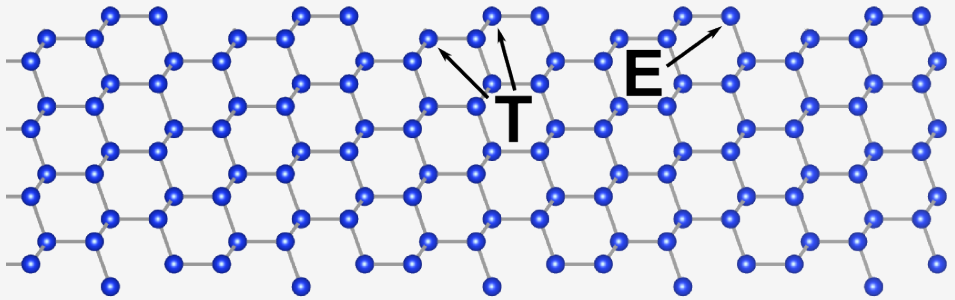
# Tilted Epitaxy on (211) Silicon

## Experimental

- (211) silicon substrates
- 500 nm films of GaSb were deposited in MBE
- GaSb and silicon have an intrinsic lattice mismatch of 13%



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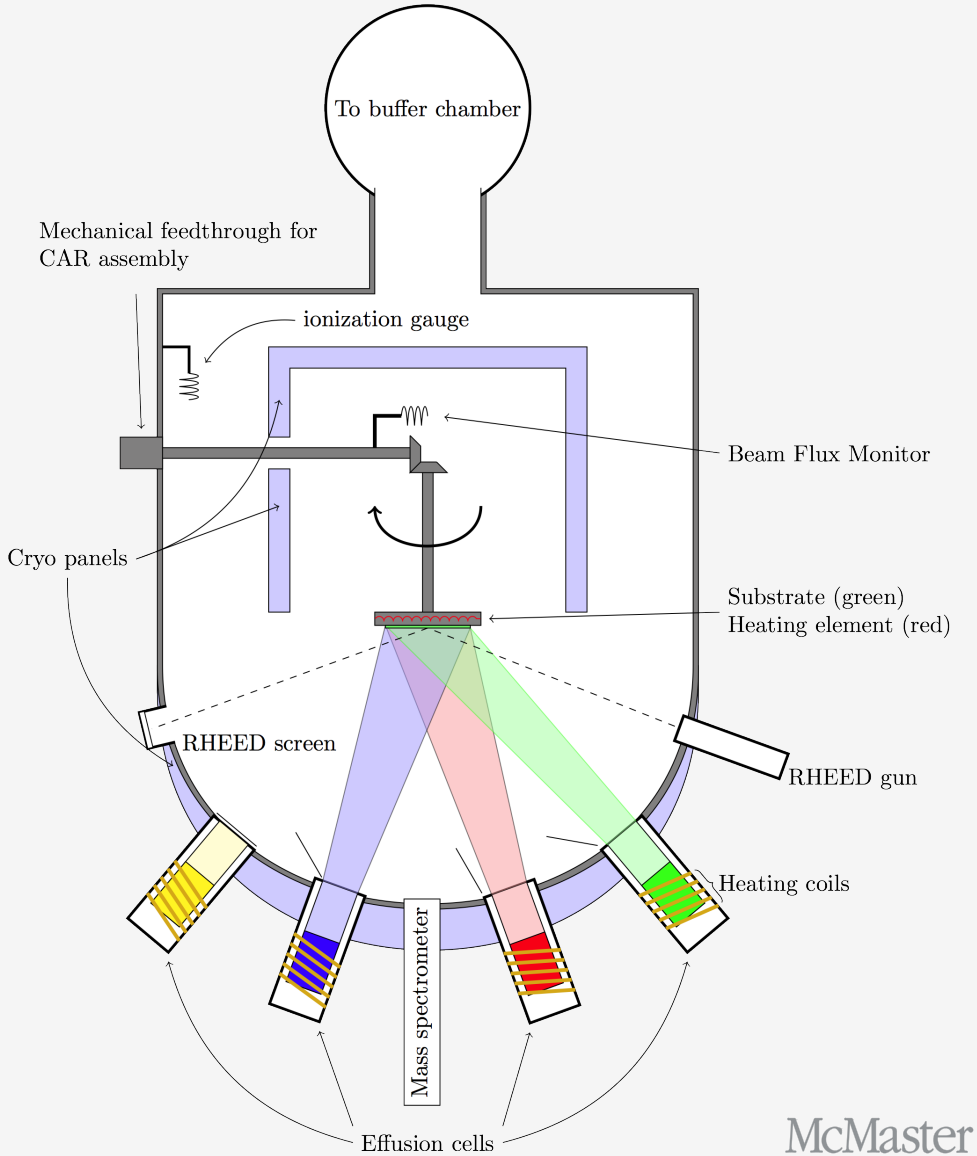

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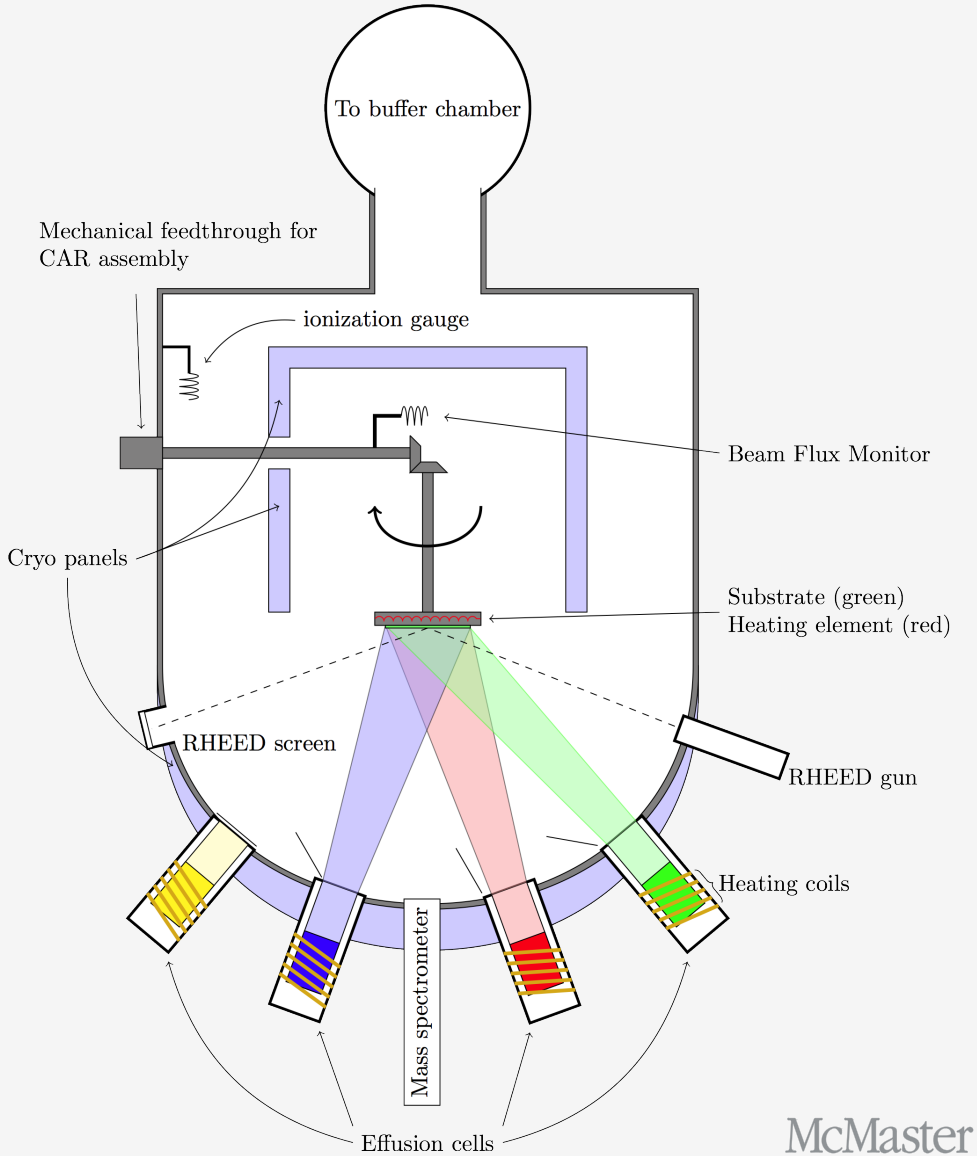
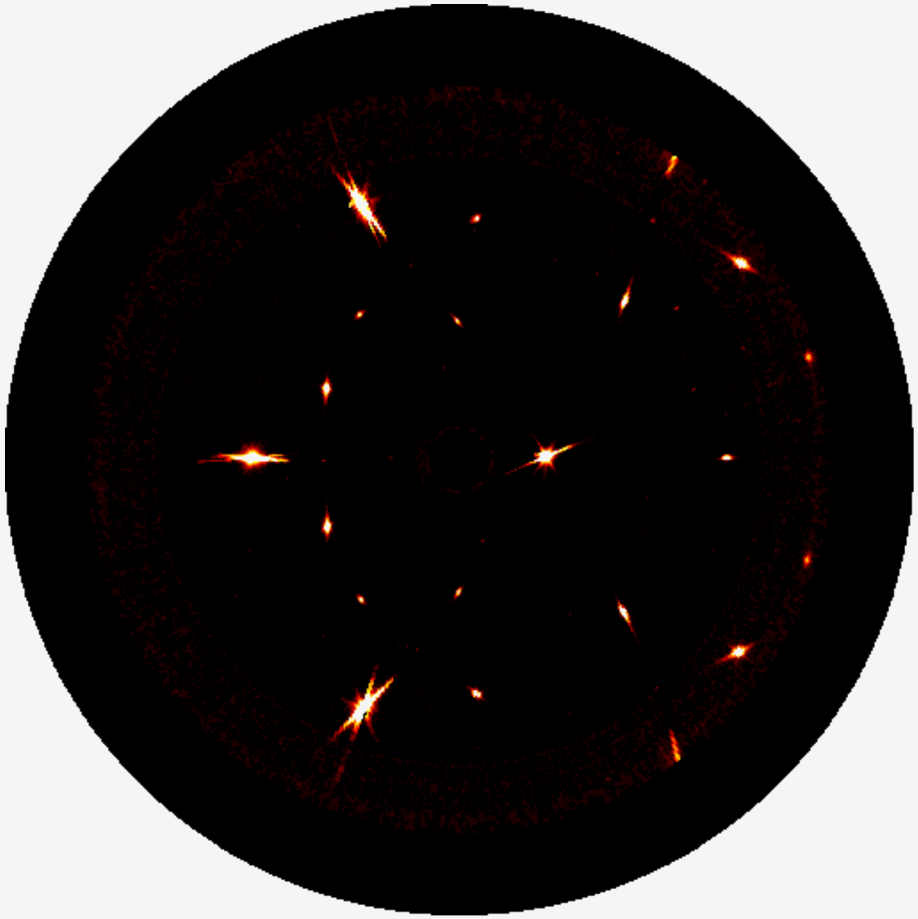
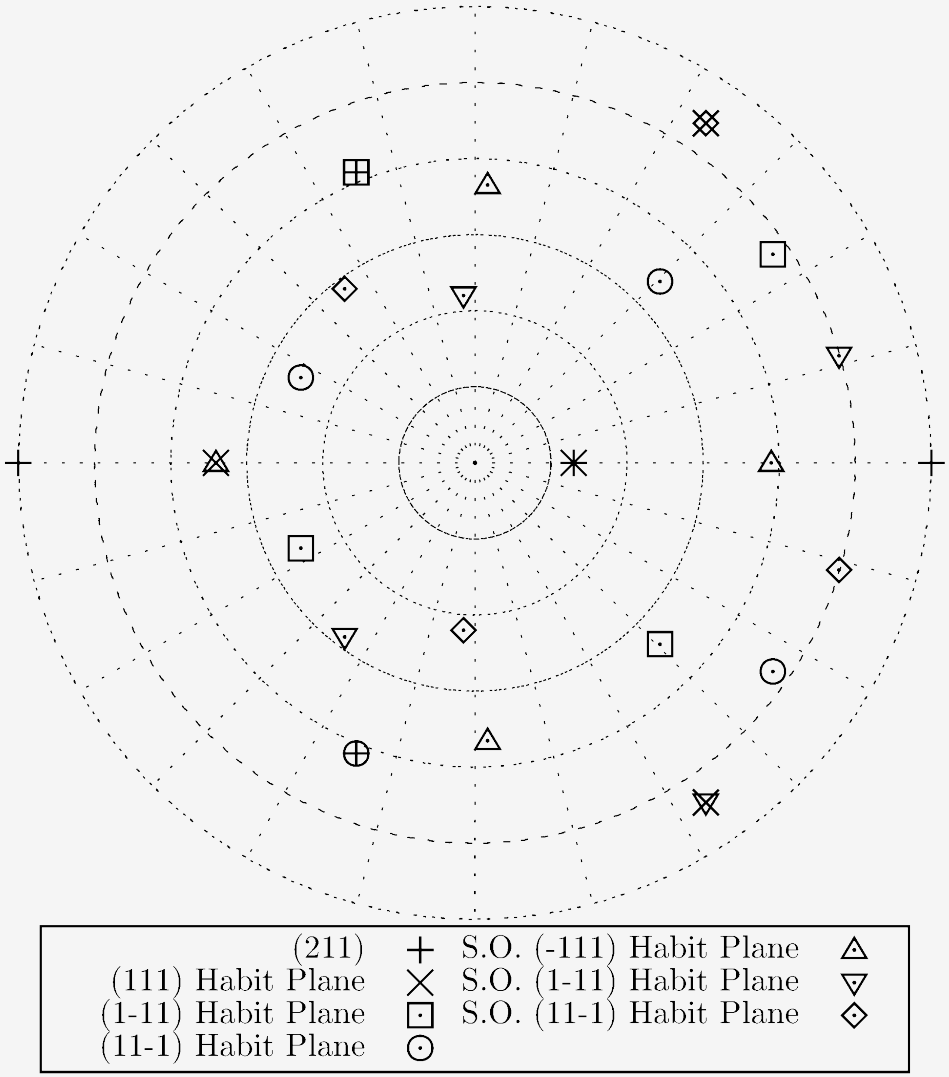


# 2DXRD Results



(a) Measured




(b) Simulated

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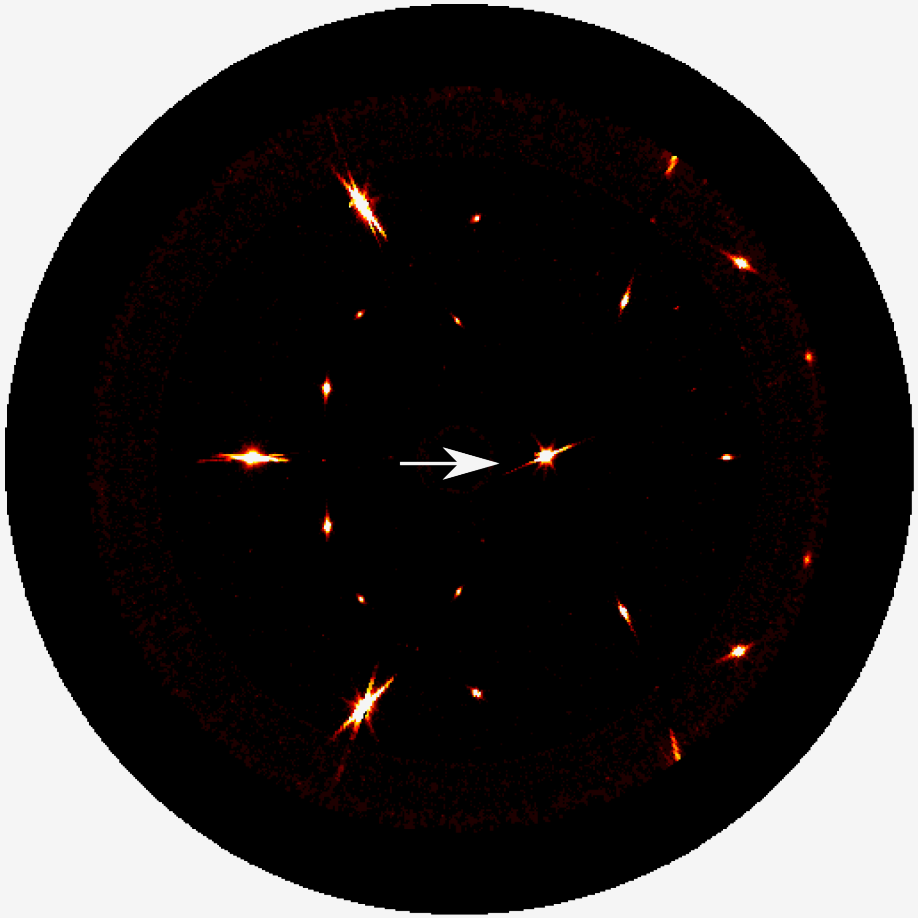

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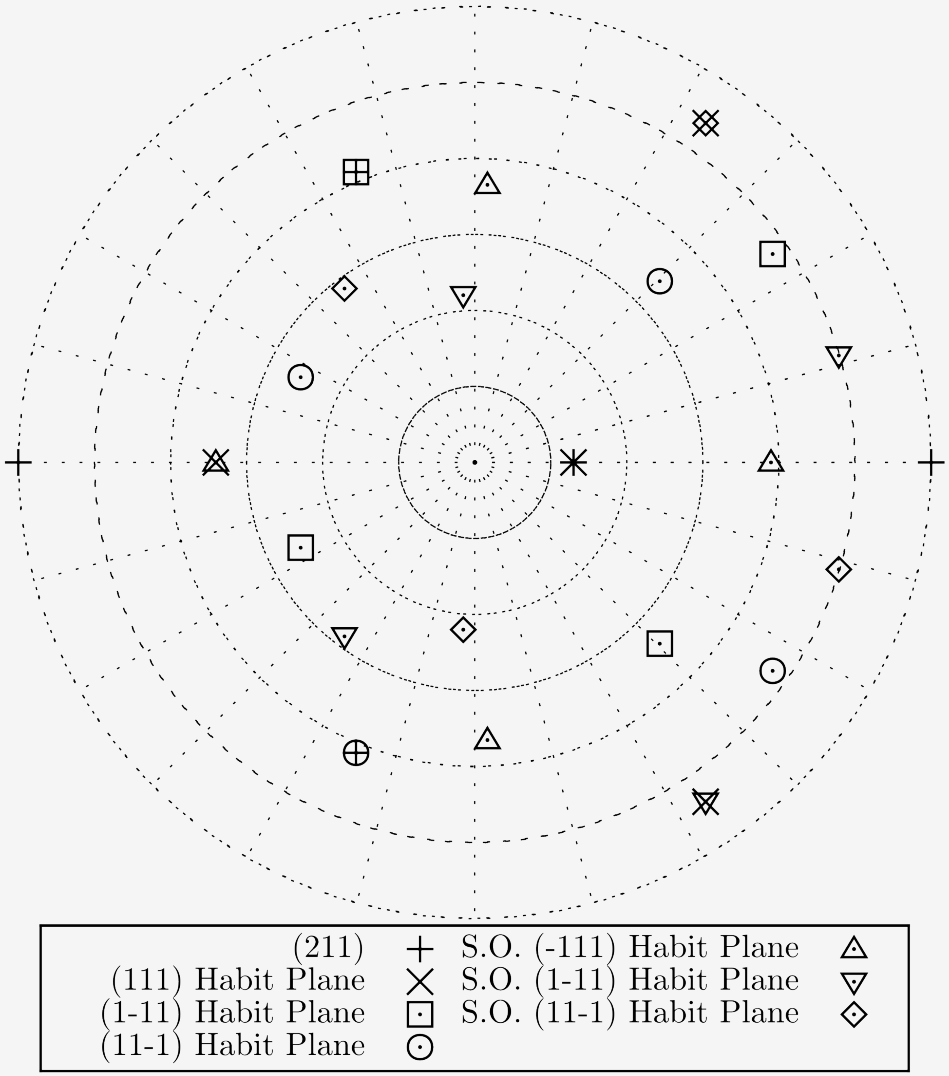


(b) Simulated

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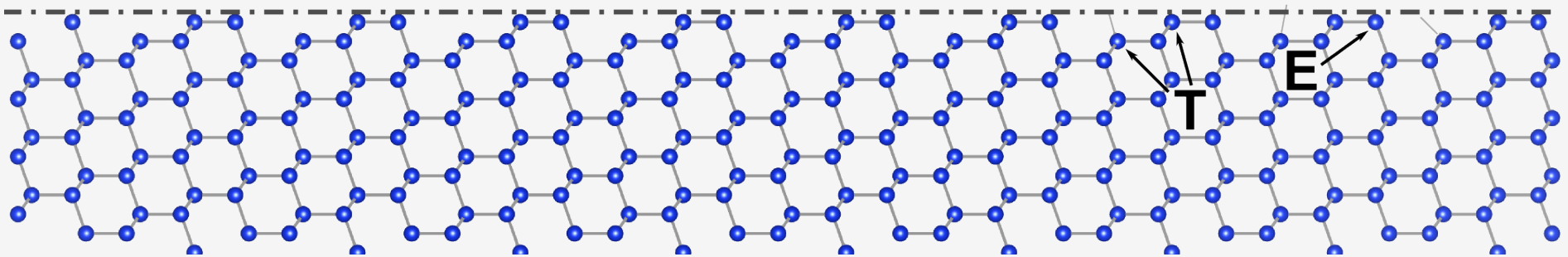
# A Toy Model



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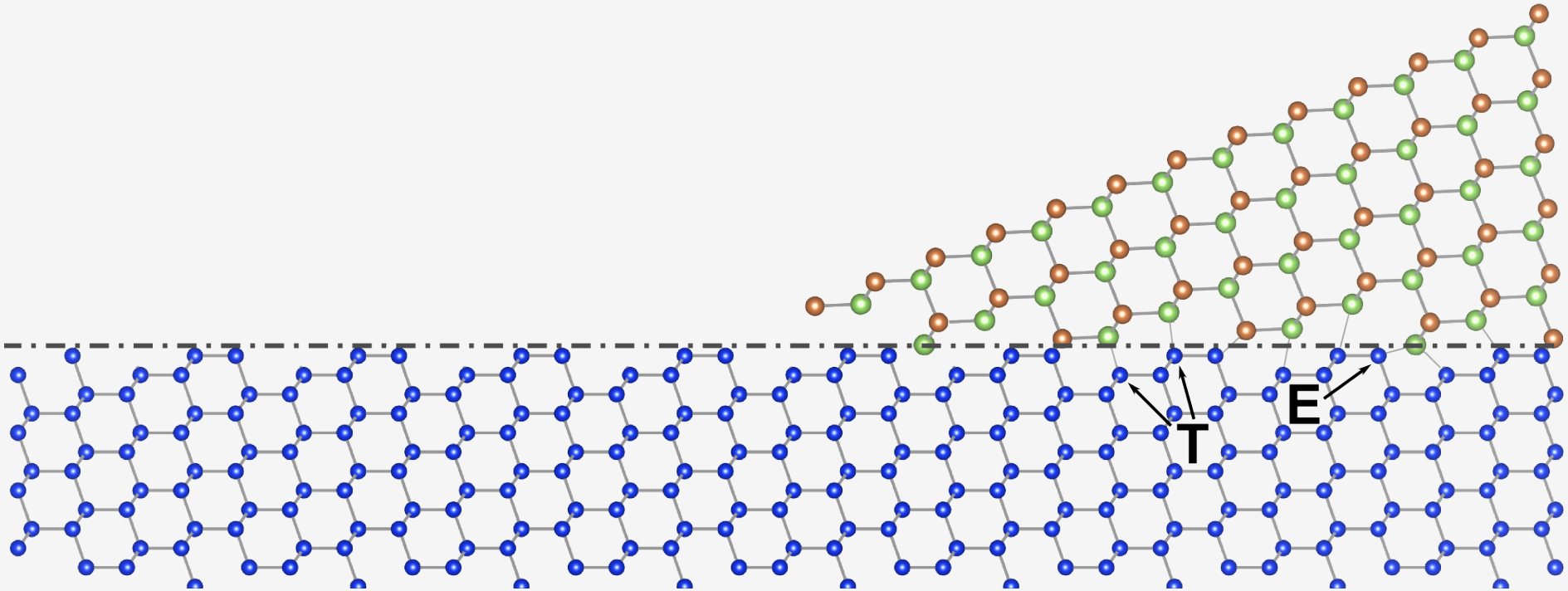


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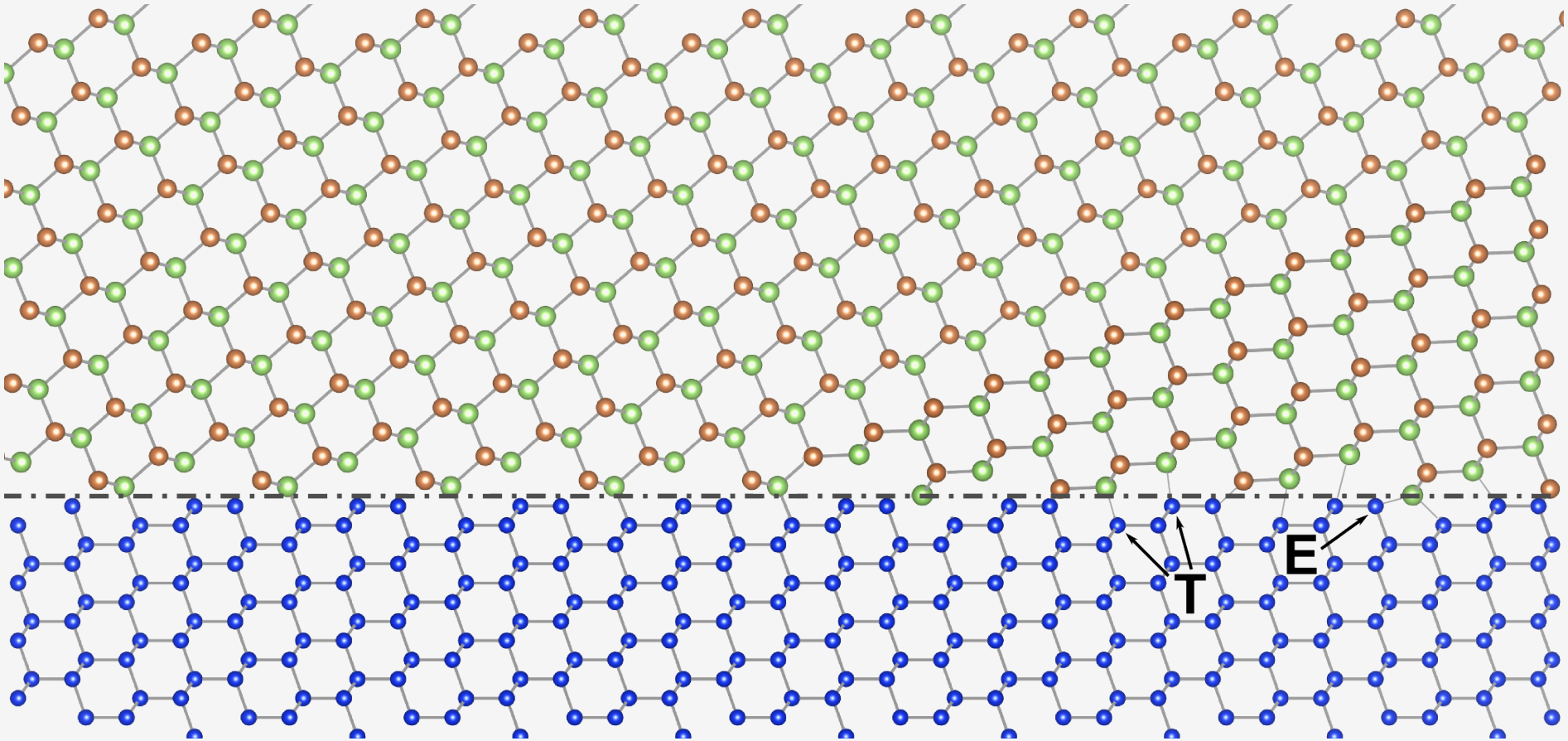


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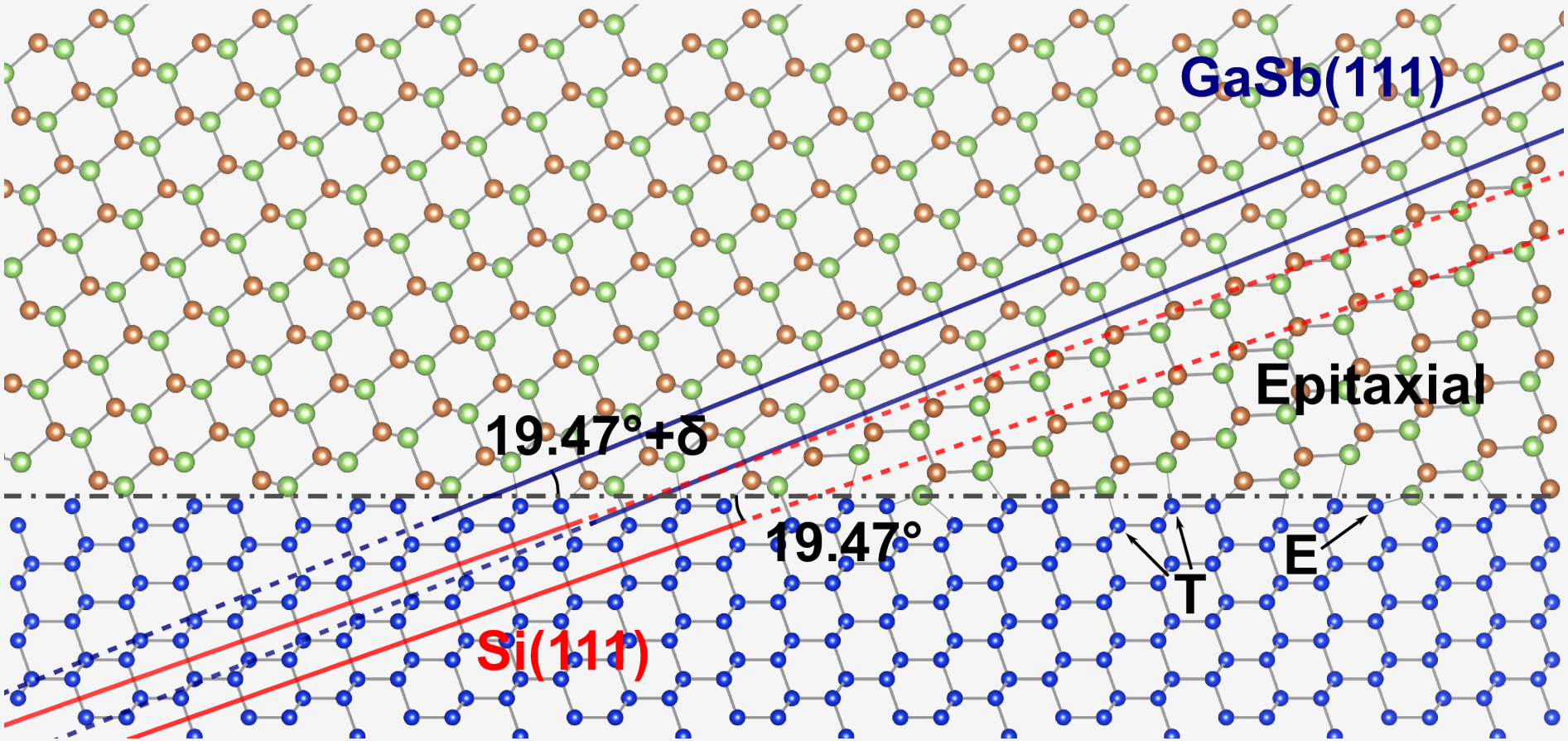


$$\frac{a_{GaSb}}{\sqrt{3}\sin(19.471^\circ + 2.5^\circ)} \simeq \frac{a_{Si}}{\sqrt{3}\sin(19.471^\circ)}$$

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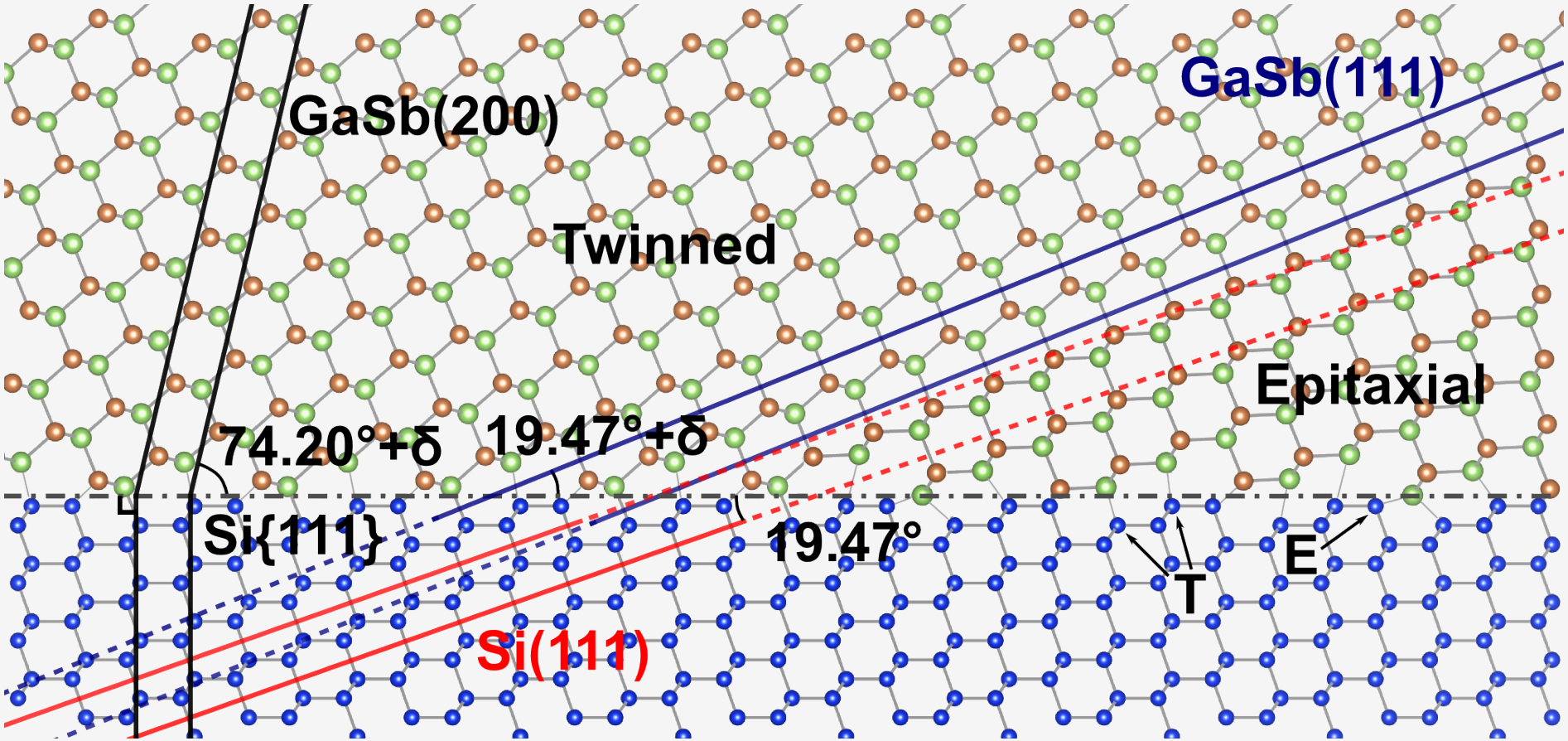


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## Generalizing the Toy Model

- Equate d-spacing of Silicon with projected d-spacing of GaSb
- Generalize for any film and substrate combination
- Strain for an arbitrary tilt is the difference between two plane spacing

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$$\varepsilon = \frac{a_{film}}{\sqrt{3}\sin(19.471^\circ + \delta)} - \frac{a_{sub}}{\sqrt{3}\sin(19.471^\circ)}$$

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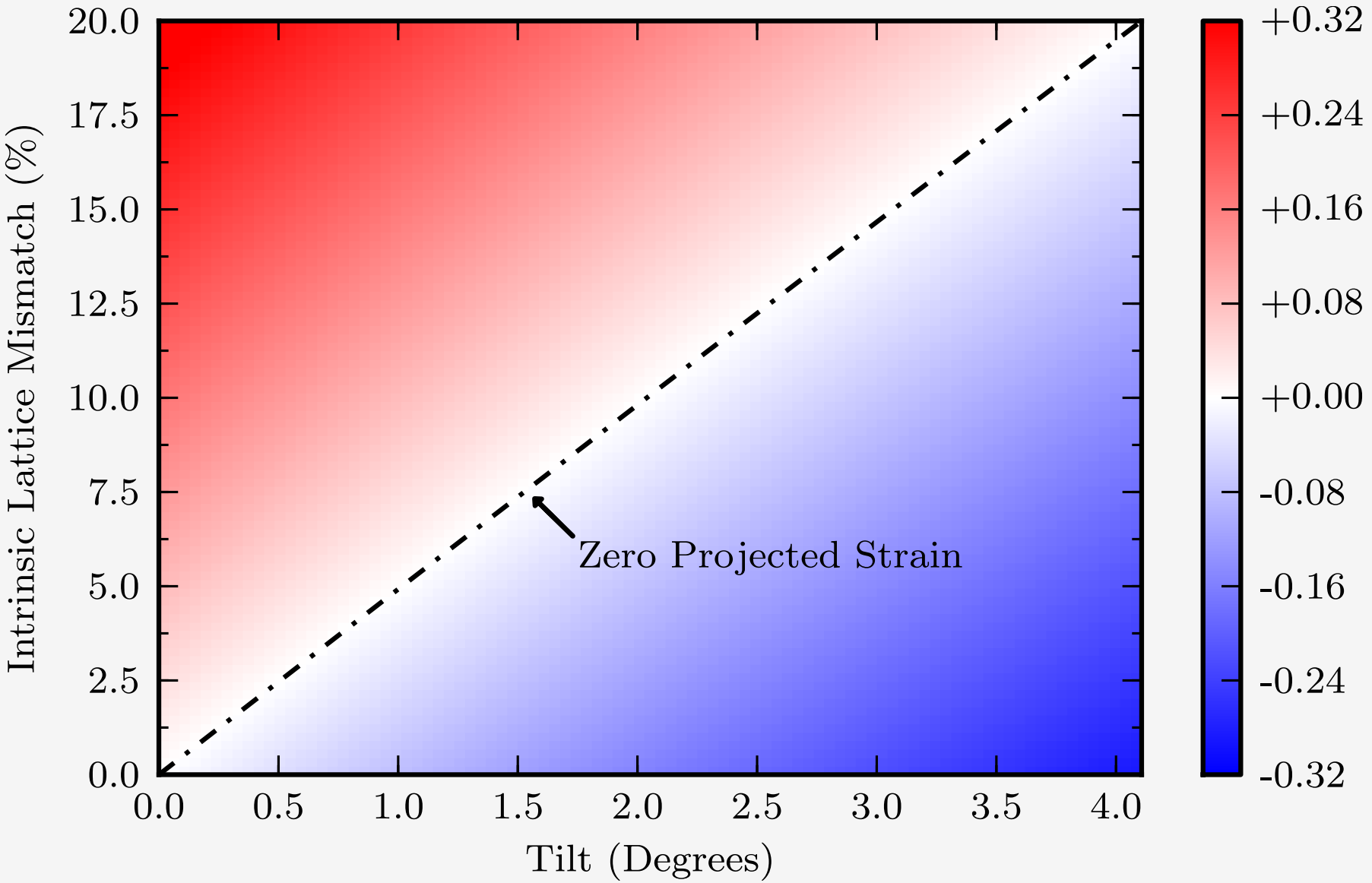


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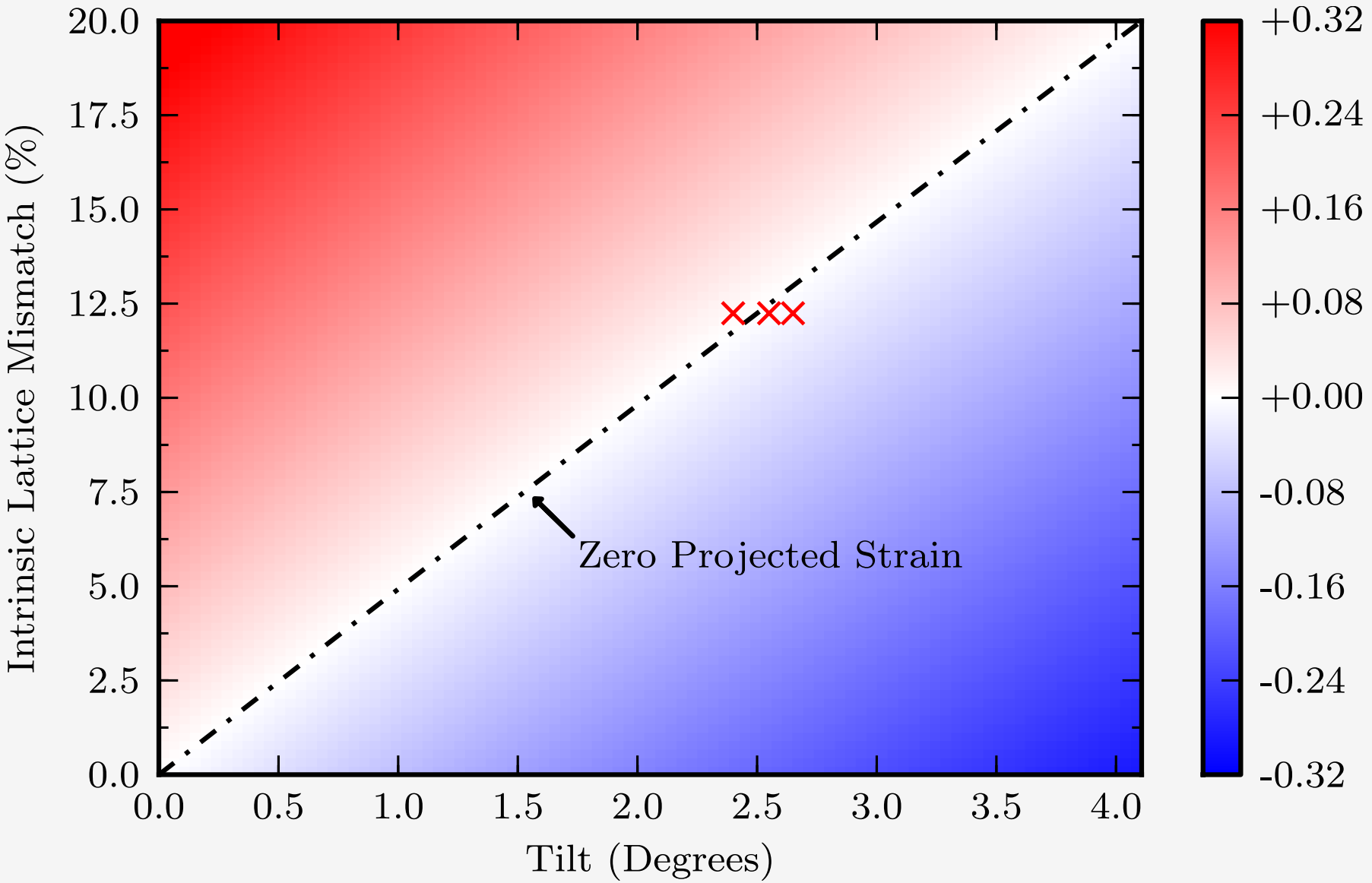


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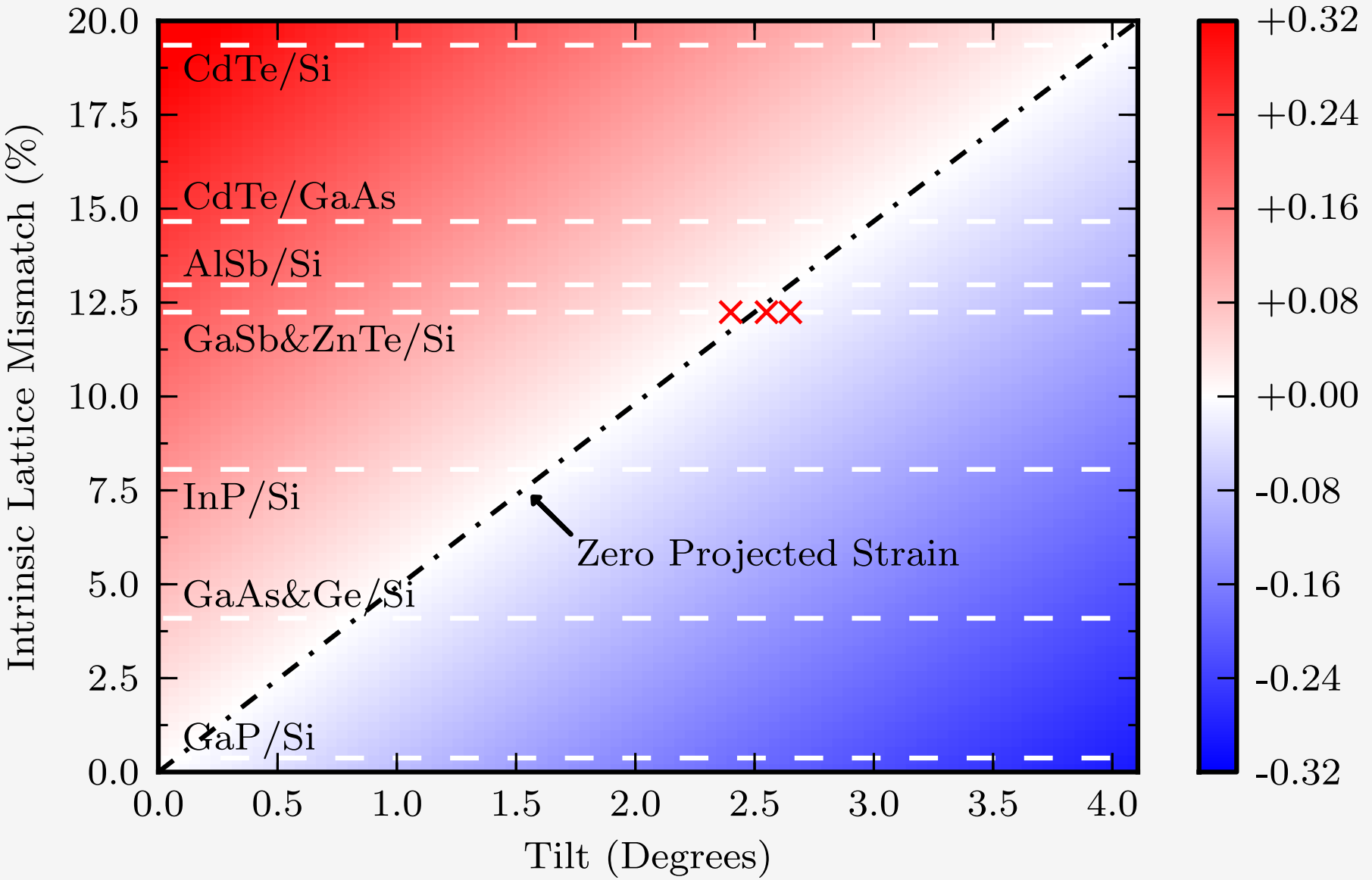
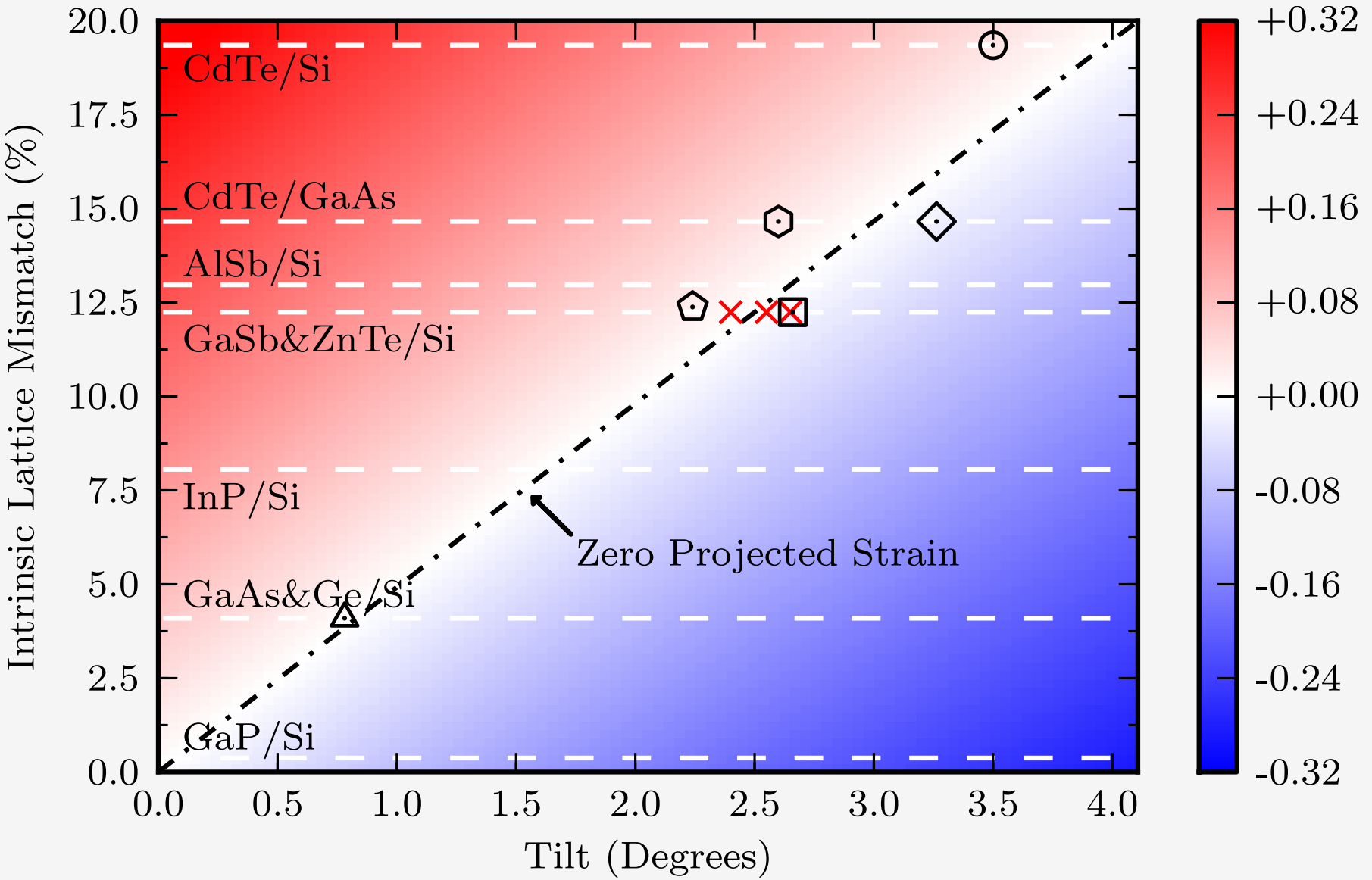

Intrinsic Lattice Mismatch (%)
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
CdTe/Si
CdTe/GaAs
AlSb/Si
GaSb&ZnTe/Si
InP/Si
GaAs&Ge/Si
GaP/Si
Zero Projected Strain
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Tilt (Degrees)
+0.32
+0.24
+0.16
+0.08
+0.00
-0.08
-0.16
-0.24
-0.32


CdTe/Si
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Tilt (Degrees)
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17.5
15.0
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5.0
2.5
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
+0.32
+0.24
+0.16
+0.08
+0.00
-0.08
-0.16
-0.24
-0.32

# Epitaxy on (211) Silicon

## Conclusions

- The natural asymmetry of (211) allows the accommodation of strain by tilting on an axis perpendicular to the asymmetry
- Tilt is driven by the alignment of (111) planes between the substrate and the thin film
- Tilt allows strain accommodation over a lattice mismatch of 0-20%

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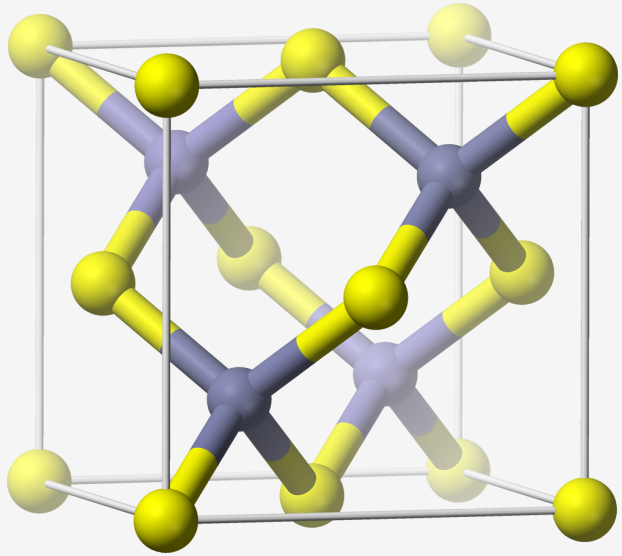
# Introduction

## Unusual Bond Energies

- Typically, epitaxial bonds are covalent or "chemisorbed" in strength
- Interface energies are comparable to in-bulk energies
- Bond energies between chemically dissimilar materials are very different
- Bond energy differences have implications for strain, post-treatment of films and defect formation



Wikipedia: Zincblende

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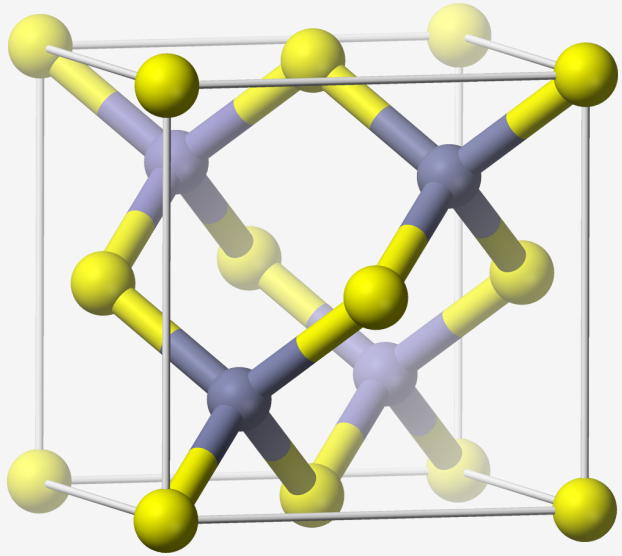

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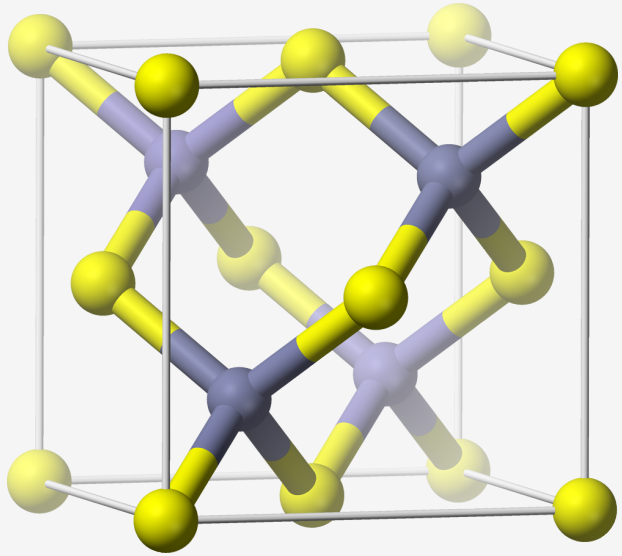
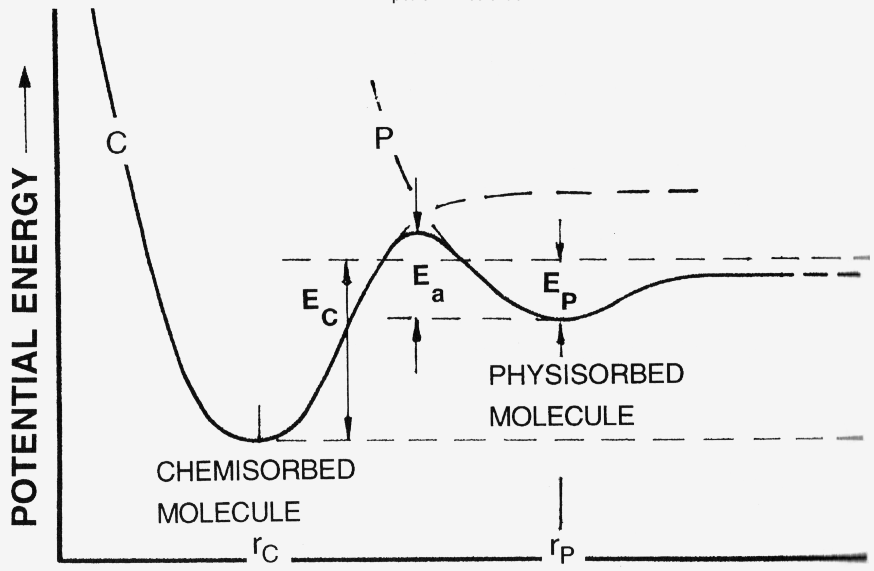


Wikipedia: Zincblende




M. Ohring, Materials Science of Thin Films, 2nd ed. San Diego: Elsevier Science, 2001.

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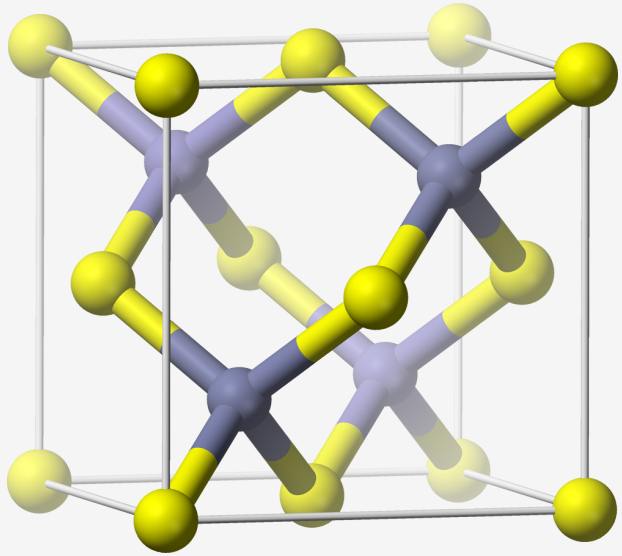
# Introduction

## Unusual Bond Energies

- Typically, epitaxial bonds are covalent or "chemisorbed" in strength
- Interface energies are comparable to in-bulk energies
- Bond energies between chemically dissimilar materials are very different
- Bond energy differences have implications for strain, post-treatment of films and defect formation



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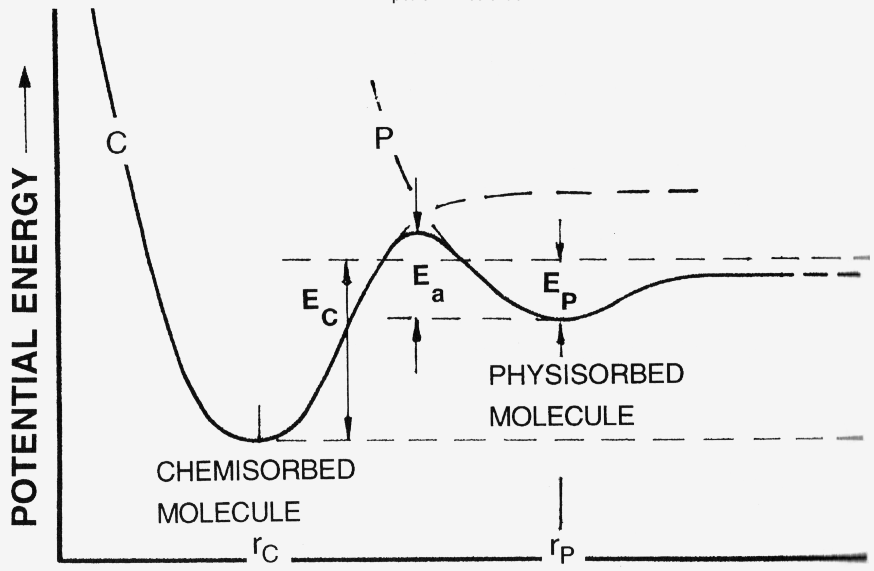


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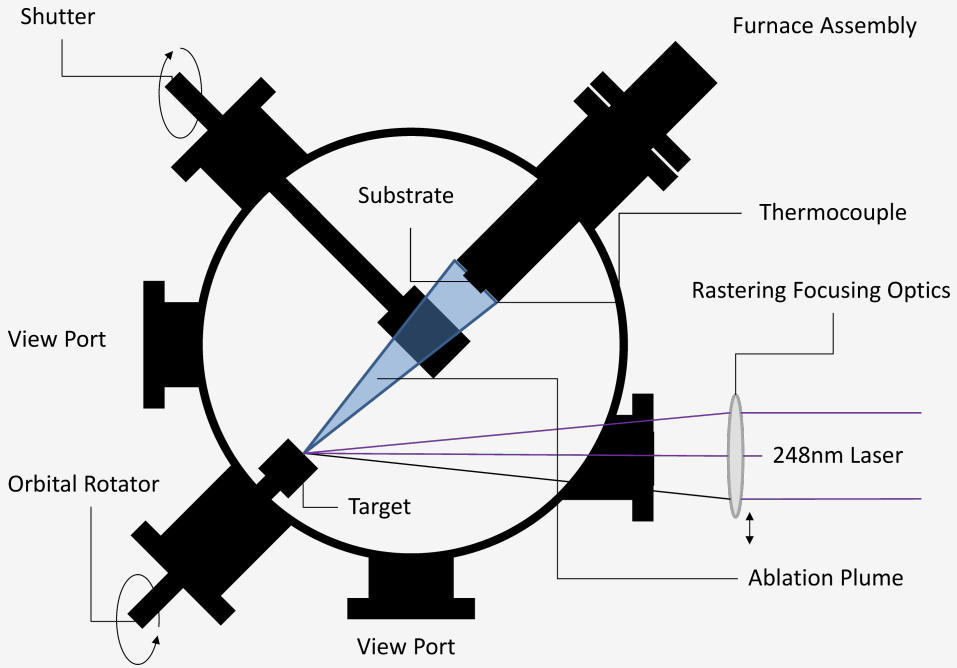
# Experimental

## Unusual Bond Energies

- Growth of CdTe thin films and nanowires has been highly successful on sapphire via PLD
- Nanowire adhesion appeared to be oddly weak despite epitaxial alignment
- How did these nanowires stay in place?
- Similar issues arose when applying contacts for electrical measurements



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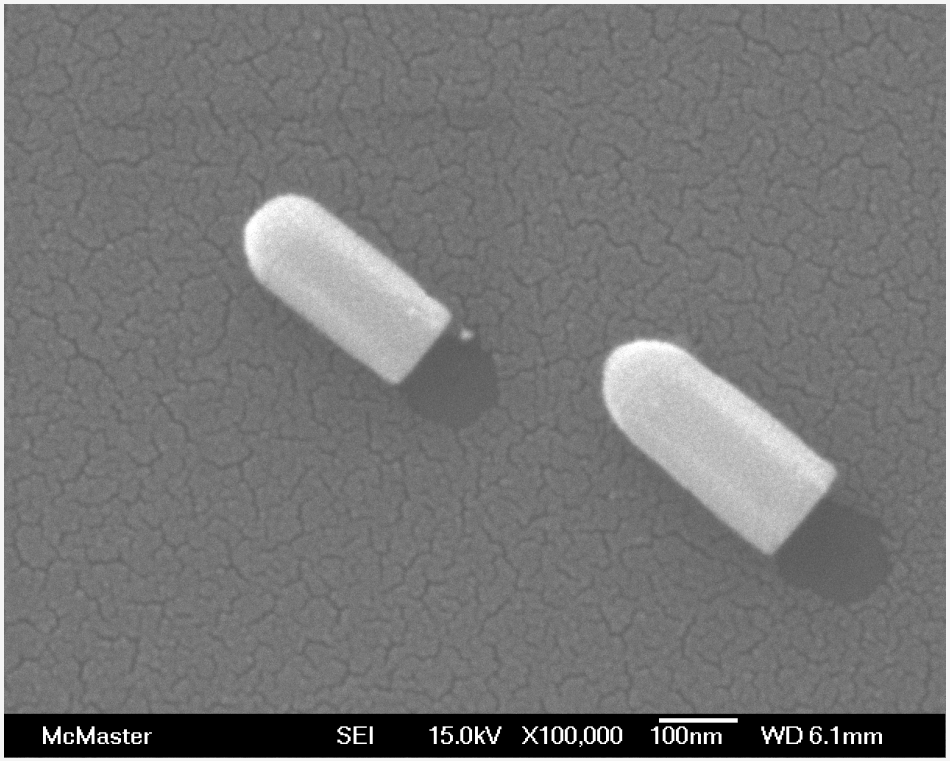


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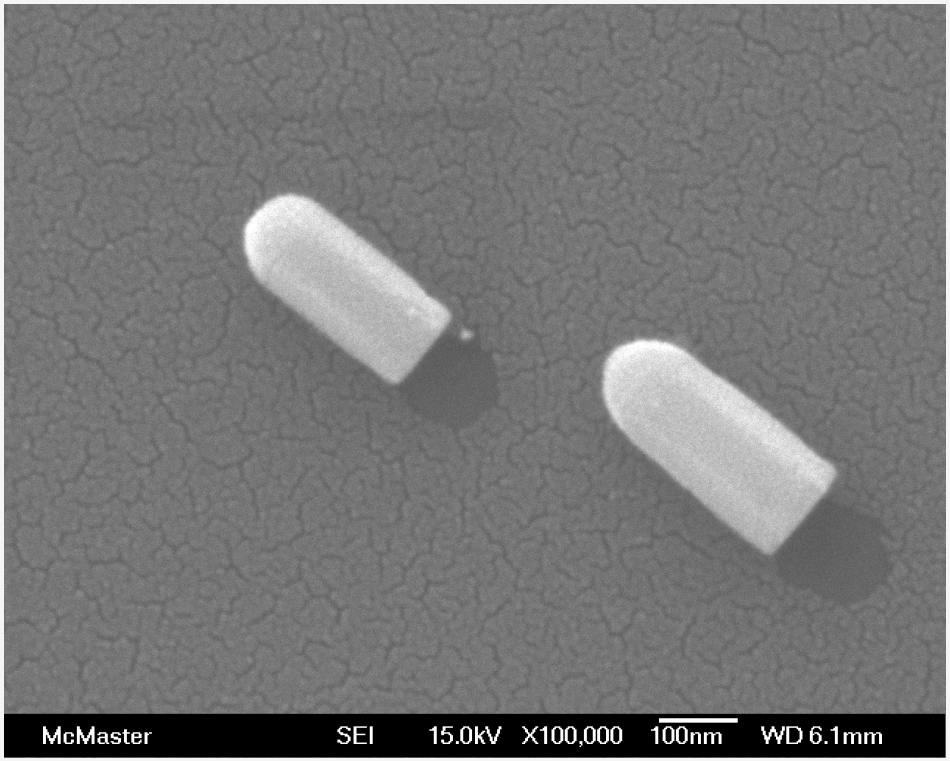


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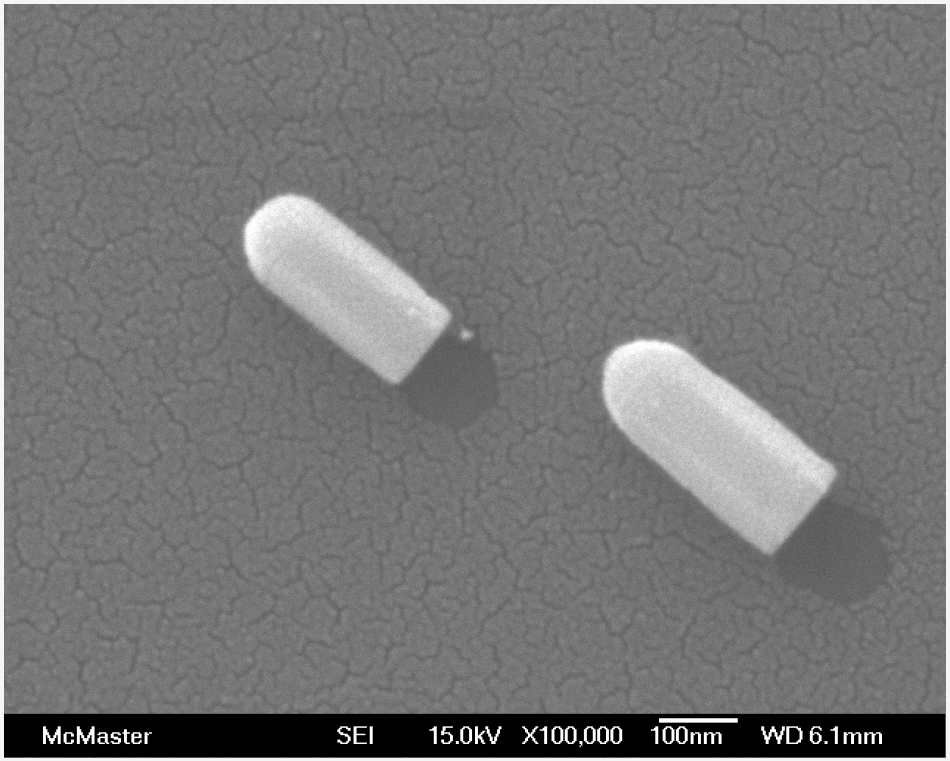


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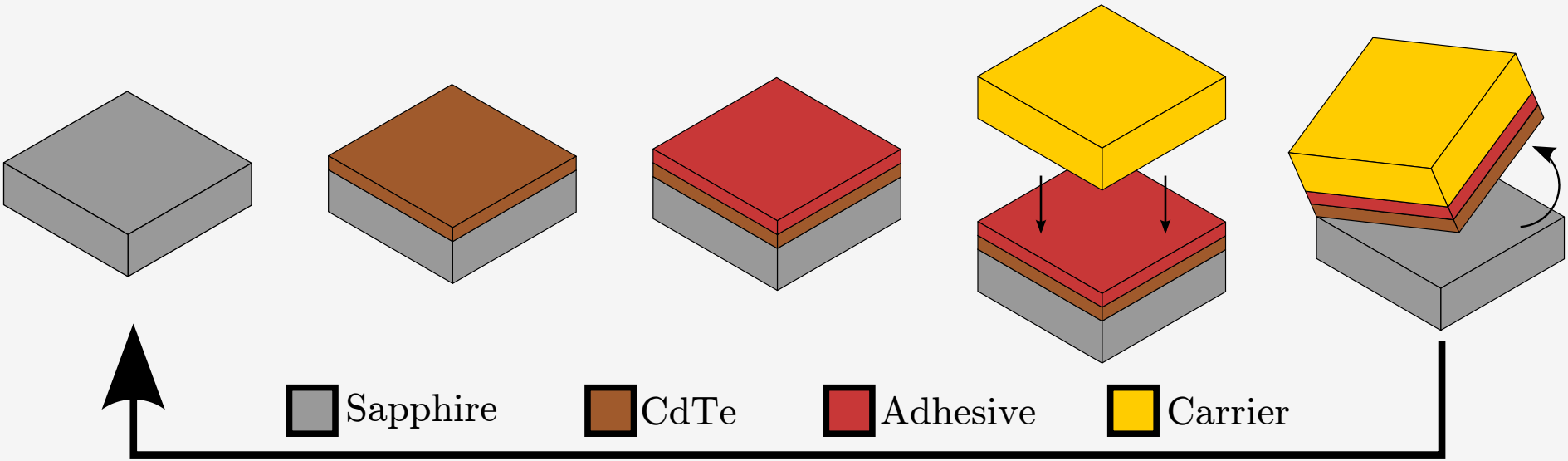
# The Process

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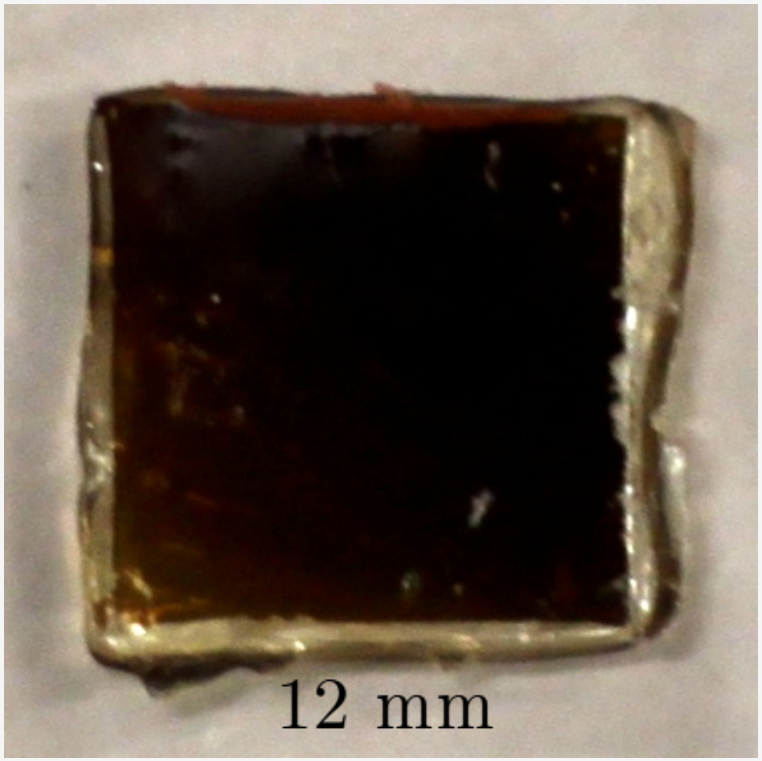
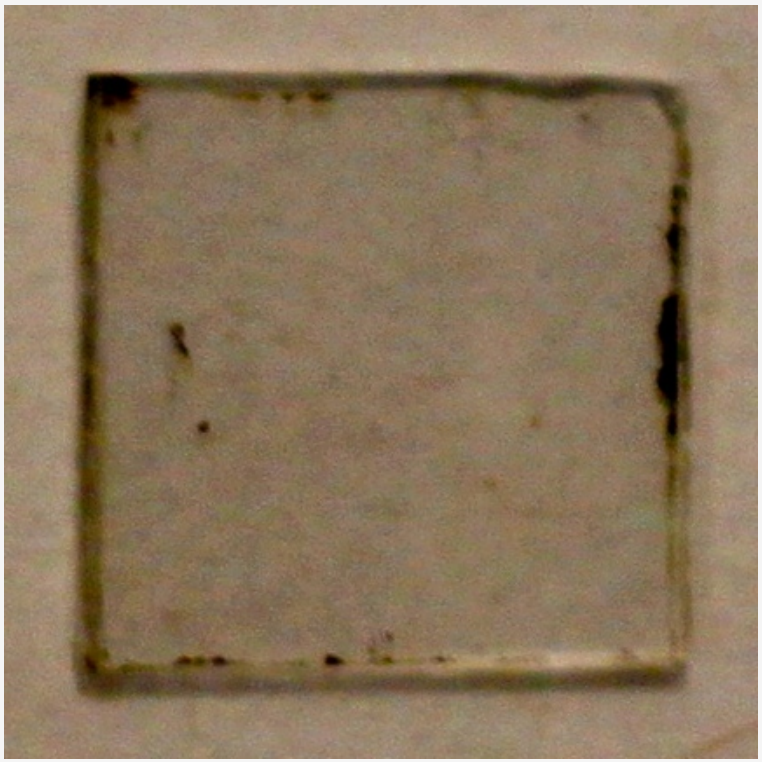
# Practical Results




CdTe on Optical Adhesive Carrier



(Mostly) Clean Sapphire Substrate

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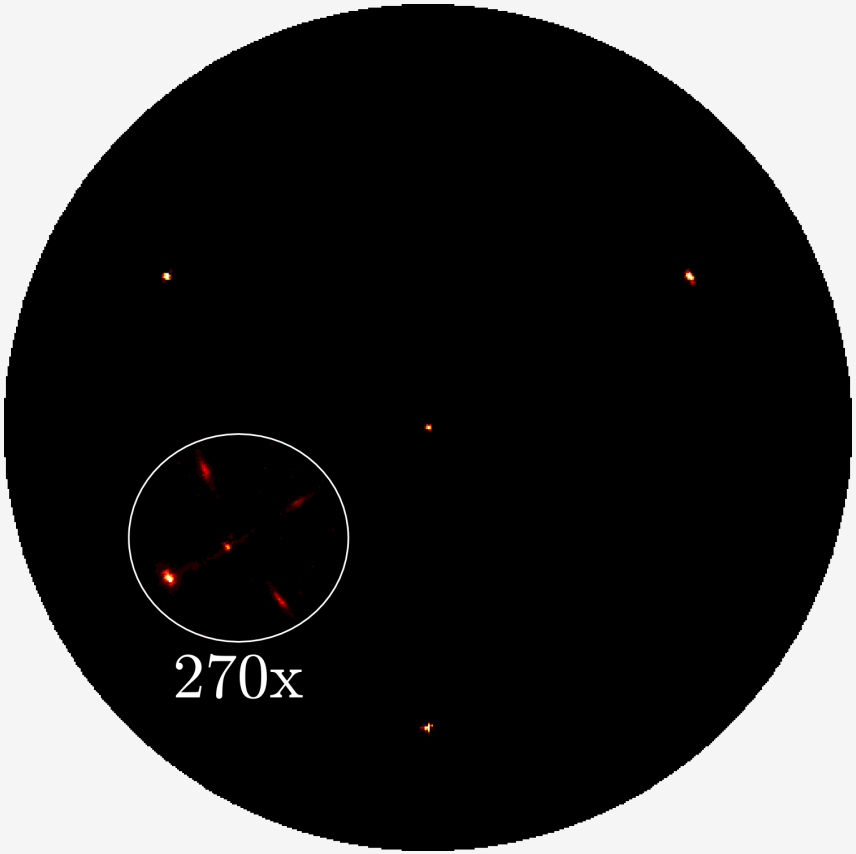
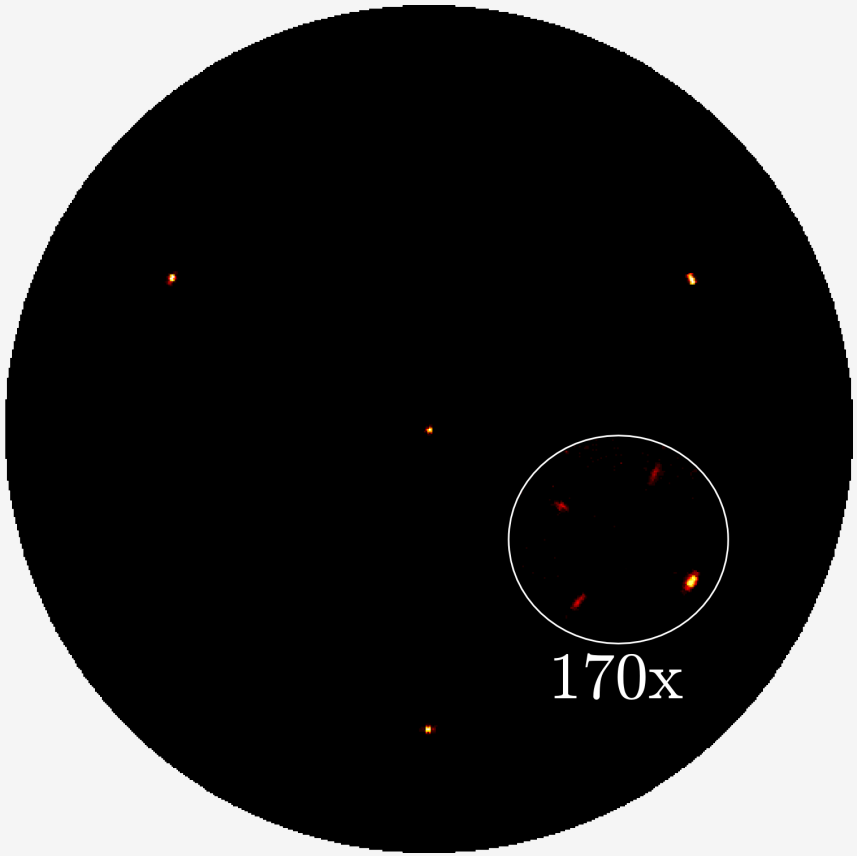
# 2DXRD Results




CdTe on Sapphire (111) Pole Figure




CdTe Liftoff on Epoxy Carrier

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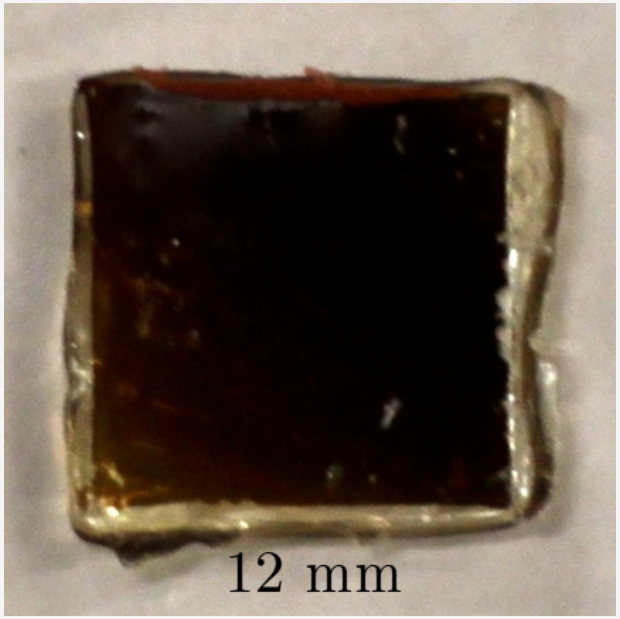
## Results

- Liftoff process is near 100% effective, subject to better processing
  - Liftoff is not destructive to crystal structure
  - Liftoff relieves strain in CdTe, improving X-ray peak widths
  - Leftover sapphire substrate is suitable for CdTe growths (after cleaning)

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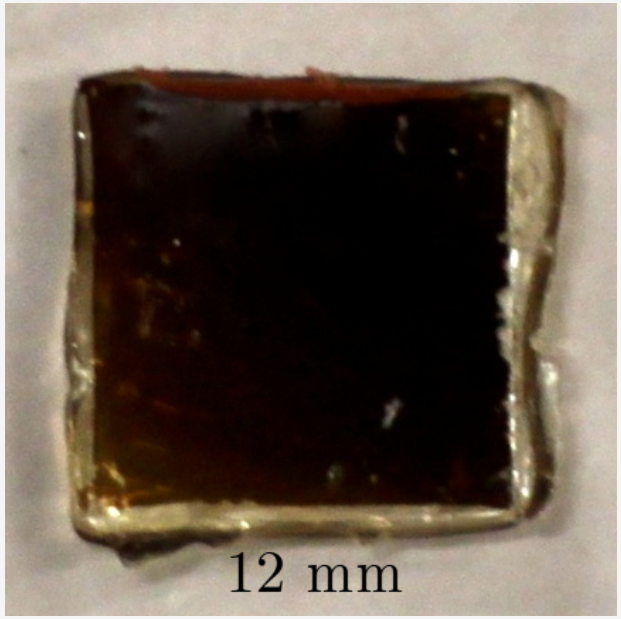


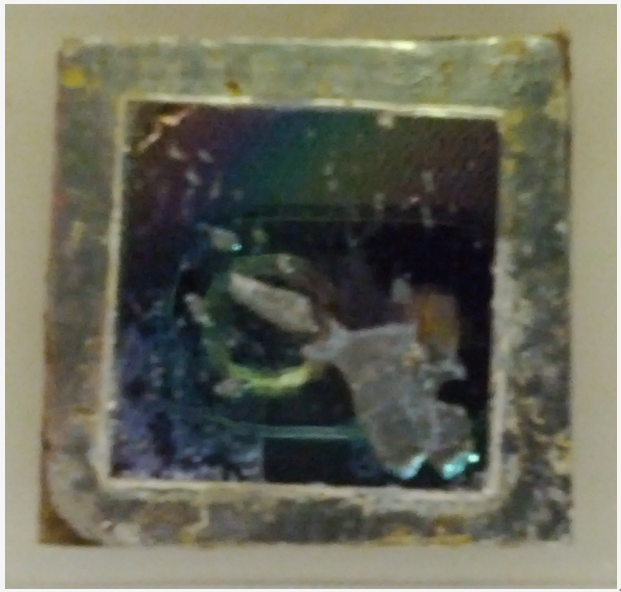

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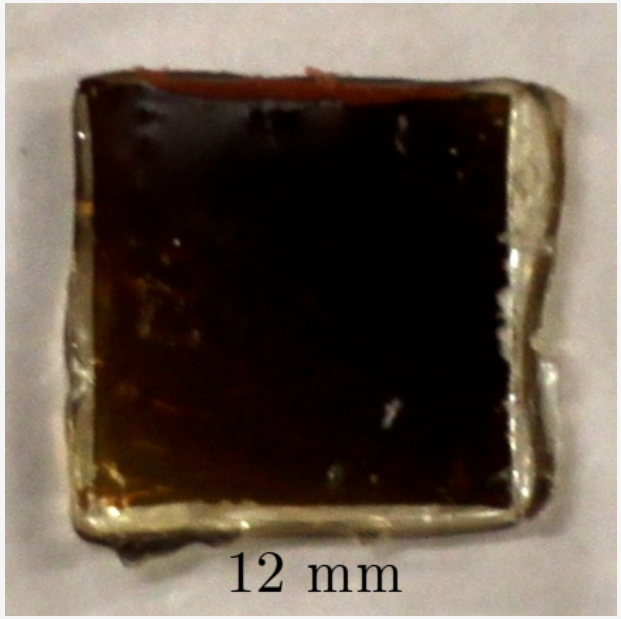


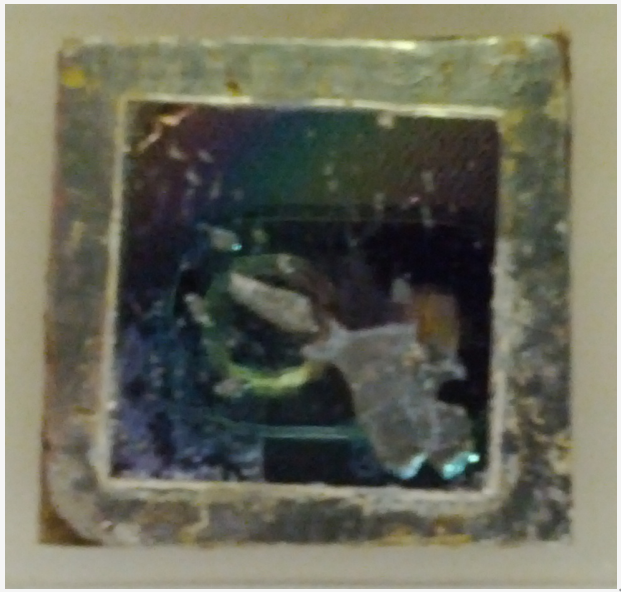

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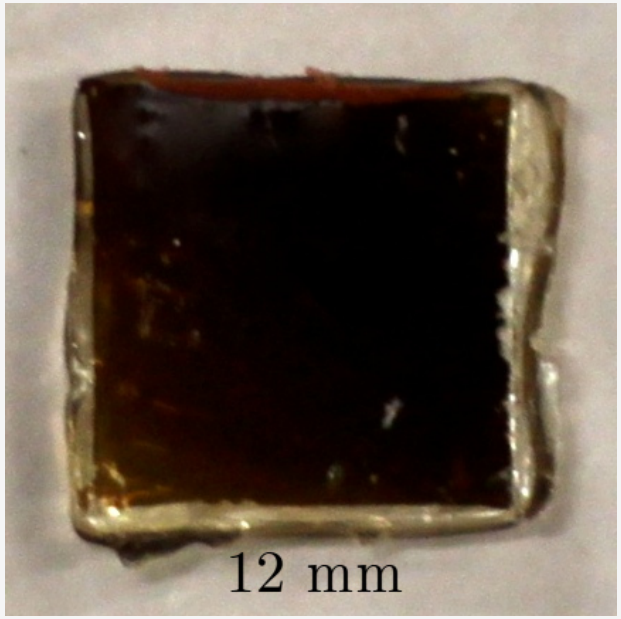


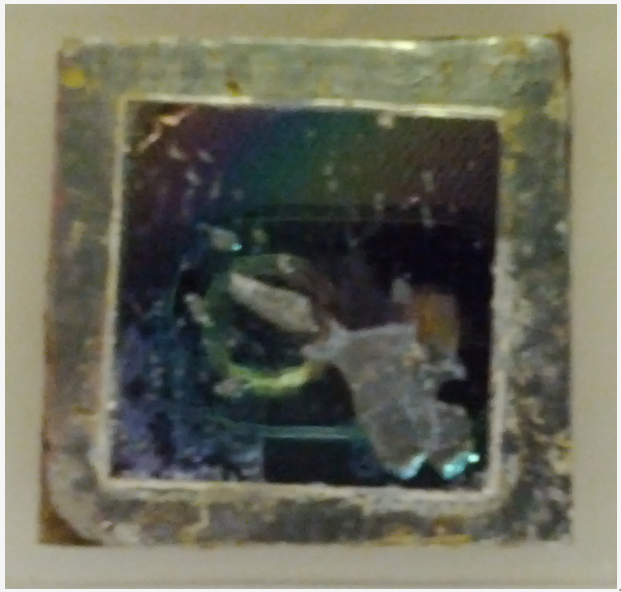

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## Results and Conclusions

- Symmetry and Symmetry Breaking
  - Vicinal substrates influence thin film growth through asymmetric enhancements of growth rate
  - Naturally asymmetric surfaces allow for strain accommodation through tilt during epitaxy
- Unusal Bond Energies at Interfaces
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# Thank You

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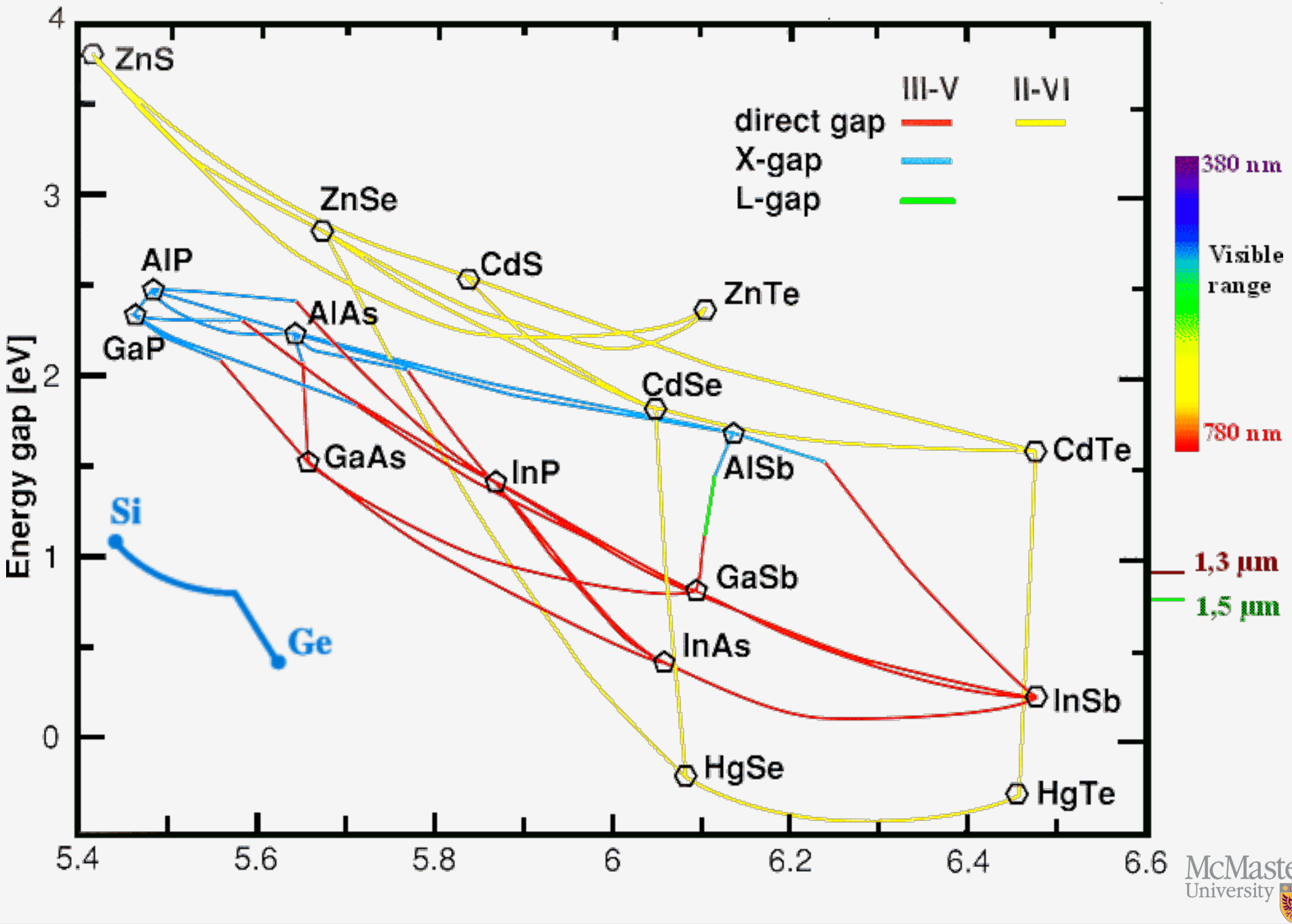
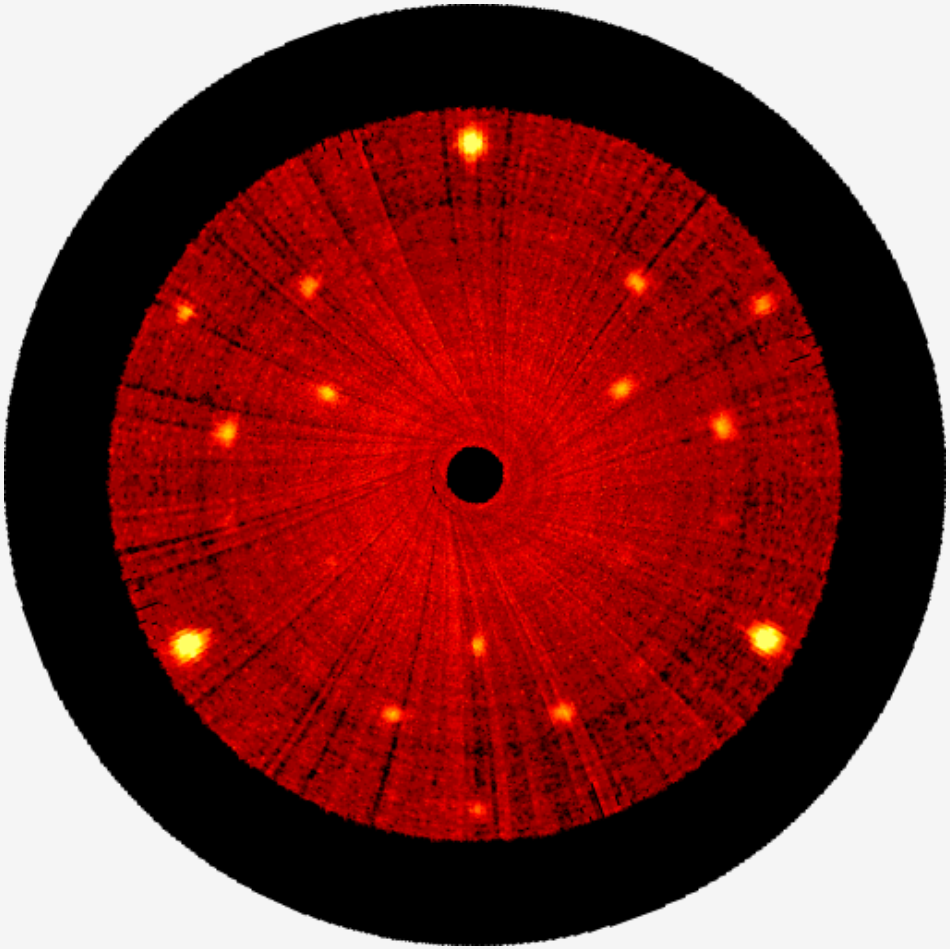
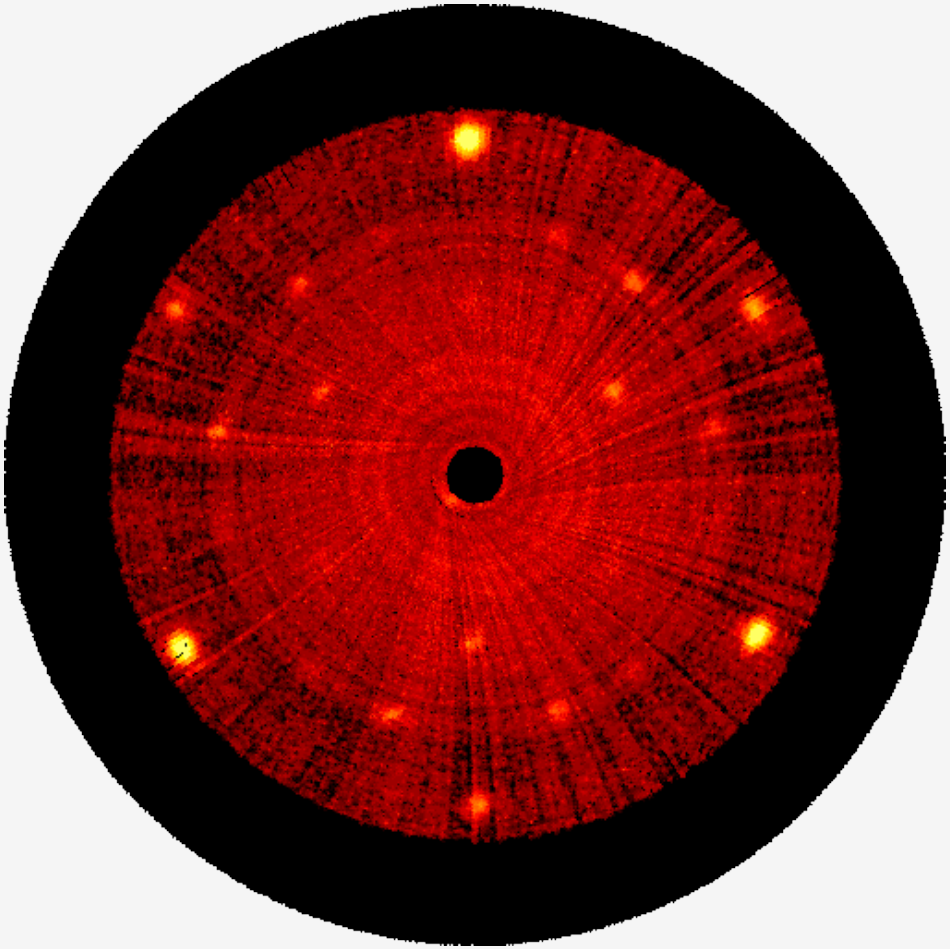

Energy gap [eV]
4
3
2
1
0
5.4
5.6
5.8
6
6.2
6.4
6.6
ZnS
ZnSe
CdS
ZnTe
AlP
AlAs
GaP
CdSe
CdTe
GaAs
InP
AlSb
Si
GaSb
Ge
InAs
InSb
HgSe
HgTe
III-V
II-VI
direct gap
X-gap
L-gap
380 nm
Visible range
780 nm
1,3 µm
1,5 µm



InSb on Sapphire



InSb on Epoxy Carrier

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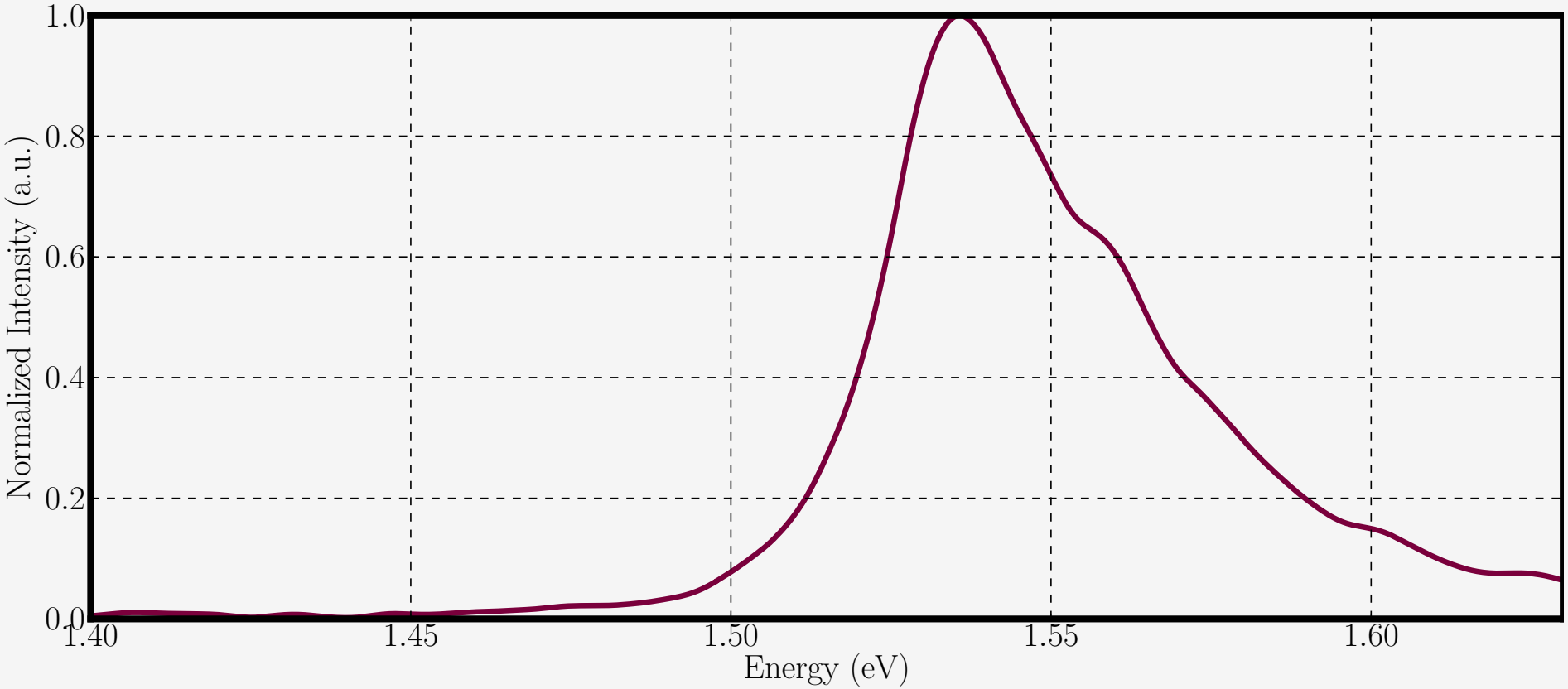
# Low Temperature Photoluminesnce

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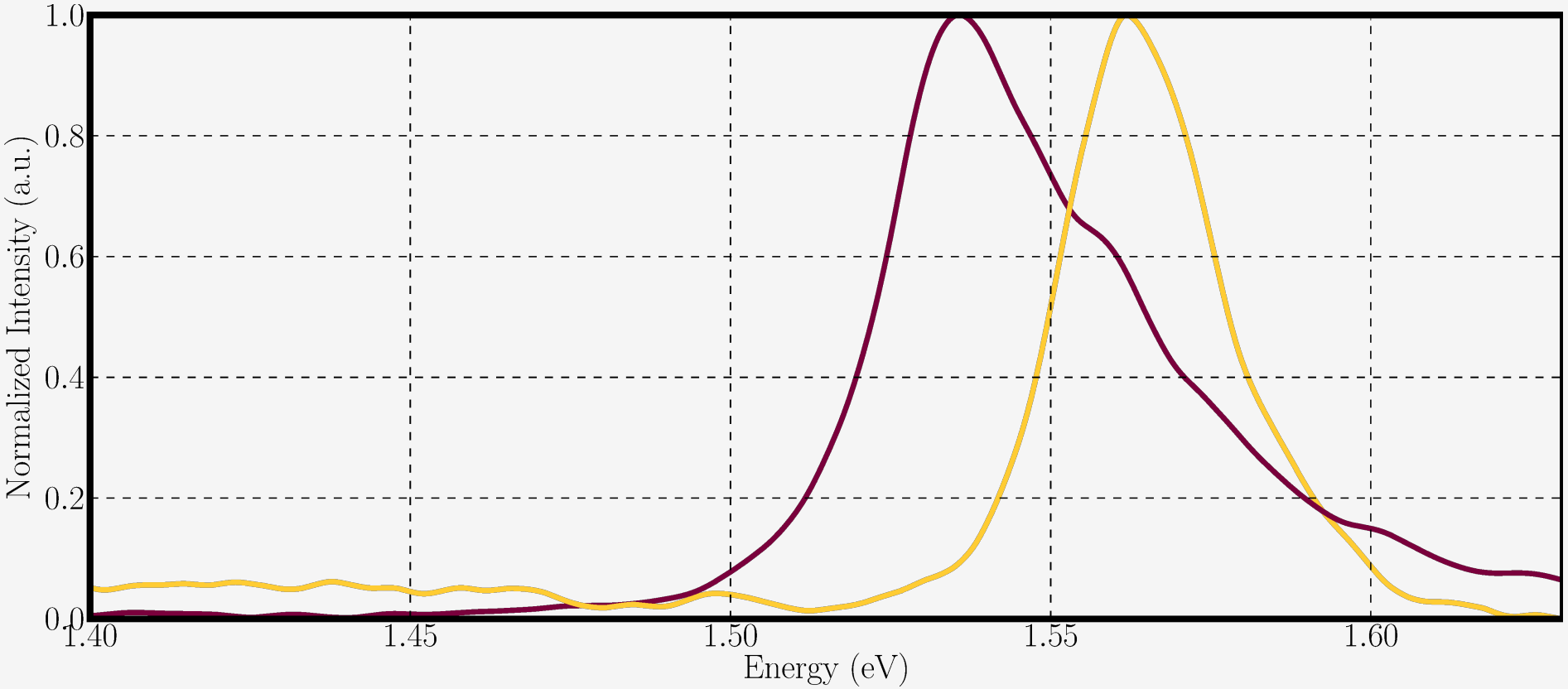


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