



ICQNM 2014

# RHOMBO-TRIGONAL EPITAXY OF SiGe ON c-SAPPHIRE

Sang H. Choi, Ph.D

Advanced Materials and Processing Branch

**NASA Langley Research Center**

Hampton, VA 23681

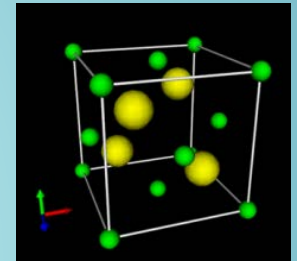


# Today's Semiconductor Bandgap Engineering

- Currently, worldwide major semiconductor alloy epitaxial growth is divided into two material groups.

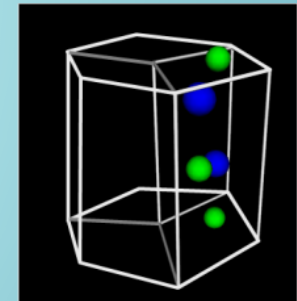
- **Cubic:**

- Diamond structures: group IV semiconductors (Si, Ge, C),
- Cubic zinc-blende structures: group III-V semiconductors (GaAs, InP), group II-VI semiconductors (ZnSe, CdTe)



- **Hexagonal:**

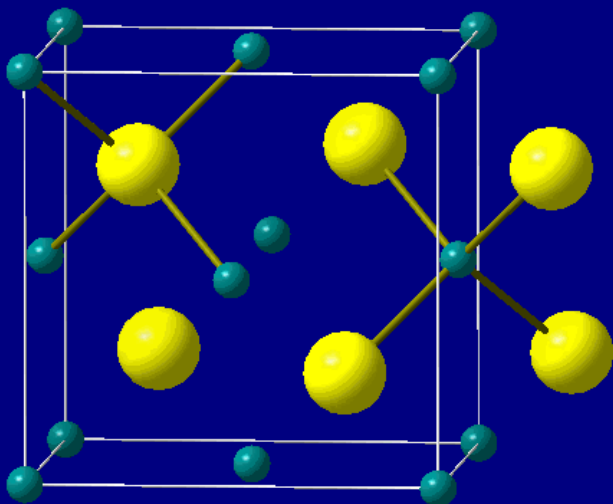
- Wurtzite structures: III-Nitride semiconductors (GaN, AlN, InN)
- II-VI semiconductor: Zinc-Oxide
- Hexagonal SiC (2H, 4H)



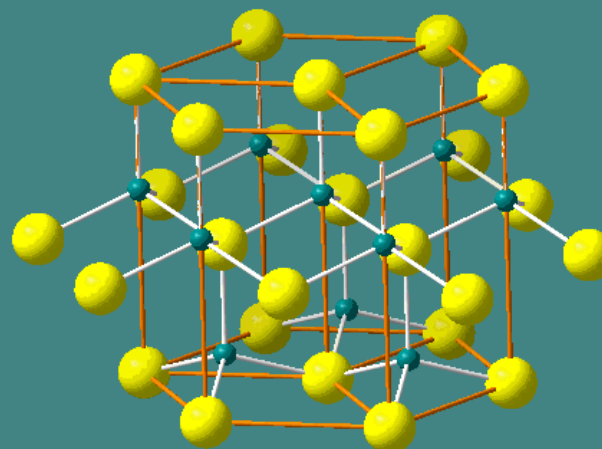
- The mixture of different crystal structures was thought to be very difficult so far. We propose a new growth technology of “**Super Hetero Epitaxy**” with SiGeC alloy in which each layer can have different materials and different crystal lattice structures.



# Comparison of Atomic Structures



Cubic Zinc Blende structure:  
GaAs, ZnS, InP, CdTe



Hexagonal Wurtzite structure:  
GaN, ZnO

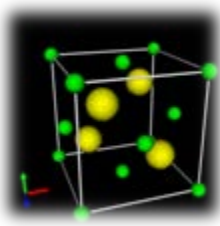


# Crystal Symmetry Relations

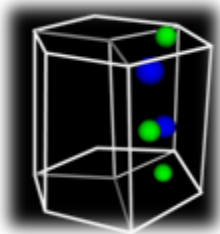
New Rhombohedral Epitaxy Technology

New Rhombohedral SiGe on c-Sapphire

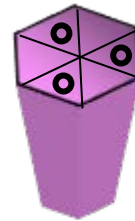
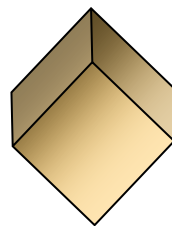
(a)



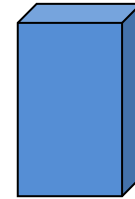
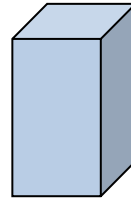
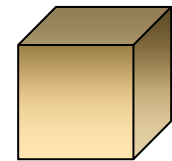
(b)



(c) Cubic Rhombohedron Trigonal



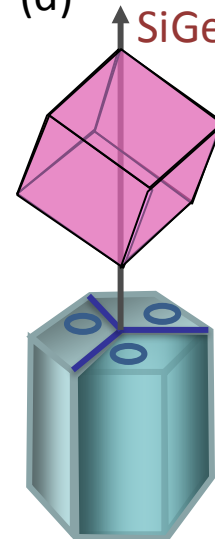
||



Cubic Tetragonal Orthorhombic

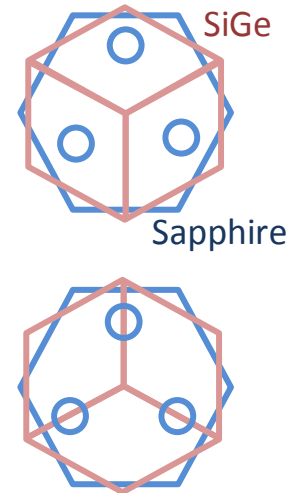
Conventional Cubic Epitaxy Technology

(d)



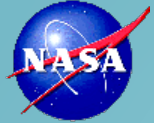
Sapphire

(e)



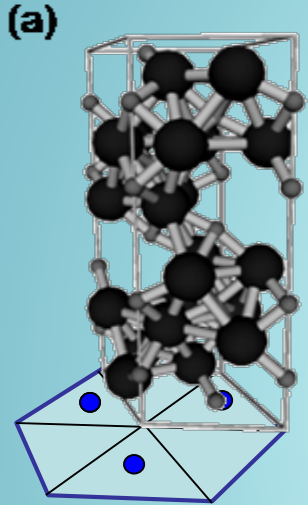
Sapphire

\* Cubic crystal also belongs to the Trigonal crystal group by the symmetry. A fundamental cross-structural epitaxy can be established beyond an accidental coincidence lattice matching!

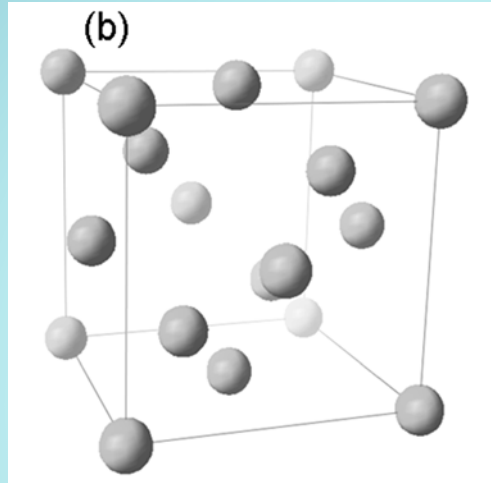


# New Super Hetero Epitaxial Technology for Hybrid Crystal Growth

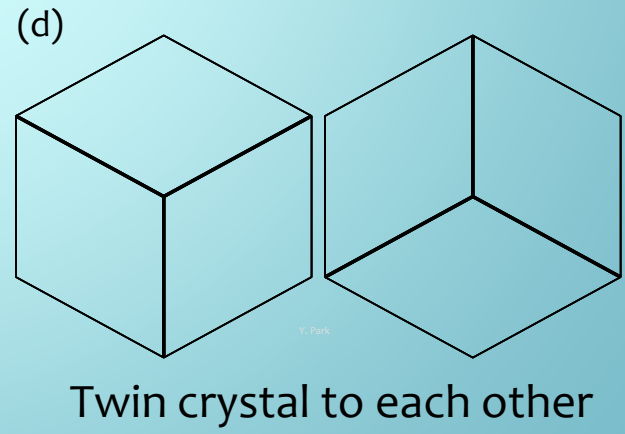
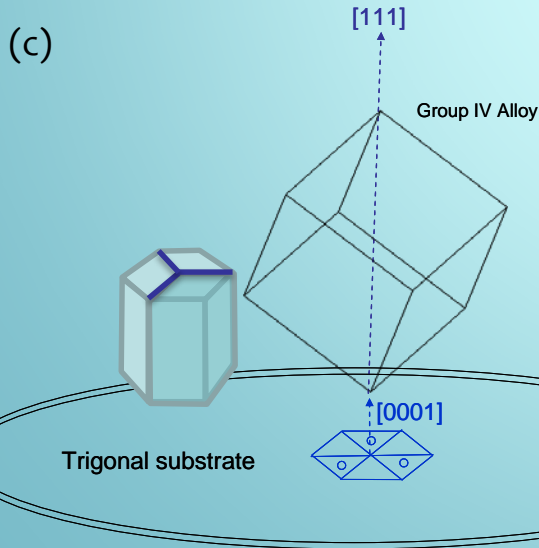
Trigonal Substrate



SiGe (Diamond Structure)



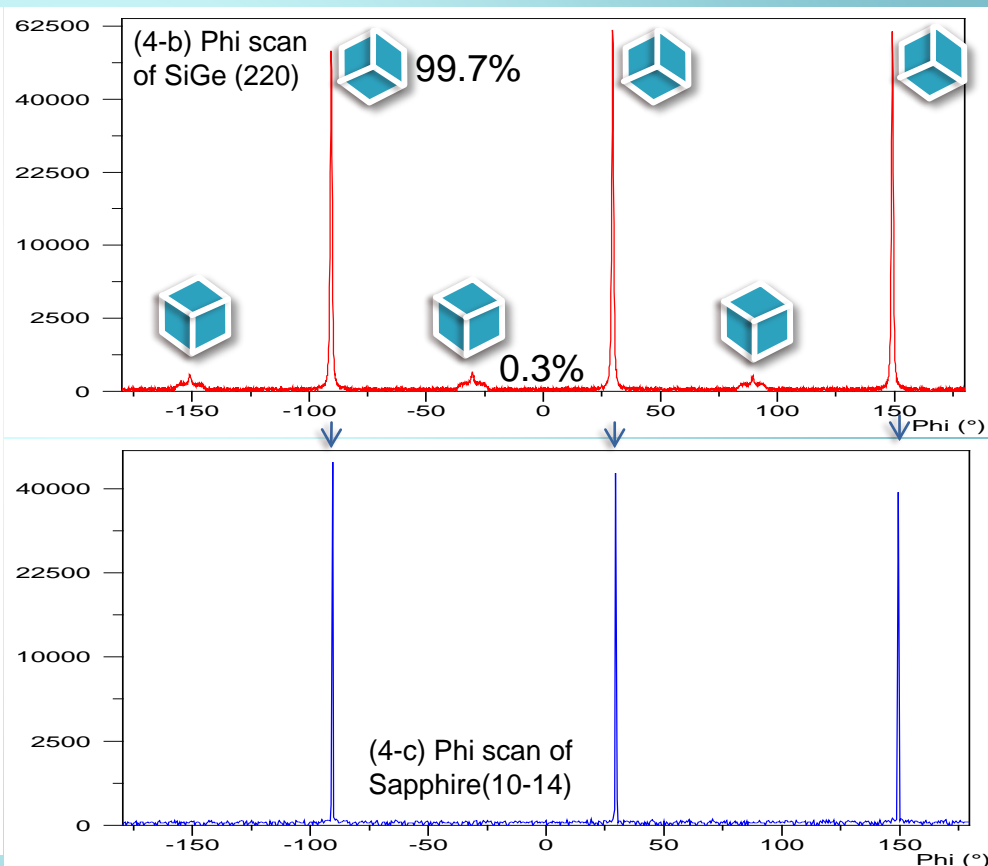
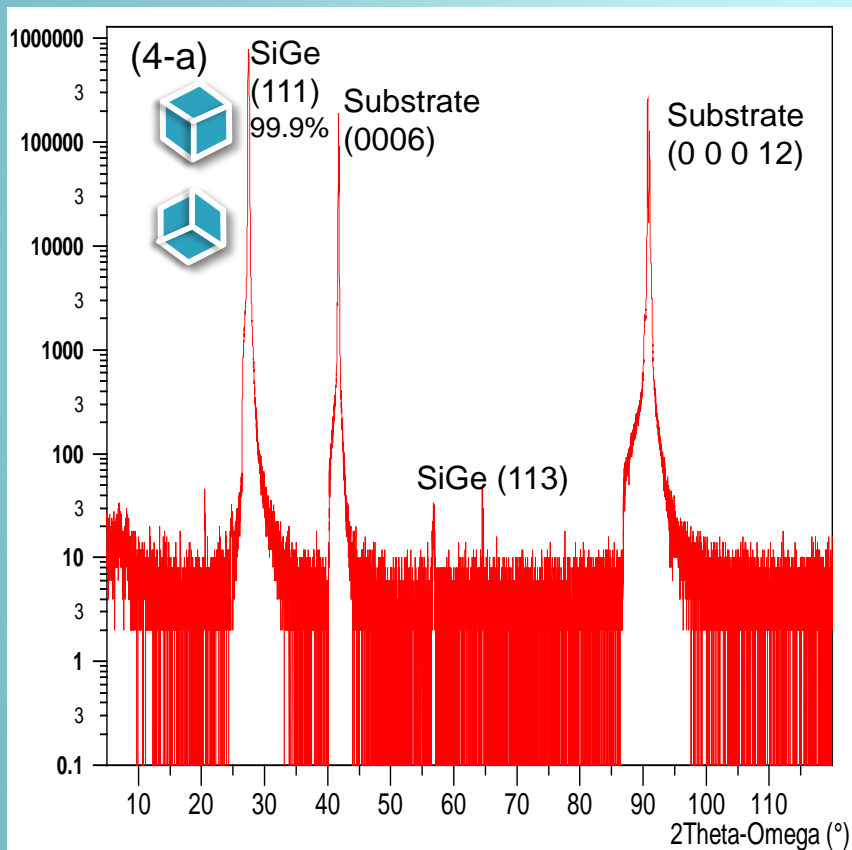
2" SiGe on trigonal substrate





# 1<sup>st</sup> Key:

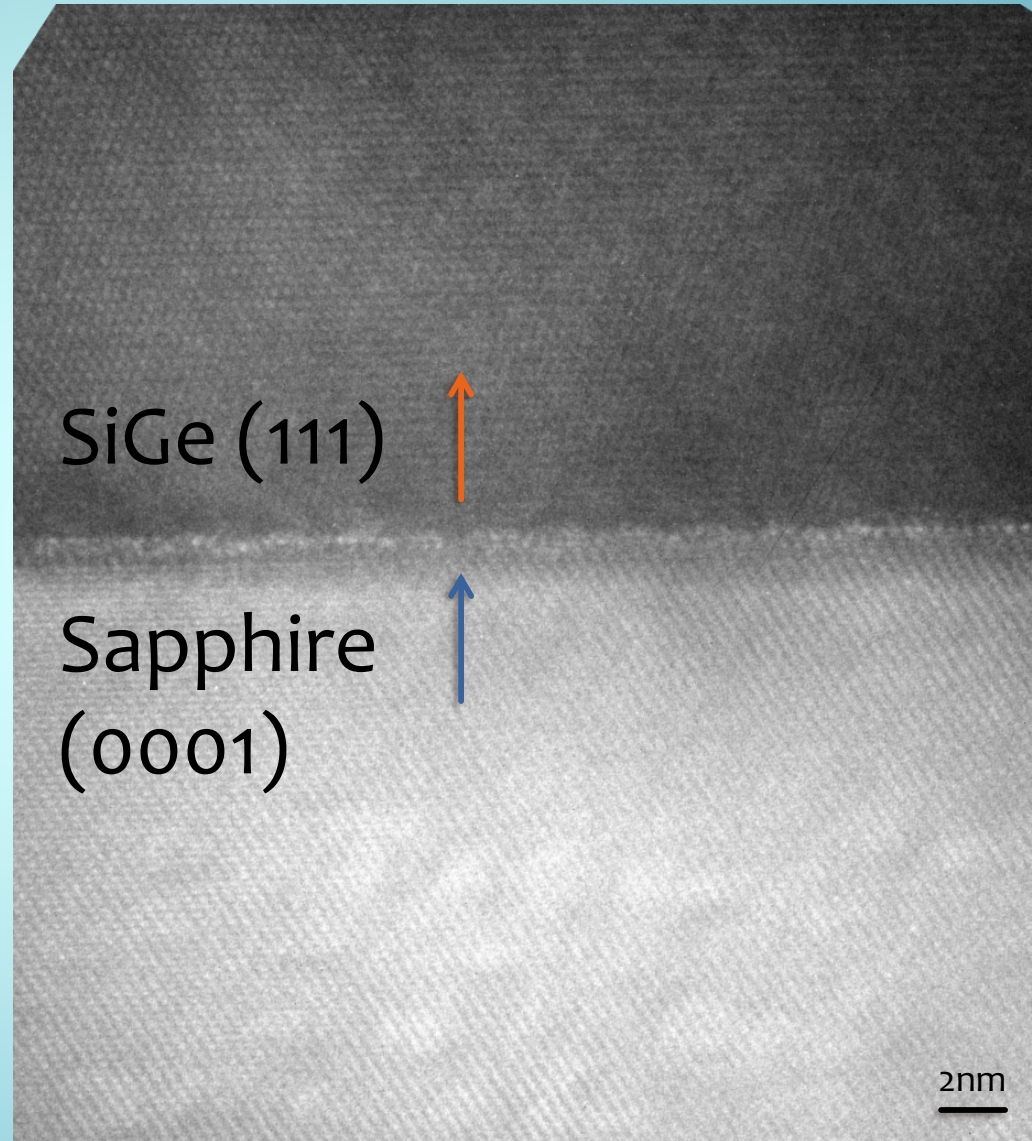
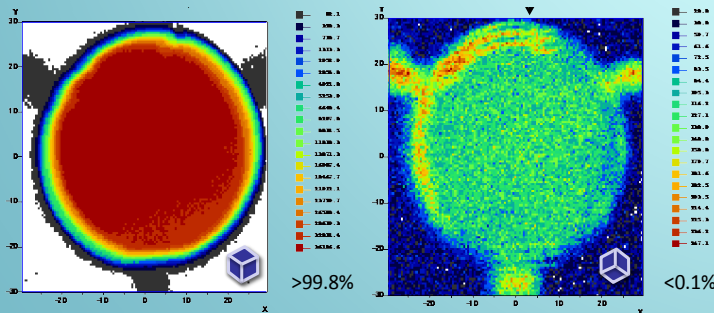
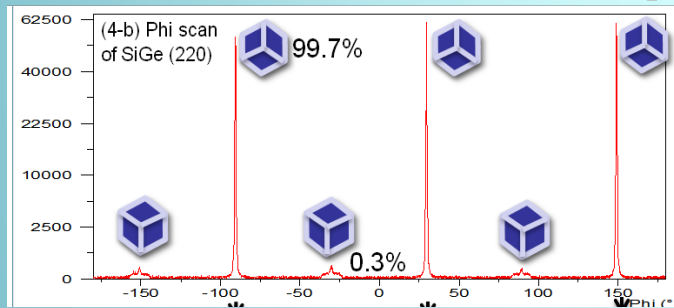
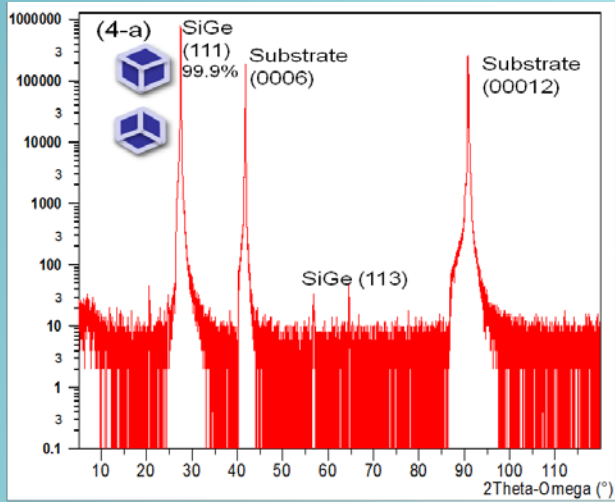
## XRD Integral Twin Density Measurement



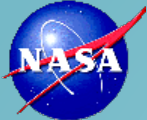


# New Rhombohedral SiGe Semiconductor Epitaxy

## Single Crystalline SiGe Atomic Layers on Sapphire



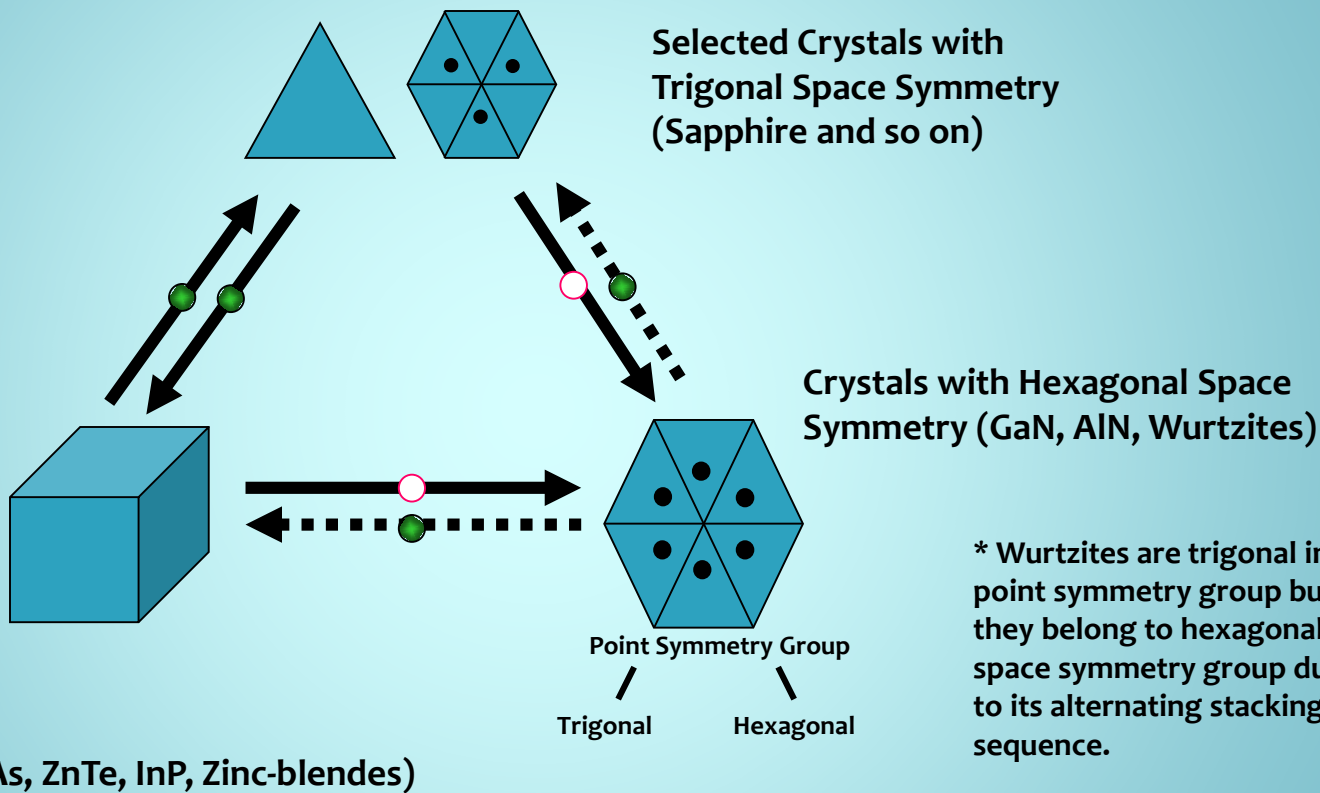
NASA patented XRD methods, materials, and fabrication processes.  
(US Patent # 7341883, 7558371, 7769135, 7906358, 8226767 and more.)



# Epitaxial Relationship with Three Space Symmetry Groups

## Inter-Crystal-Lattice Epitaxial Relation

Three different crystals can be integrated into one continuous epitaxial structure.



Substrate Epitaxial Layer : No Double Position Defect

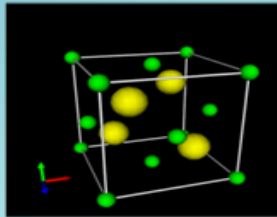
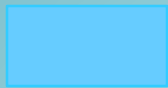
Substrate Epitaxial Layer : Double Position Defect at Stepped Interface

Twin detection XRD works



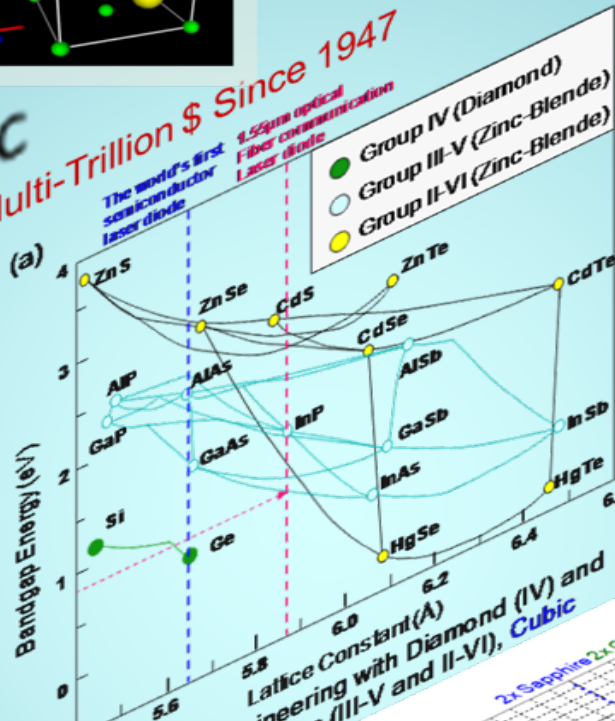
Twin detection XRD does not work





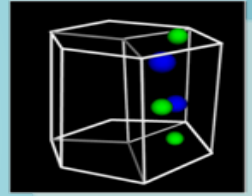
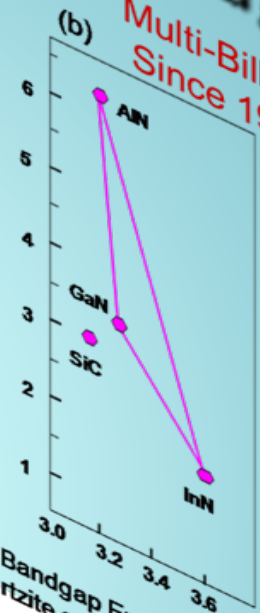
Cubic

Multi-Trillion \$ Since 1947



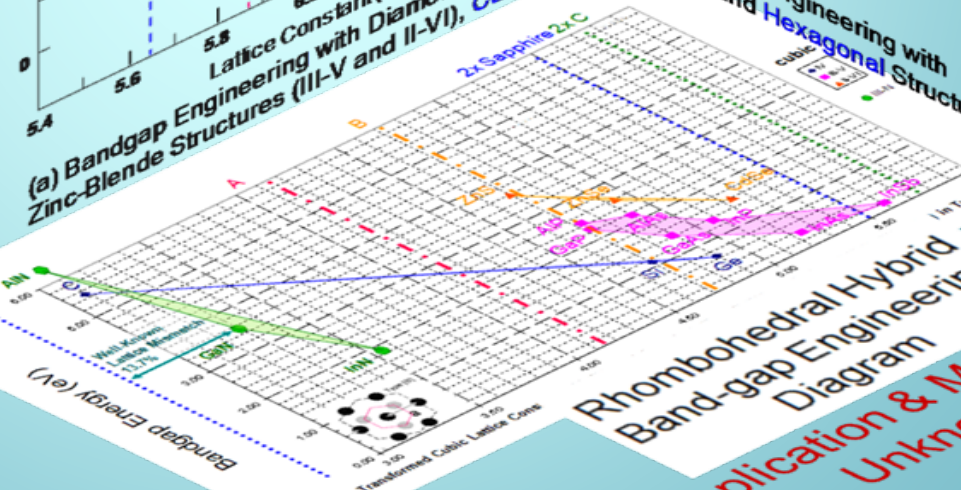
Hexagonal

Multi-Billion \$ Since 1990



(b) Bandgap Engineering with Wurtzite and Hexagonal Structures

New Rhombohedral Semiconductor Epitaxy



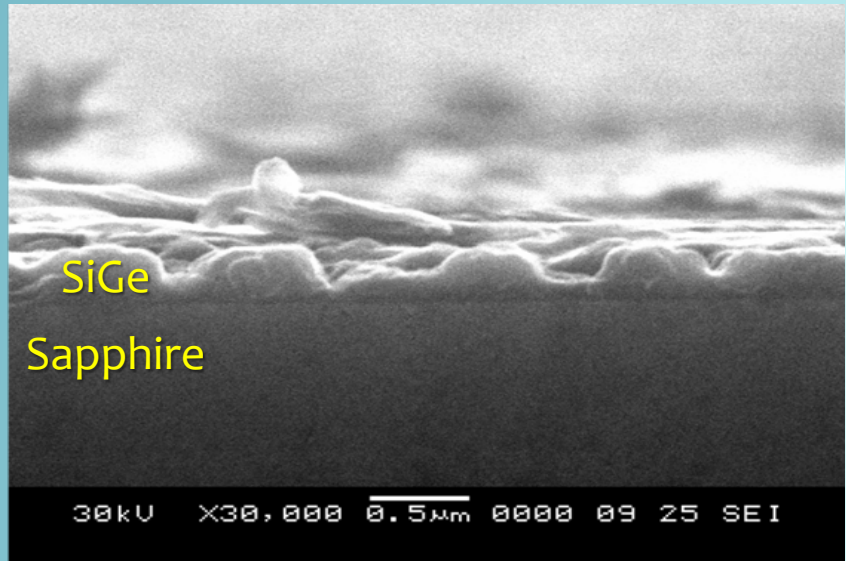
Rhombohedral Hybrid Band-gap Engineering Diagram Application & Market Size: ? Unknown Yet

Rhombohedral

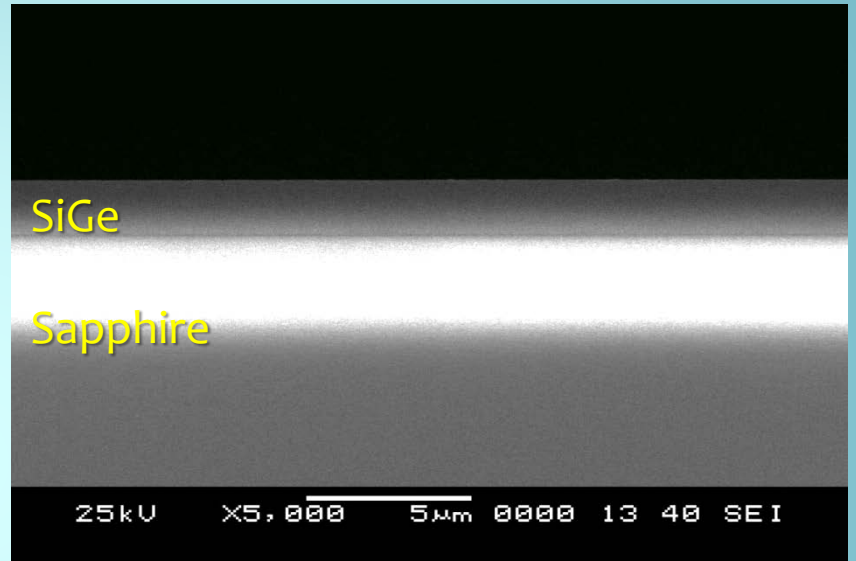


# Epitaxial Layer Growth Optimization

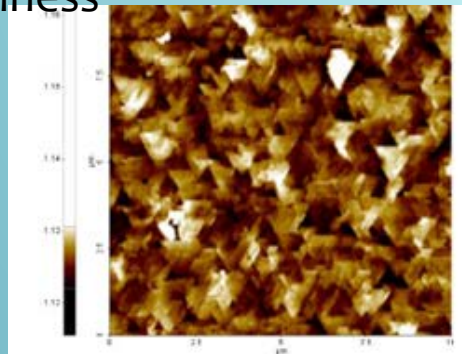
SEM: Unstable island growth



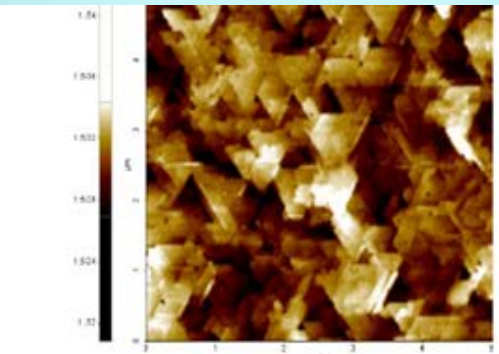
Stable layer-by-layer growth



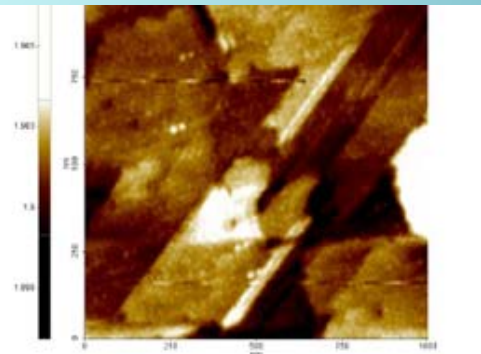
AFM: Triangular Crystal Planes of SiGe (Atomic Steps), Smooth Surface with 2.2nm Roughness



10µm x 10µm Image  
RMS Roughness = 2.24nm

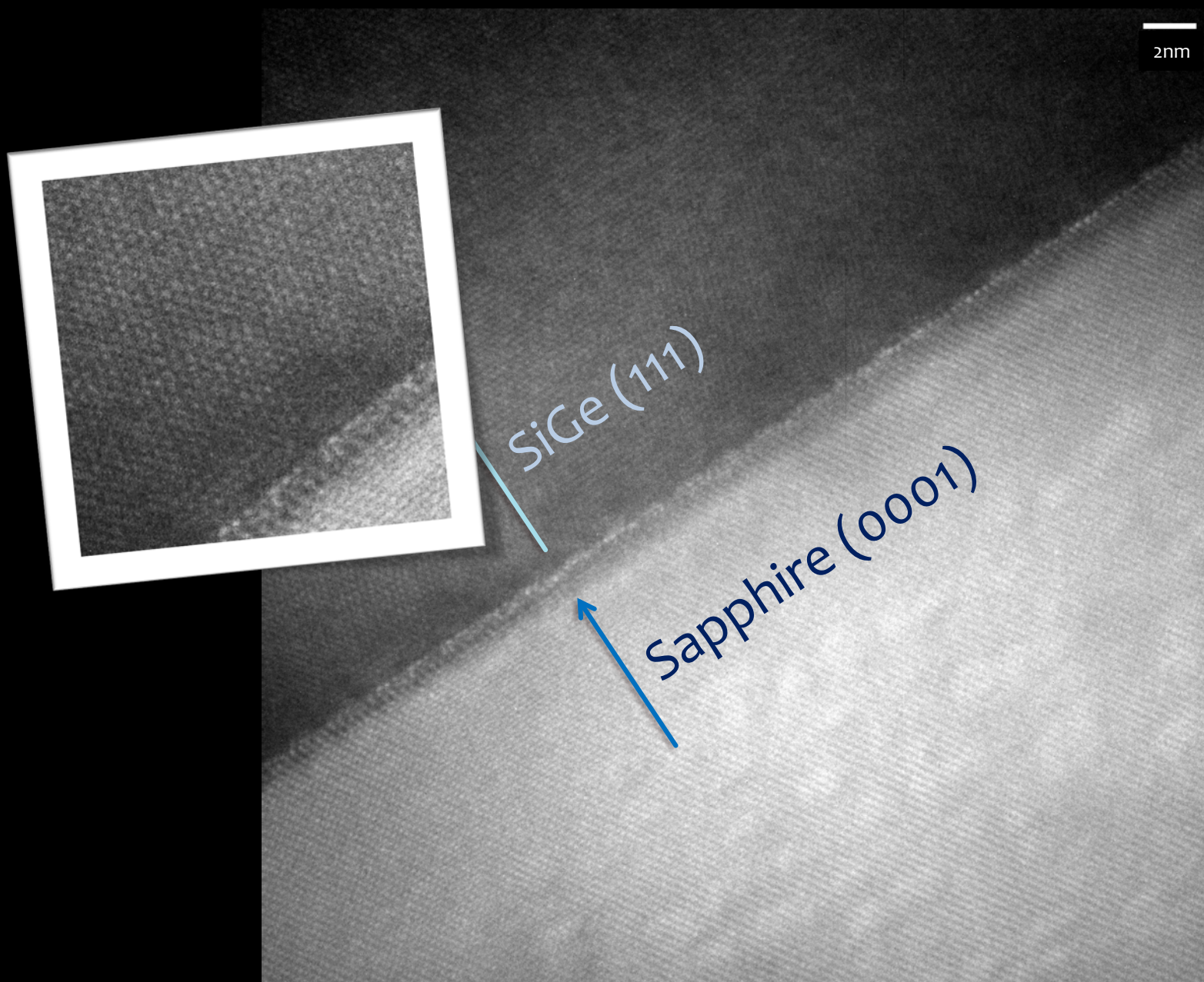


5µm x 5µm Image  
RMS Roughness = 1.87nm



1µm x 1µm Image  
RMS Roughness = 1.06nm

# Atomic Resolution TEM Image of Rhombohedral-Trigonal Super Structure





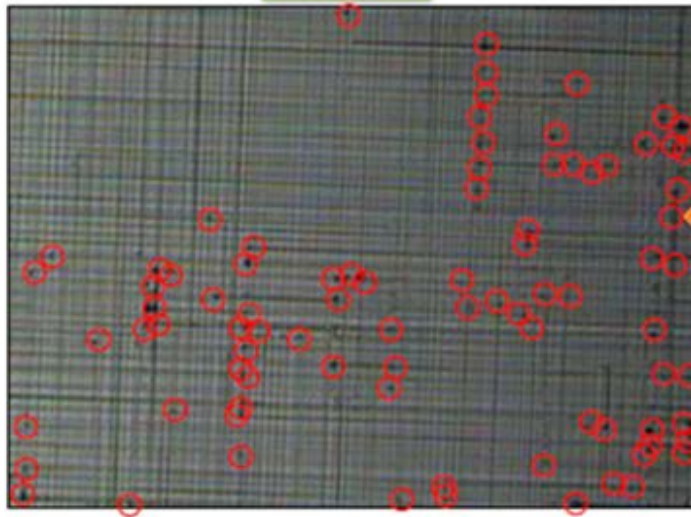
# Comparison of Etch-Pit Densities

## Threading Dislocation Pit Density after Secco Etching

IBM's SiGe

SiGe on Si substrate Si(100)

35 % Ge

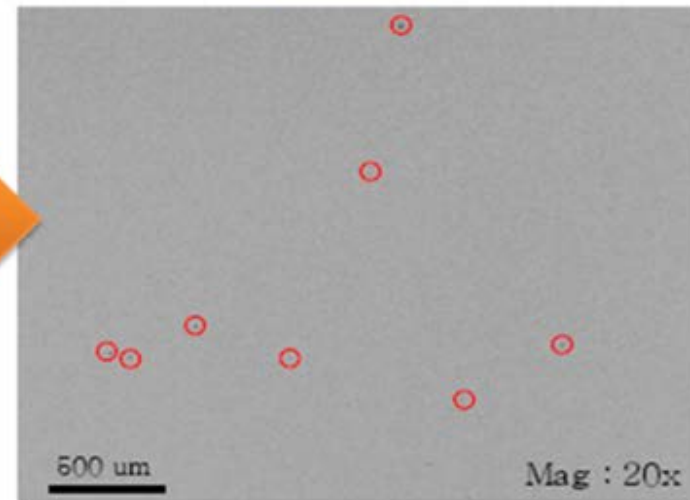


- ❖ TDP density :  $3.90 \times 10^4/\text{cm}^2$
- ❖ LD density :  $1.73 \times 10^4/\text{cm}$
- ❖ Cross-hatch pattern

NASA Langley's SiGe

SiGe on sapphire substrate Sapphire(0001)

78 % Ge



- ❖ TDP density :  $1.9 \times 10^2/\text{cm}^2$
- ❖ LD density : 0/cm
- ❖ No Cross-hatch pattern

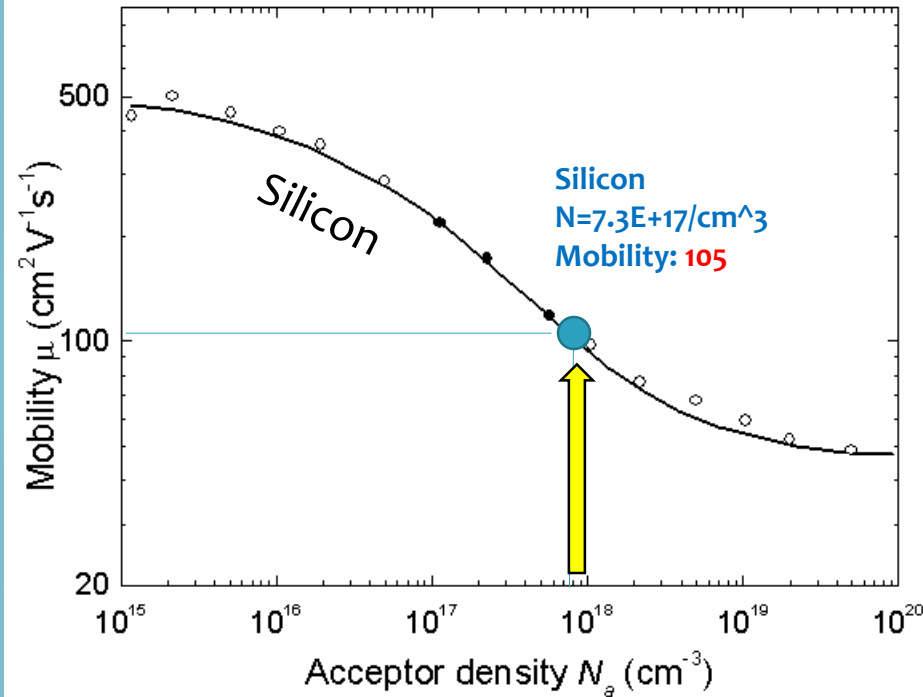
The surface was etched by using Secco Etchant for 3 seconds.

(Etch rate: 25nm/sec)

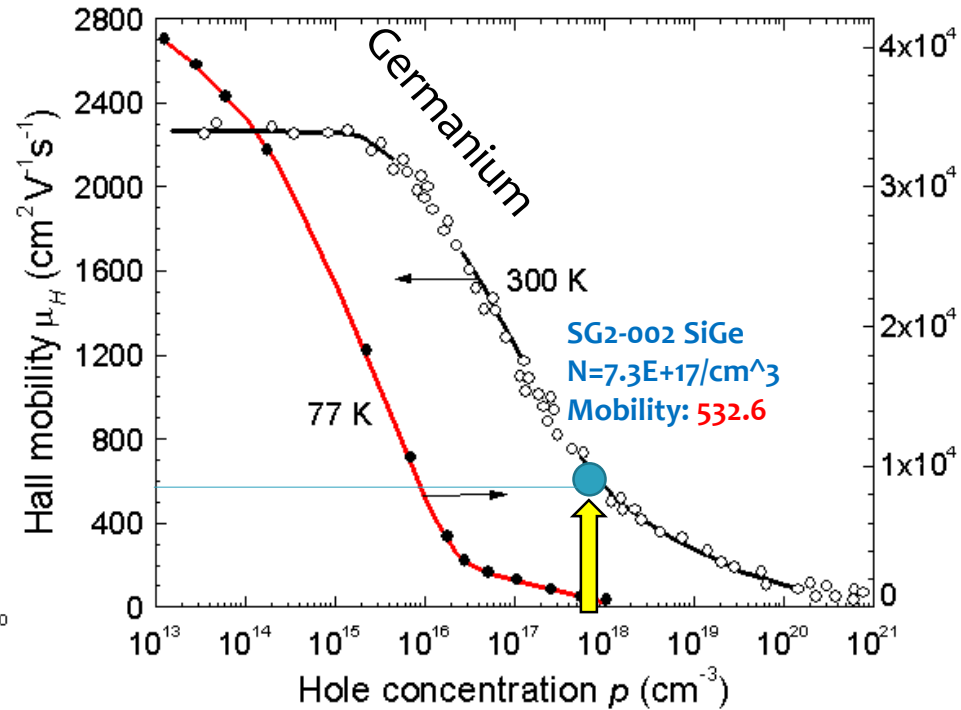


# Hole (p-type) Mobility of SiGe

500% Faster Than Silicon (Si=105 vs. SiGe=532)



P-type Silicon's Mobility vs. Doping

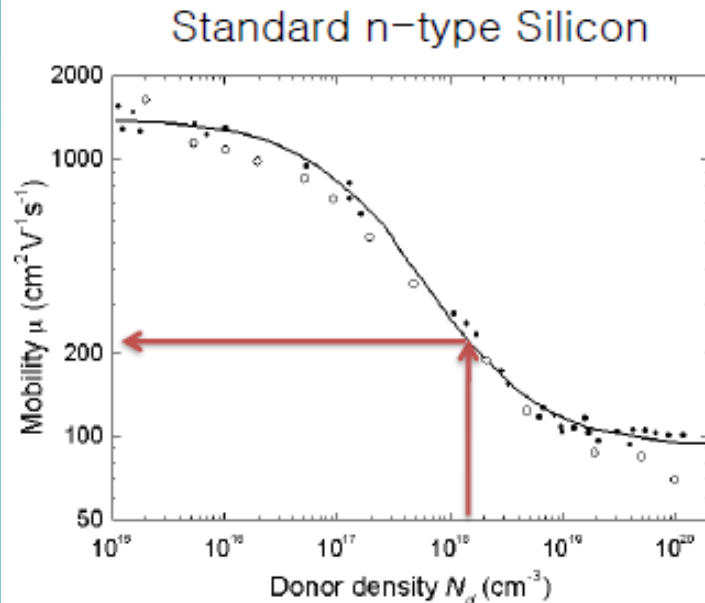


P-type Germanium's Mobility vs. Doping



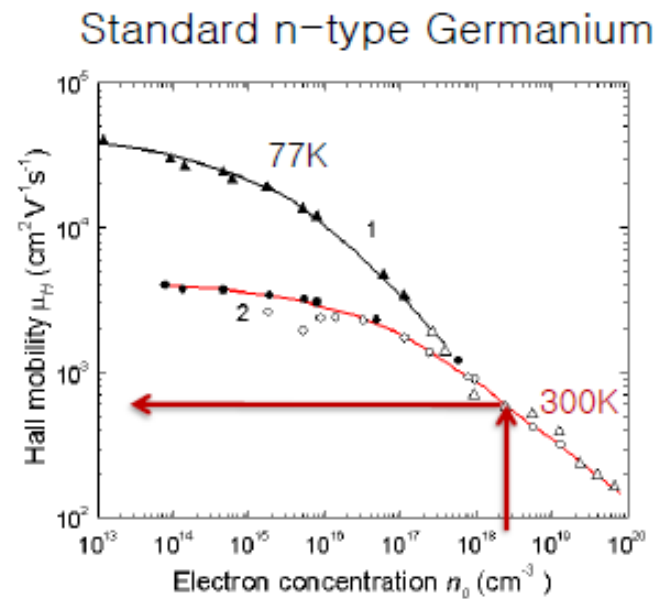
# Electron (n-type) Mobility of SiGe

**280% Faster Than Silicon (Si=220 vs. SiGe=616)**



Jacoboni, C., C. Canali, G. Ottaviani, and A. A. Quaranta, *Solid State Electron.* 20, 2(1977) 77-89.

**220 cm<sup>2</sup>/V·s** at 1.5x10<sup>18</sup>/cm<sup>3</sup> doping



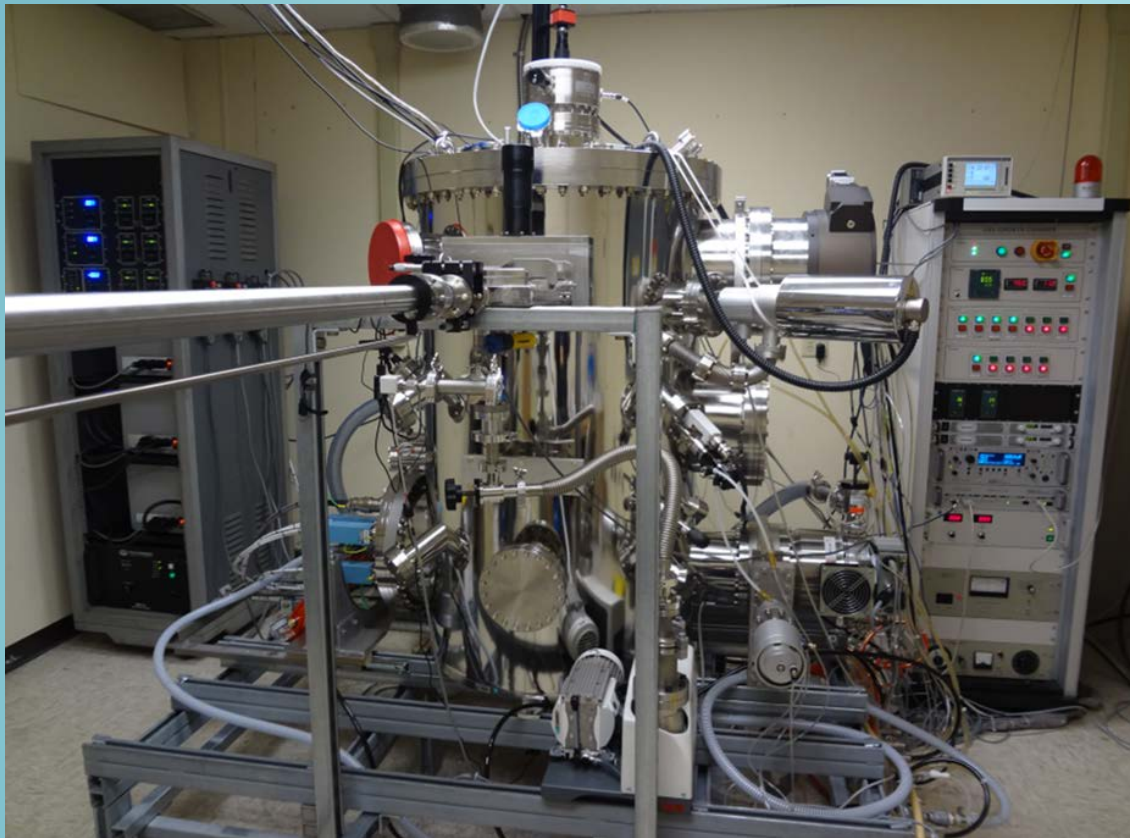
Fistul V. I., M. I. Iglitsyn, and E. M. Omelyanovskii, *Sov. Phys. Solid State* 4, 4 (1962) 784-785.

**780 cm<sup>2</sup>/V·s** at 1.5x10<sup>18</sup>/cm<sup>3</sup> doping

Note: Our Thin Rhombohedral SiGe Sample#2 has **616 cm<sup>2</sup>/V·s** at 1.5x10<sup>18</sup>/cm<sup>3</sup> doping which is **2.8 times higher electron mobility** than single crystalline Silicon wafer at the sample doping level. **μ<sub>SiGe</sub> is 2.8 times higher than μ<sub>Si</sub>**



# Super Hetero Crystal Growth Chamber



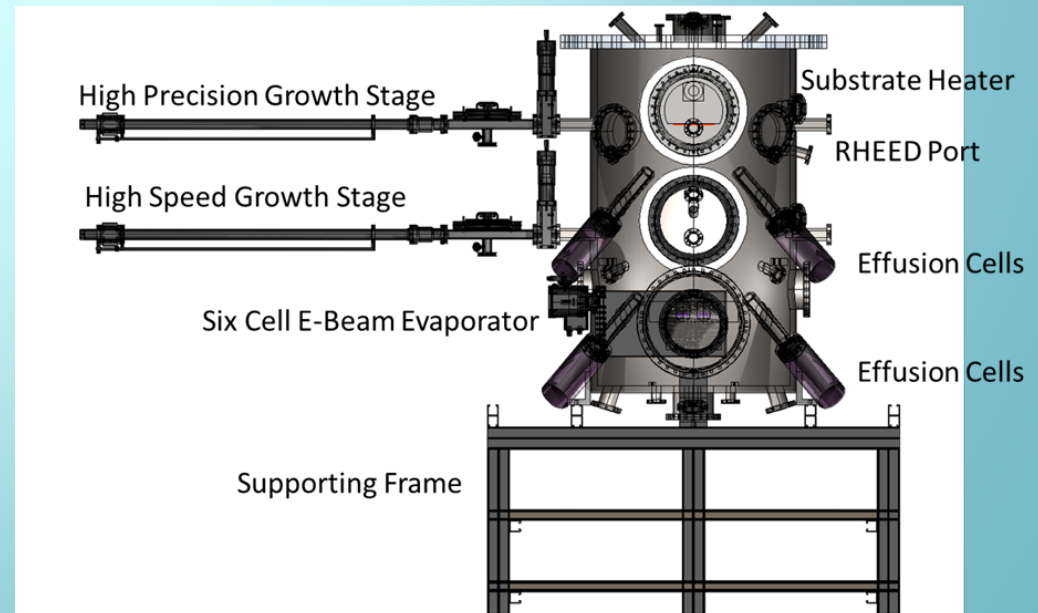
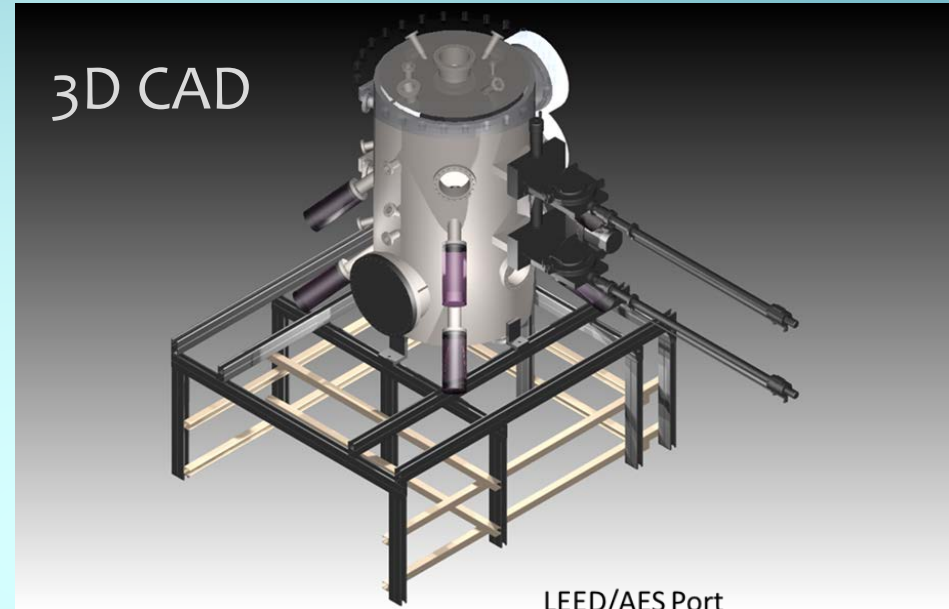
- About \$1 Million was invested to build the super hetero-crystal crystal growth chamber. Additional financial support was made from Department of Transportation (DoT).
- The system can accept standard 2"~6" wafers with a load-lock.
- The system is ready for full computer control.





# Super Crystal Structure Growth Chamber Designed by NASA Langley Team

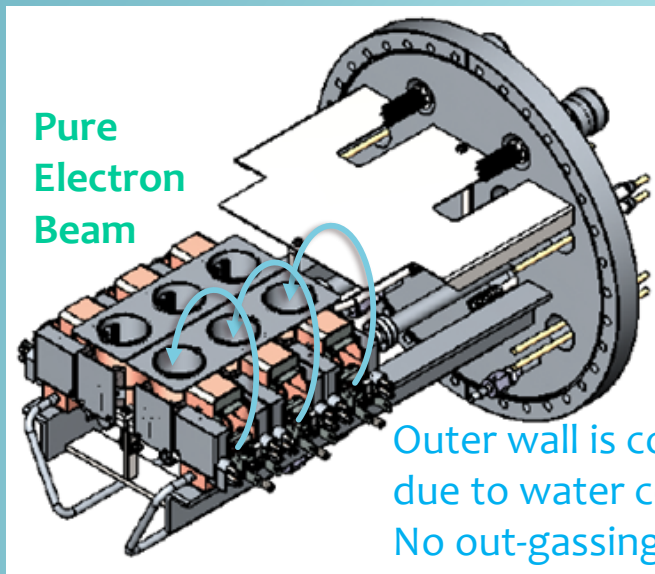
- New atomic resolution growth machine was designed and built by NASA Langley Team.
- Unique two stage design to support (1) High Precision Growth Mode, (2) High Speed Growth Mode.
- Six cell E-beam evaporator to evaporate source materials up to 8130°F (4500°C).
- Multi effusion cells for dopants
- Reflective High Energy Electron Diffraction (RHEED) system to monitor in-situ growth.
- Low Energy Electron Diffraction (LEED) system with Auger Electron Spectroscopy (AES).







# Functions of Super Growth Chamber

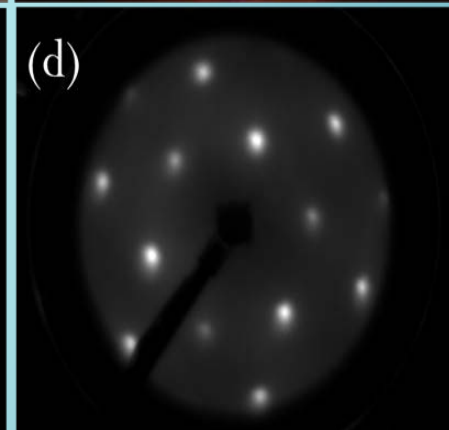
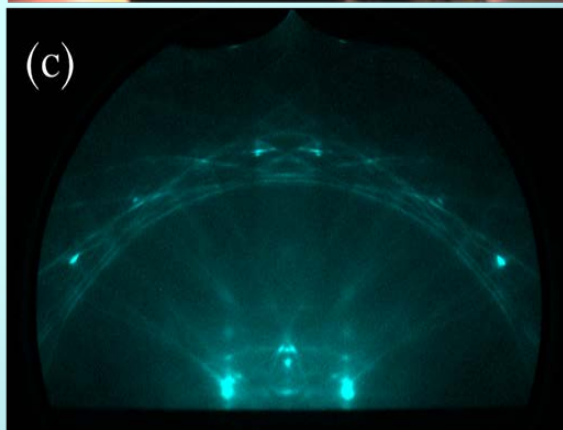
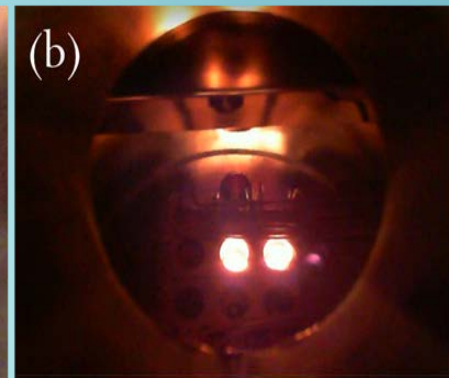
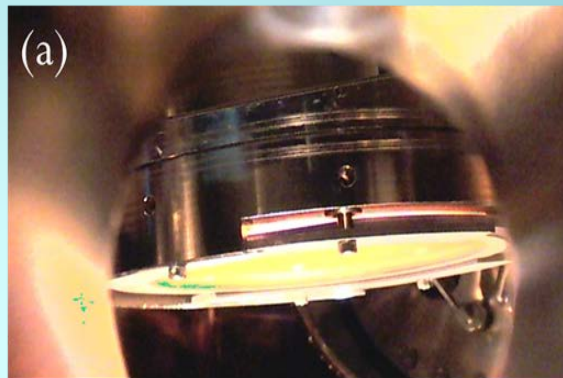


Pure  
Electron  
Beam

Outer wall is cold  
due to water cooling.  
No out-gassing!

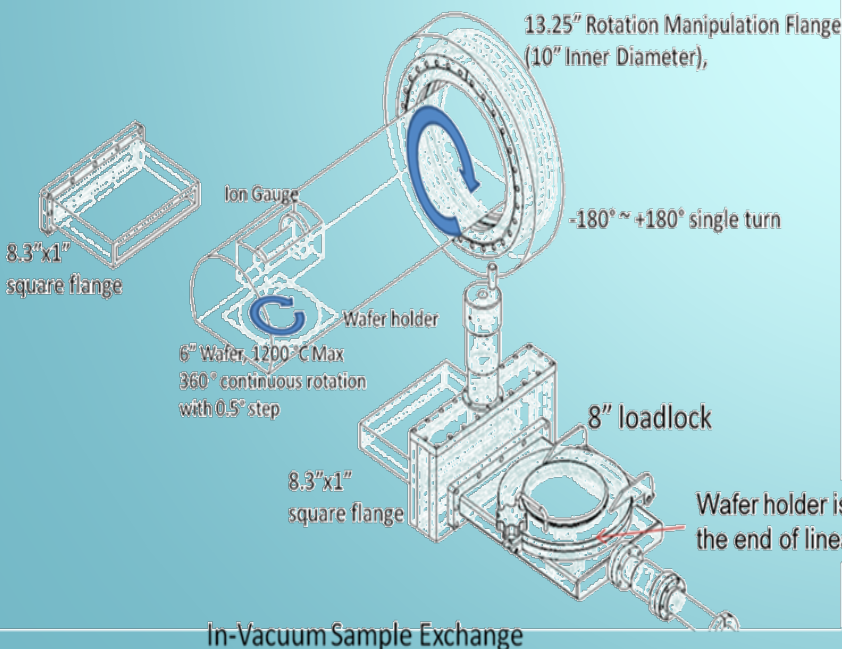
6" Wafer Heater

6-Cell E-Beam Evaporator



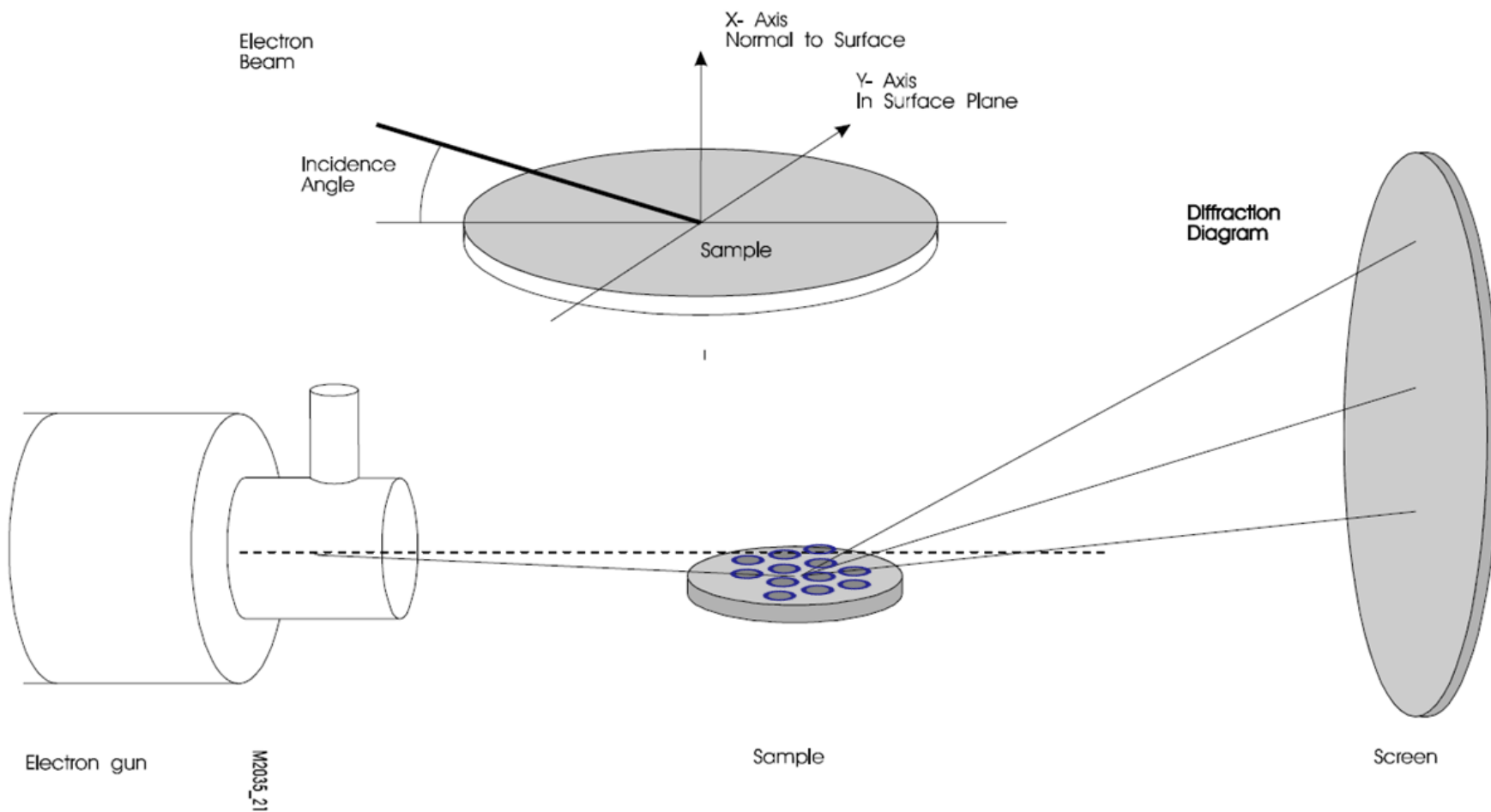
RHEED Monitoring

LEED Monitoring





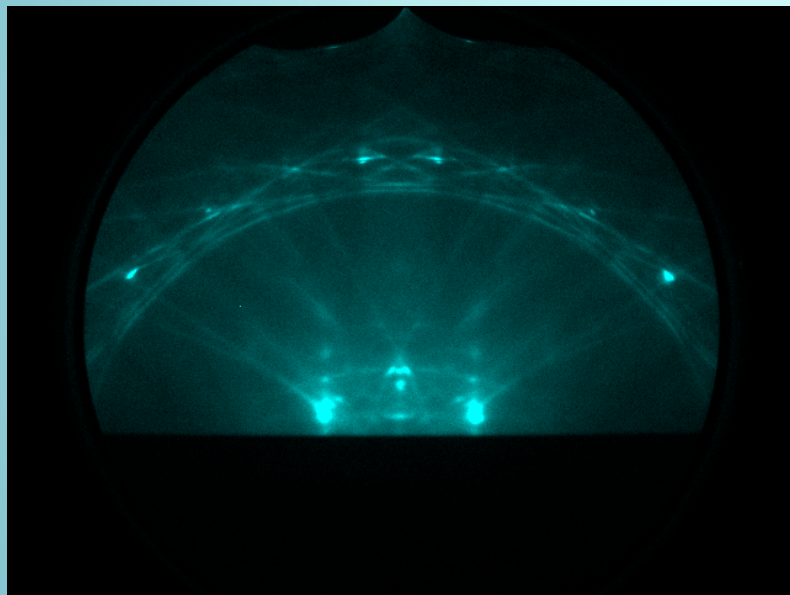
# Reflective High Energy Electron Diffraction (RHEED) System Configuration



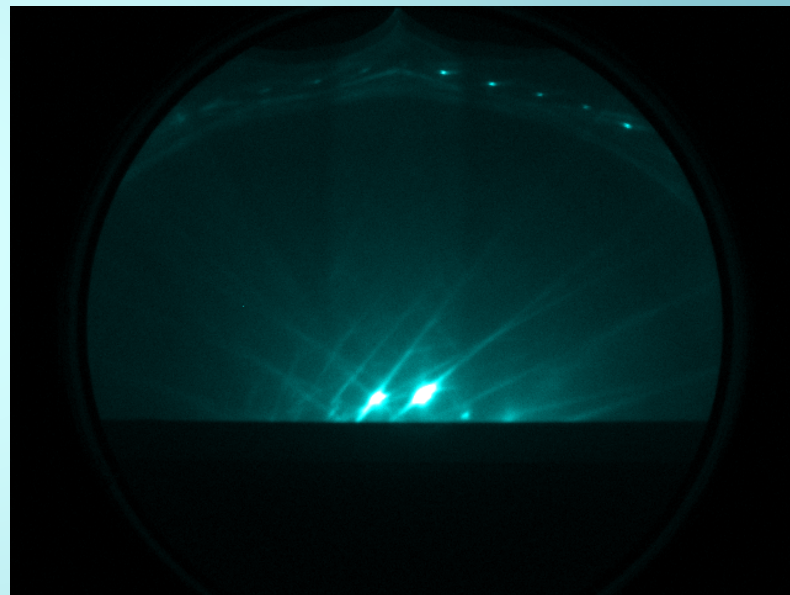


# Atomic Precision In-Situ Growth Monitoring

RHEED patterns obtained from Sapphire (0001) surface



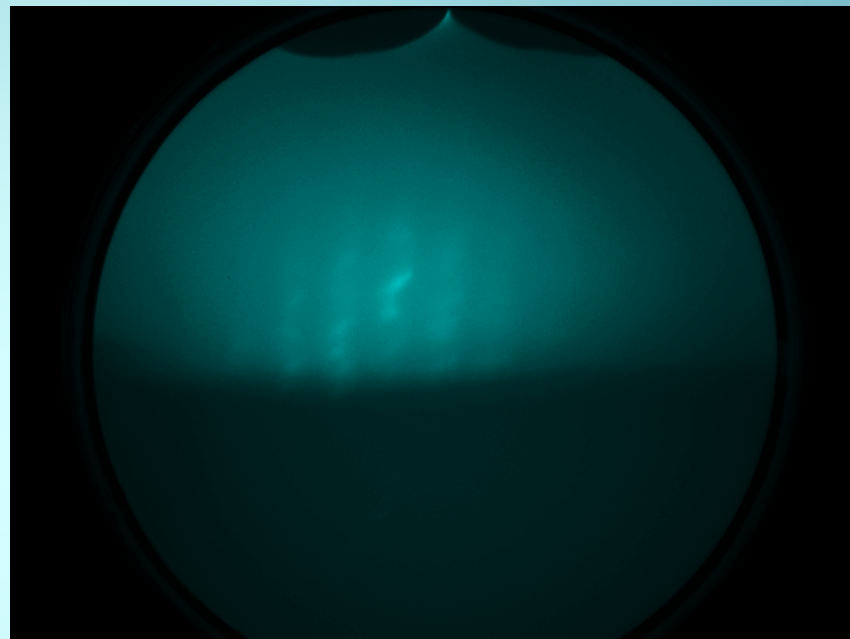
$[2\bar{1}\bar{1}0]$  Direction



$[1\bar{1}00]$  Direction



# RHEED Pattern of SiGe Epi-Layer



RHEED Pattern of  
SiGe Epitaxial Layer

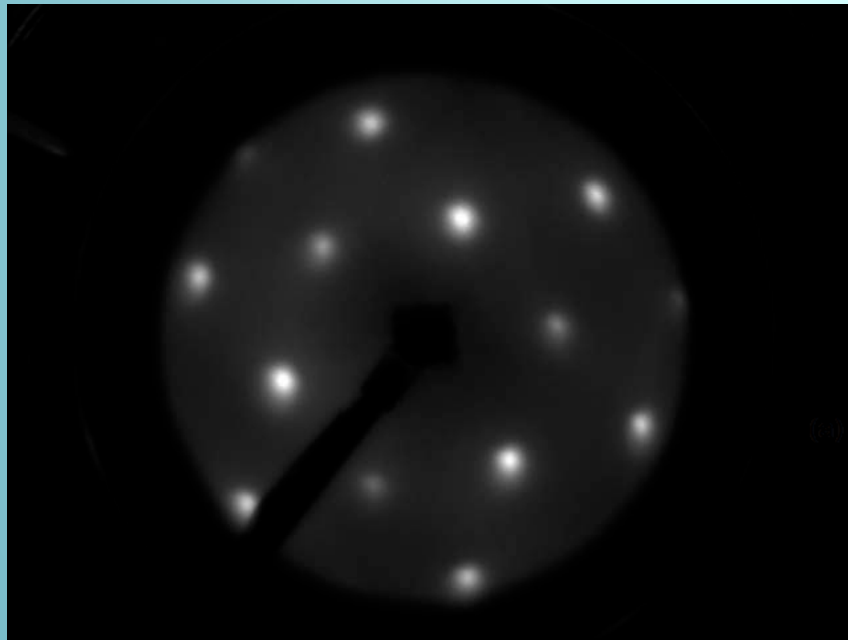
\*Fuzzy lines are due to 60Hz noise  
from AC current substrate heater.



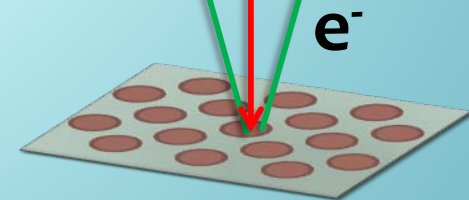
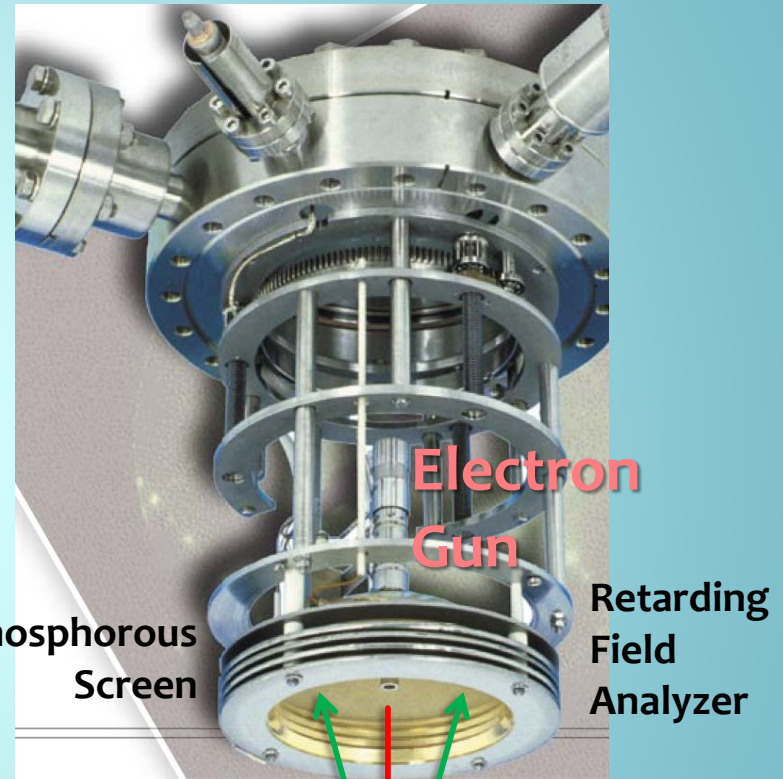
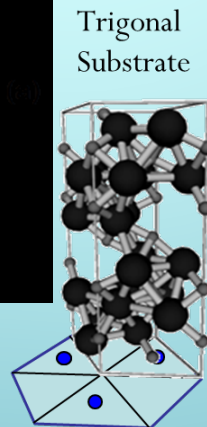
# Atomic Precision Substrate Surface Monitoring

## Low Energy Electron Diffraction (LEED)

- Three bright spots and three dark spots indicate the atomic surface of trigonal symmetry. As the substrate temperature and gas condition change many new LEED patterns appear as different surface reconstructions occur.

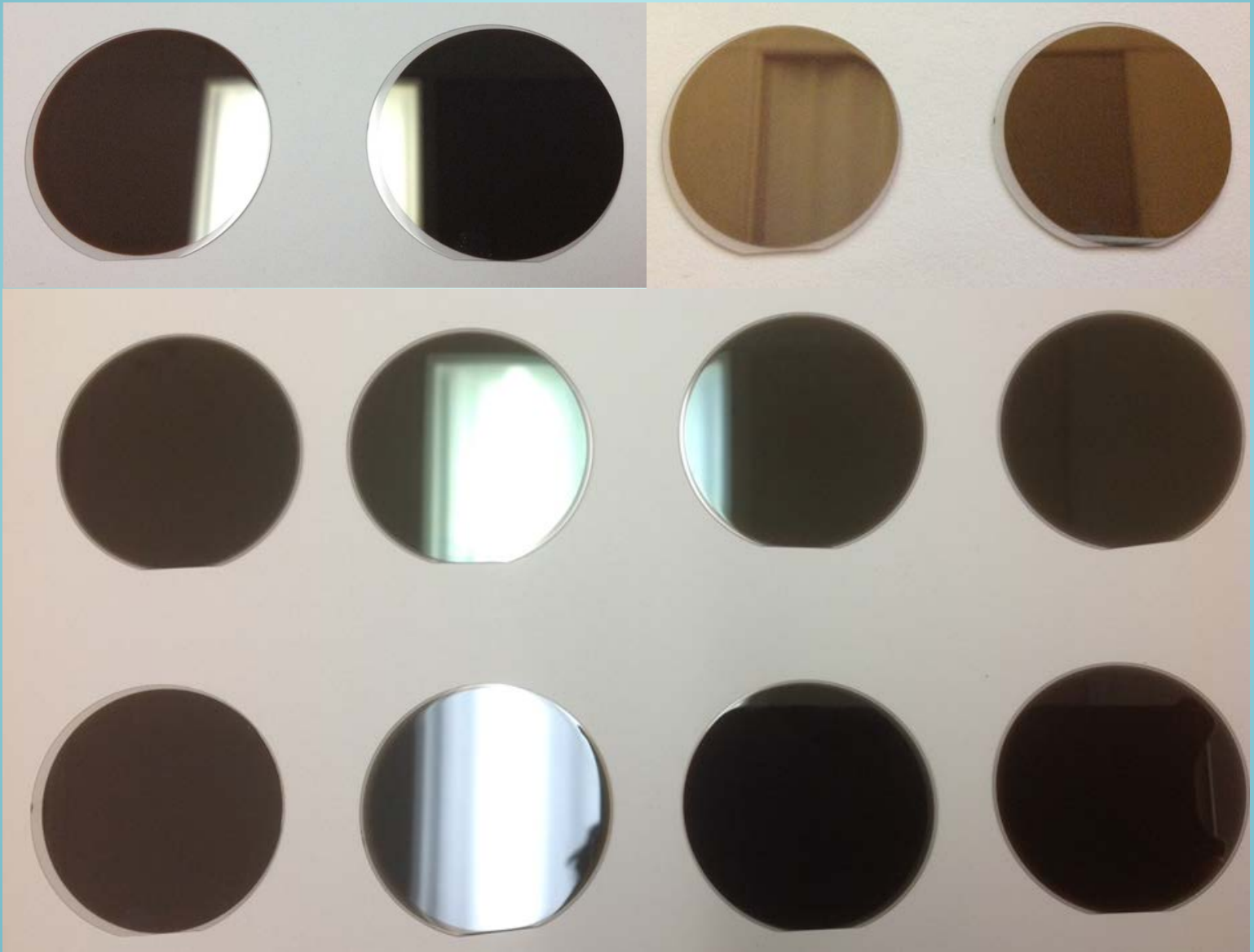


100eV LEED Pattern



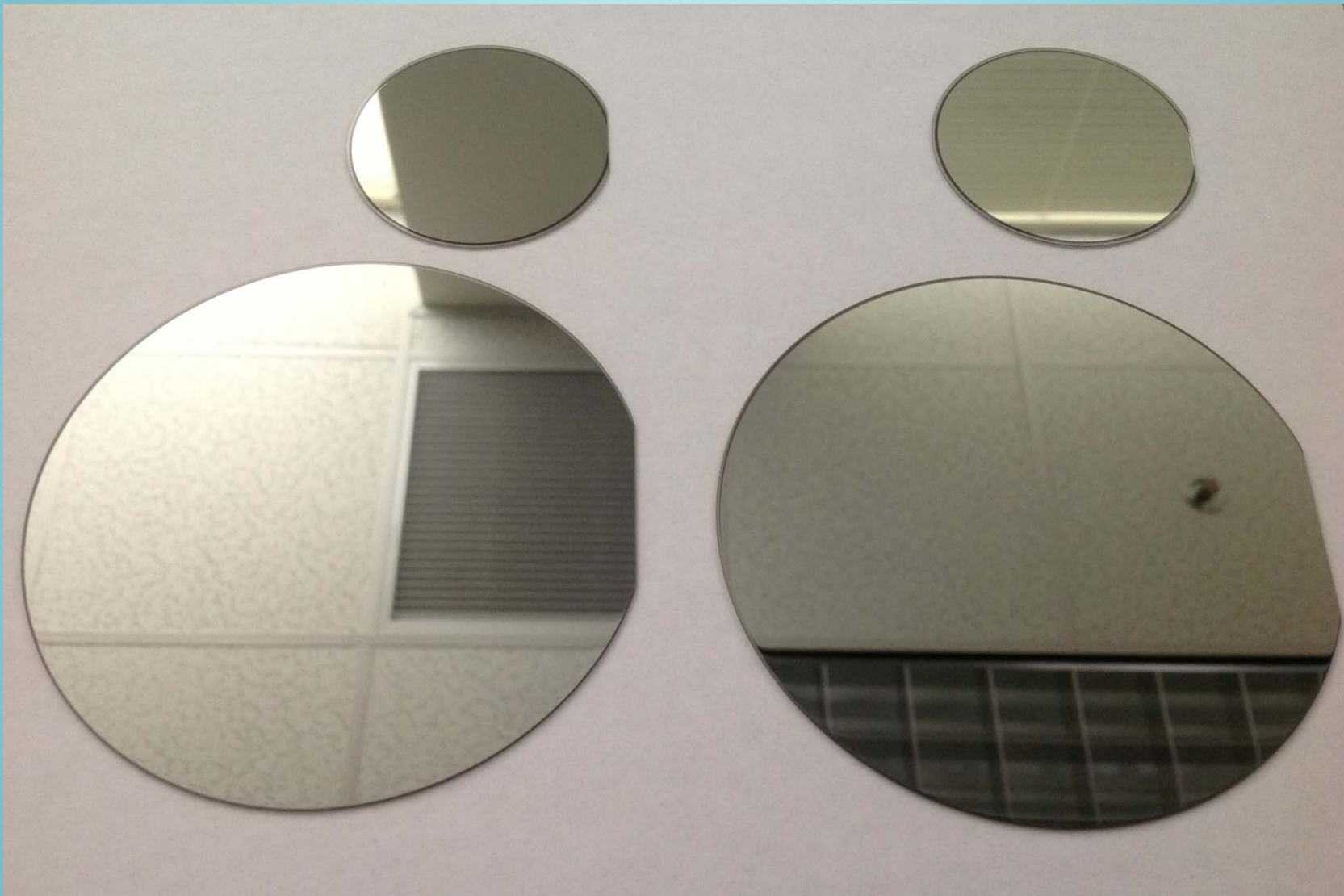


# 2" SiGe on c-Sapphire Samples





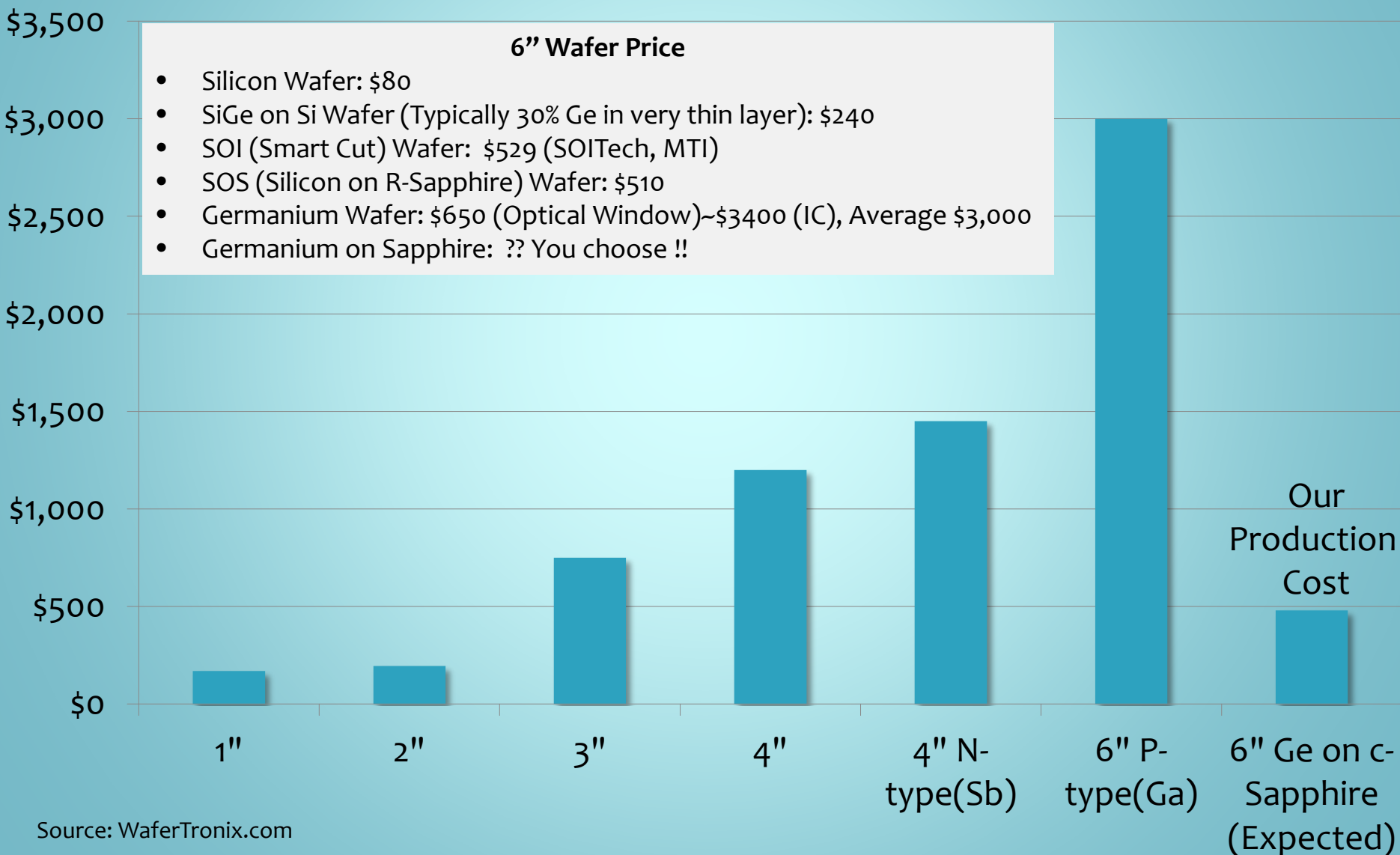
# 4" SiGe on c-Sapphire Samples





# 2013 Germanium Wafer Market

## Germanium Wafer Market Price

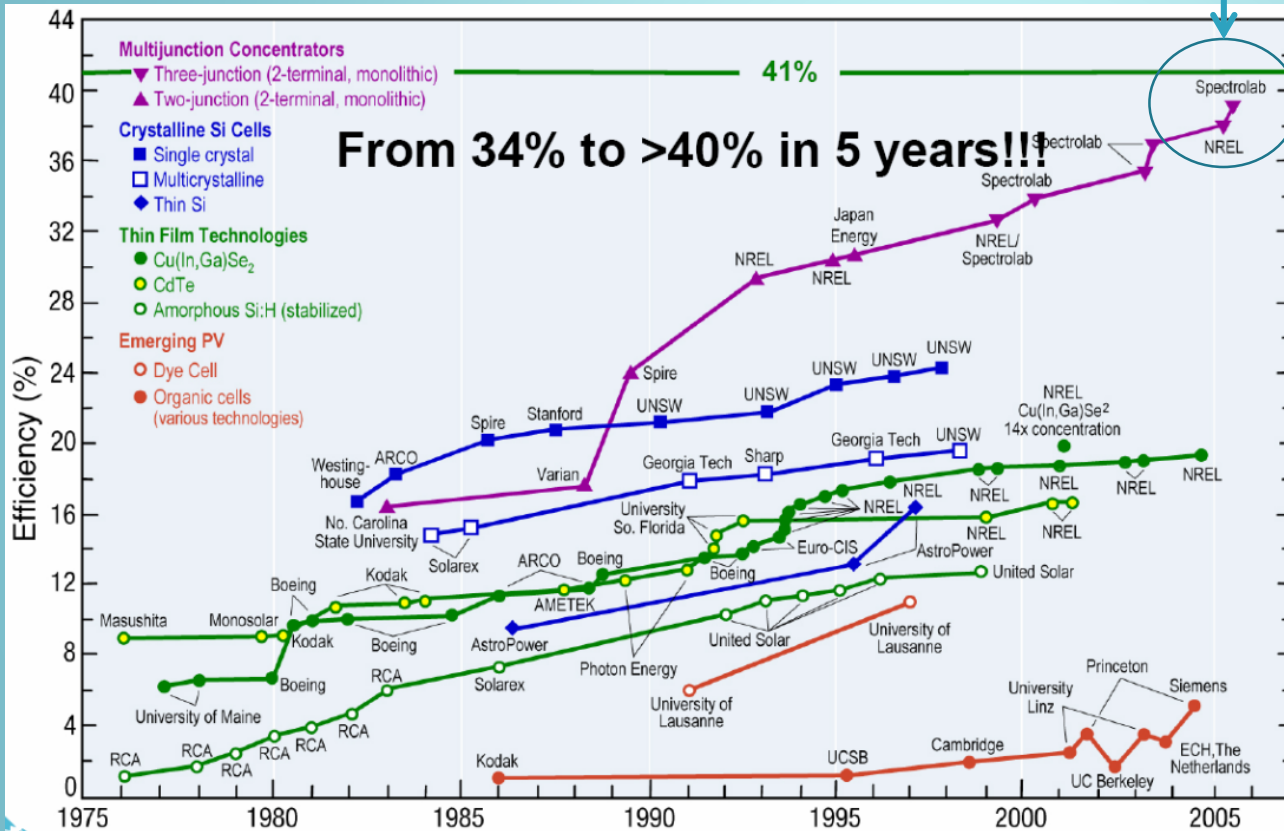




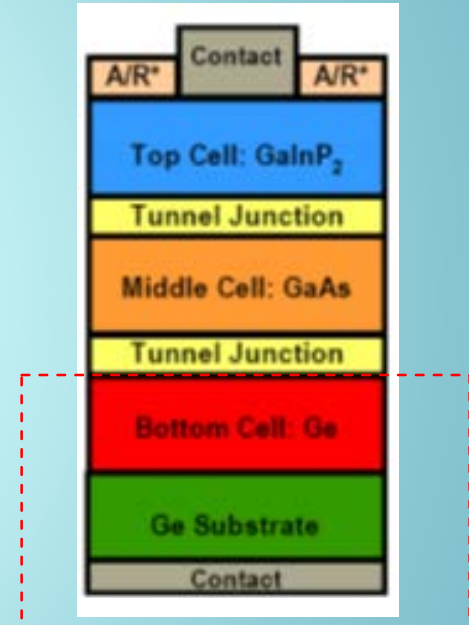


# Toward The World's Best Solar Cell

The World's Highest Efficiency Solar Cell: III-V Multi-Junction Cells on Ge/Si Wafer (44%)



III-V Multi-Junction Solar Cell On Germanium Solar Cell Wafer



Commercial 6" Germanium Wafer is about \$3,000.

NASA's new technology can make 6" SiGe/Sapphire under \$300.

Our SiGe on Sapphire uses transparent substrate: It can receive light in both sides.

**Our Goal: 40% Efficiency with 1/10<sup>th</sup> of price.**



# Summary

- Rhombohedral super-hetero-crystal epitaxy technology is invented. The world's first triangular crystal-plane epitaxy technology can combine cubic semiconductors with trigonal crystals.
- Germanium-rich single crystal SiGe layers on c-Sapphire are fabricated with high reliability (>99.9% single-crystal).
- US Patents: #8,257,491. #8,226,767. #7,906,358. #7,769,135. #7,558,371. #7,514,726 and so on.
- Super growth chamber was designed and manufactured to fabricate highly sophisticated quantum well solar cells and devices.
- Characterization shows single-crystalline SiGe layers on c-Sapphire with some residual defects. Surface morphologies are being improved with the reduction of RMS roughness.
- Rhombohedral Hybrid Bandgap (RHB) Technology expansion to III-V, III-Nitride and II-VI is underway.
- Pre-processor for high yield and Post-processor for high quality are under development.