Essence and Mechanism for Rhombohedral Hybrid Bandgap Engineering

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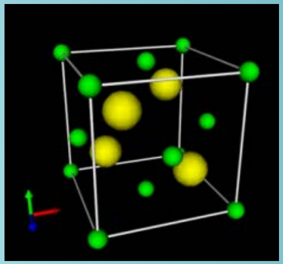
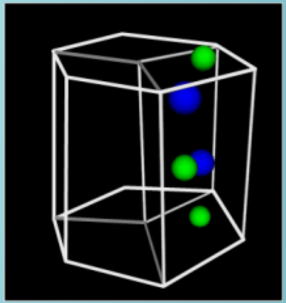
Today's Semiconductor Bandgap Engineering

- Currently, 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)

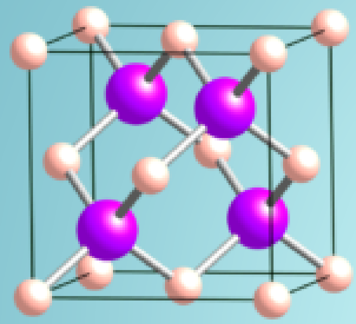


  - Hexagonal:
    - Wurtzite structures: III-Nitride semiconductors (GaN,AlN,InN)
    - II-VI semiconductor: Zinc-Oxide
    - Hexagonal SiC (2H, 4H)

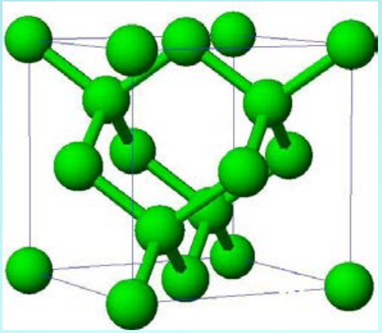


- The mixture of different crystal structures was thought to be very difficult. We developed a new growth technology of "Super Hetero Epitaxy" with SiGeC alloy in which each layer can have different materials and different crystal lattice structures.

Epitaxy Technology

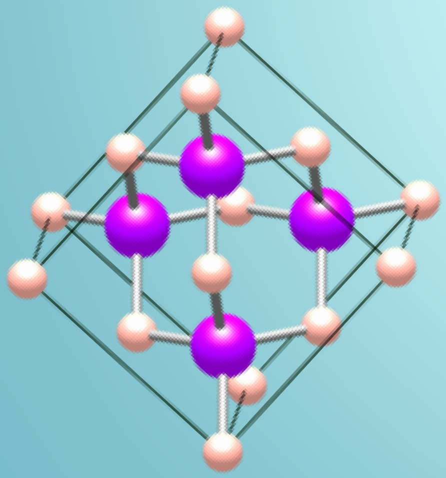


Cubic Zinc-Blende

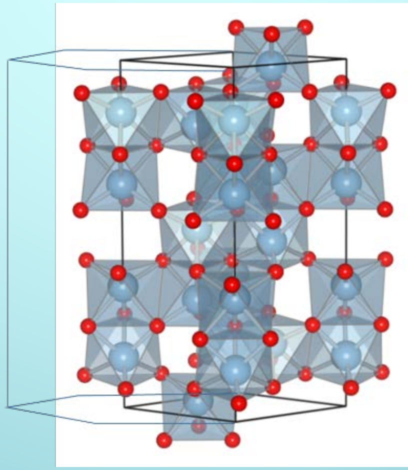


Cubic Diamond

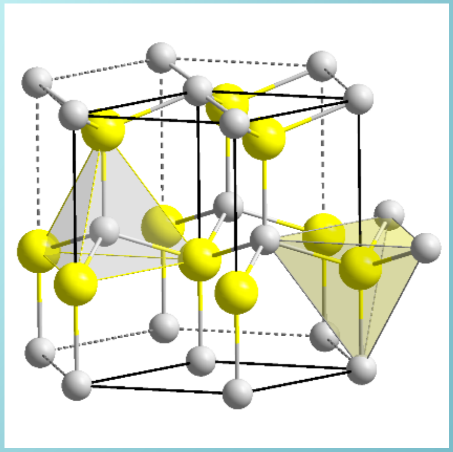
- Homo Epitaxy: One on One with same crystal structure
- Hetero Epitaxy: One on Different but same crystal structure
- Super-Hetero Epitaxy: One on Different with Different crystal structure



[111]-oriented Cubic Zinc-Blende

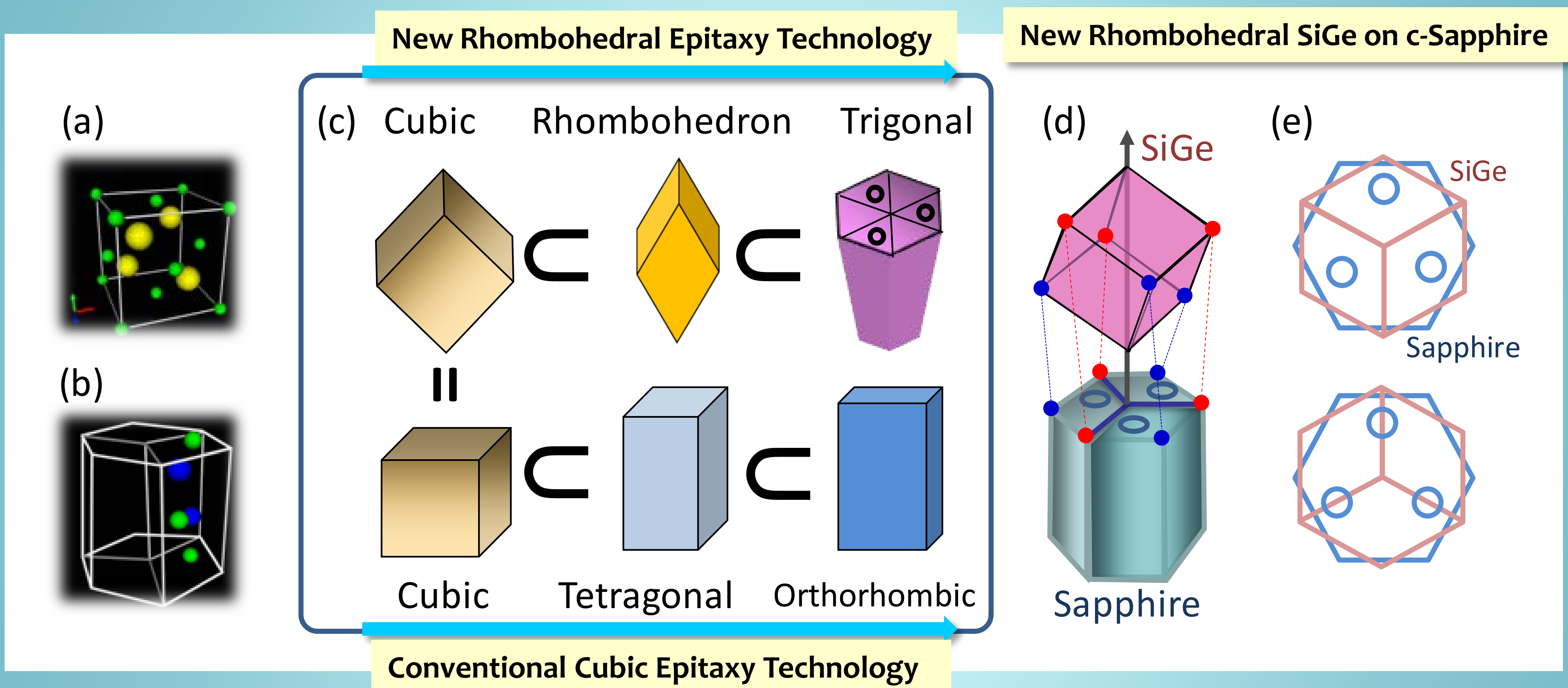


Trigonal Sapphire



Wurtzite Structure

Crystal Symmetry Relations

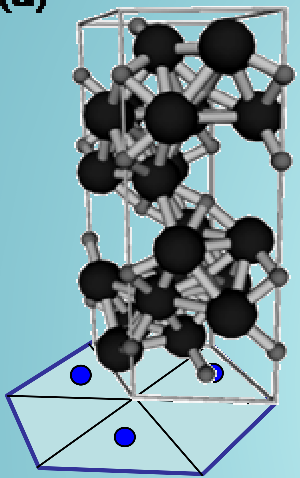


Cubic crystal also belongs to the Trigonal crystal group by the symmetry. A fundamental cross-structural epitaxy can be established beyond an accidental coincidence lattice matching!

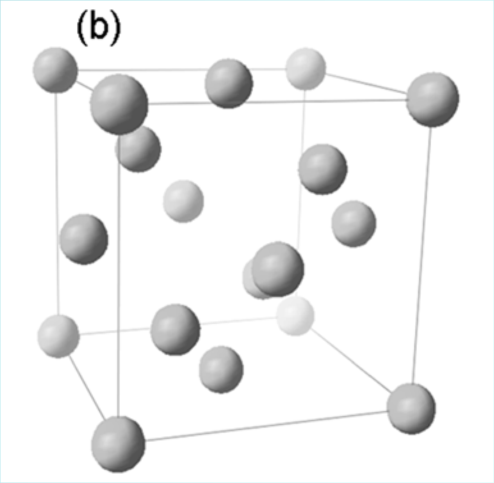
New Super Hetero Epitaxial Technology for Hybrid Crystal Growth

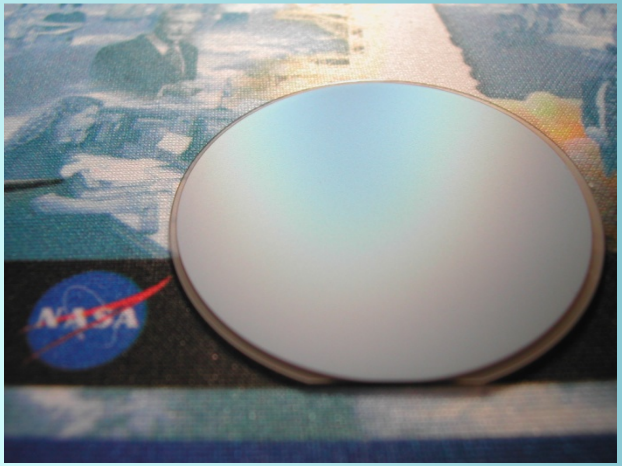
Trigonal Substrate

(a)



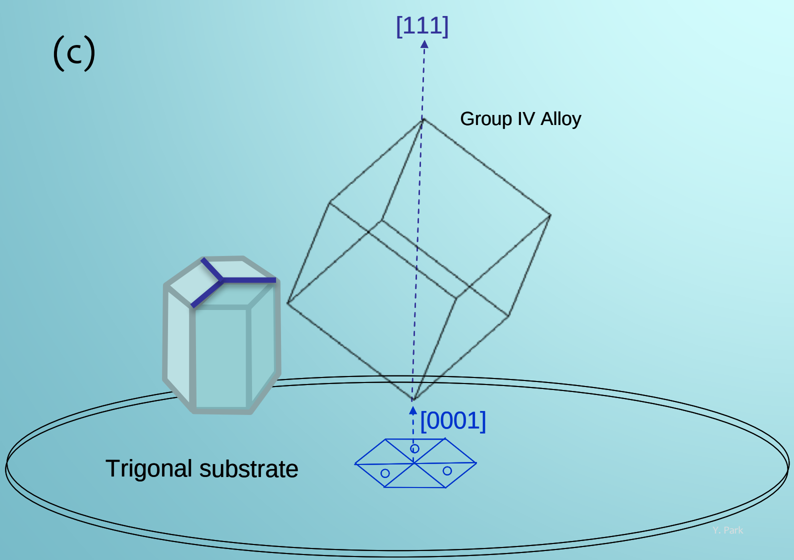
SiGe (Diamond Structure)



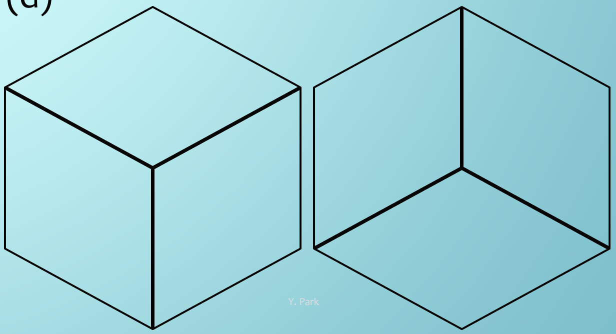


2” SiGe on Trigonal Substrate

(c)

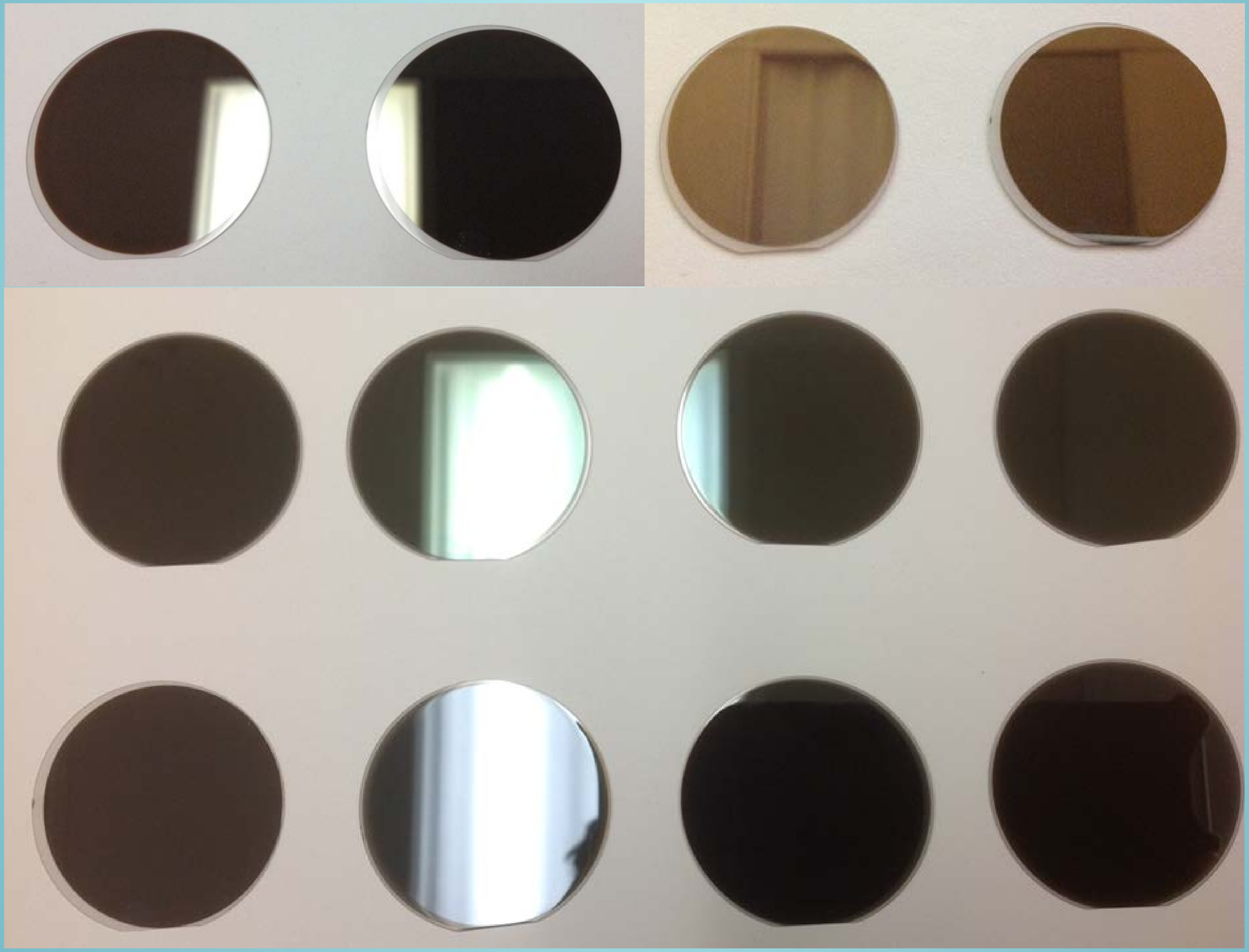


(d)

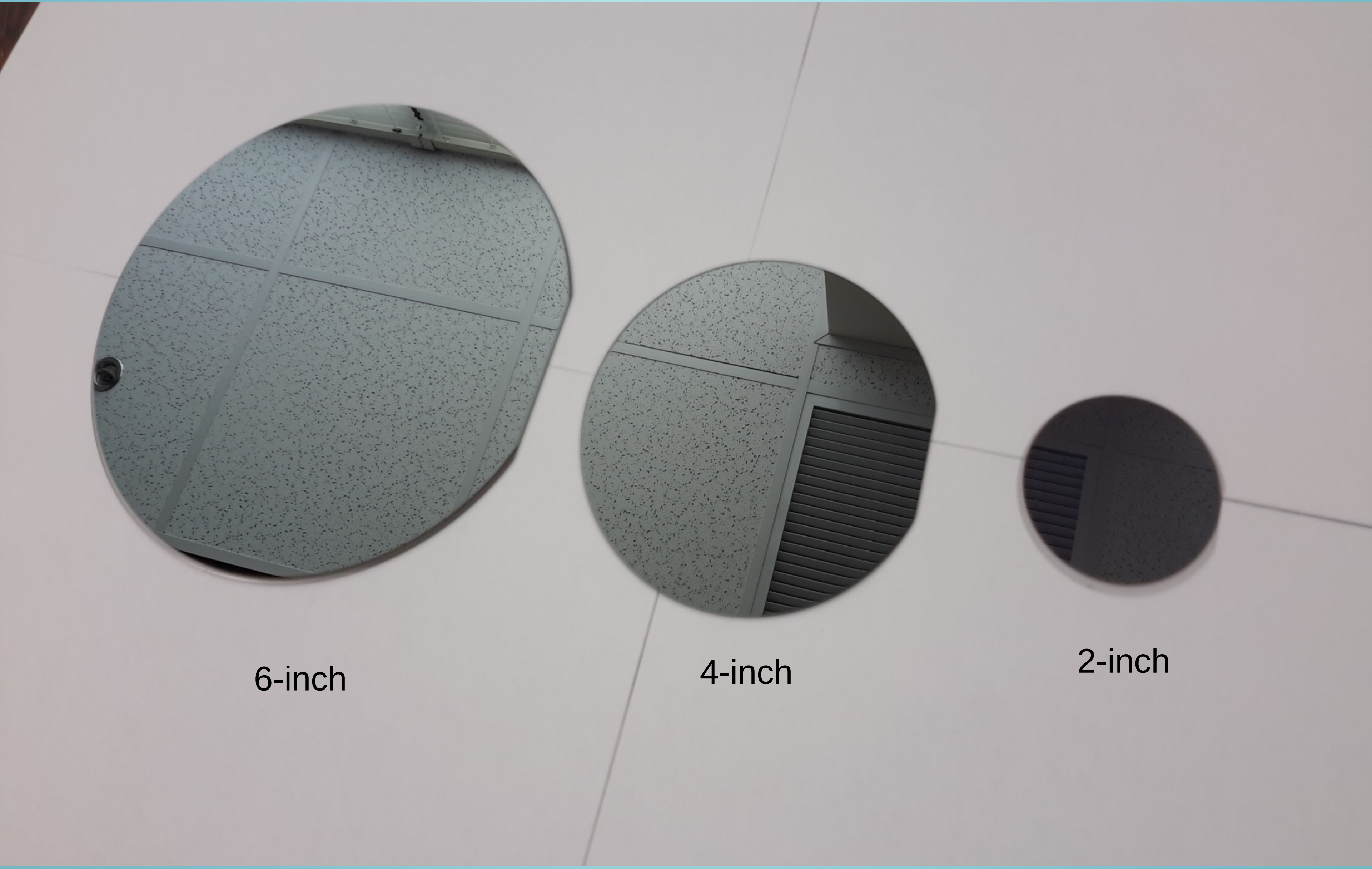


Twin Crystal to Each Other

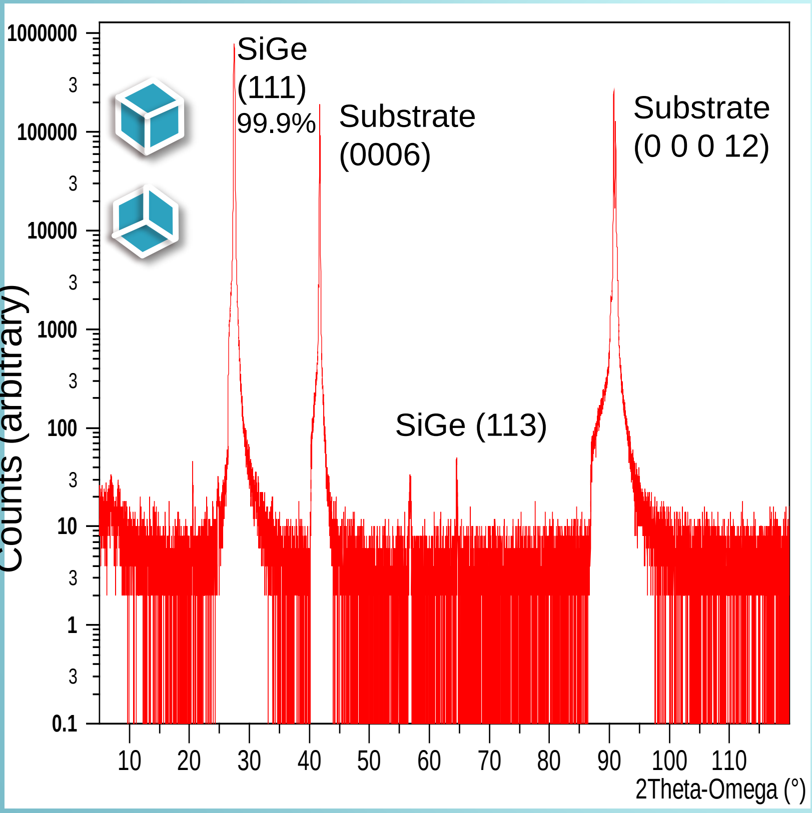
2" SiGe on c-Sapphire Samples

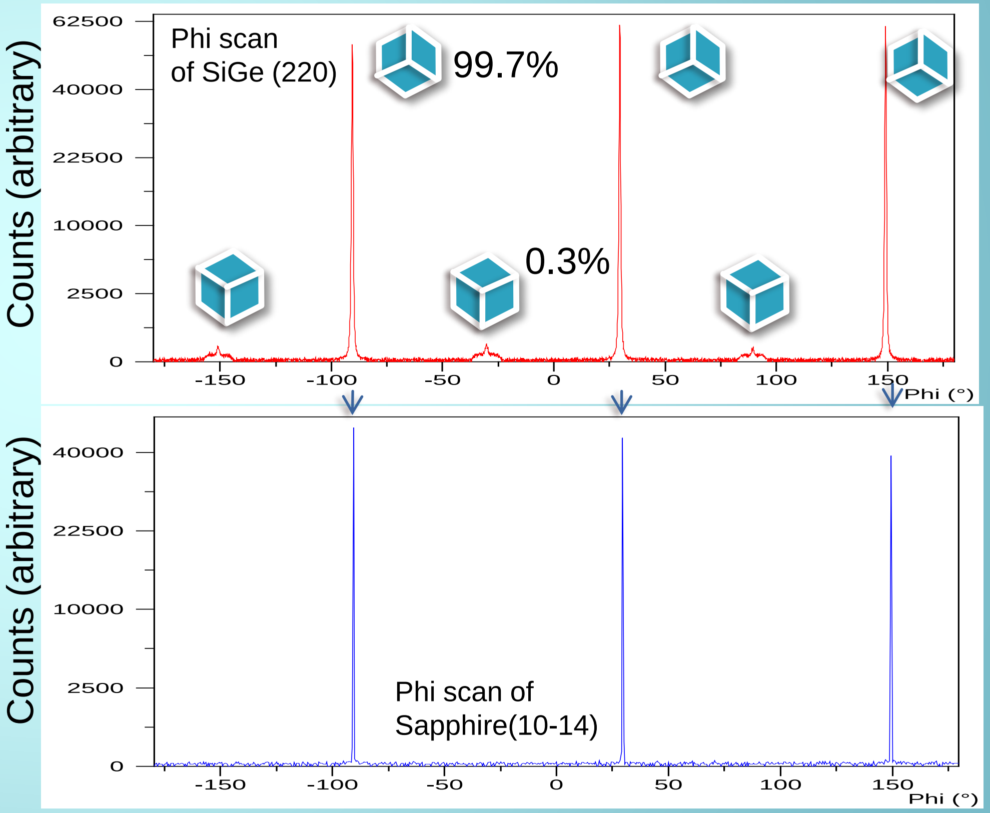


6” SiGe on c-Sapphire Samples

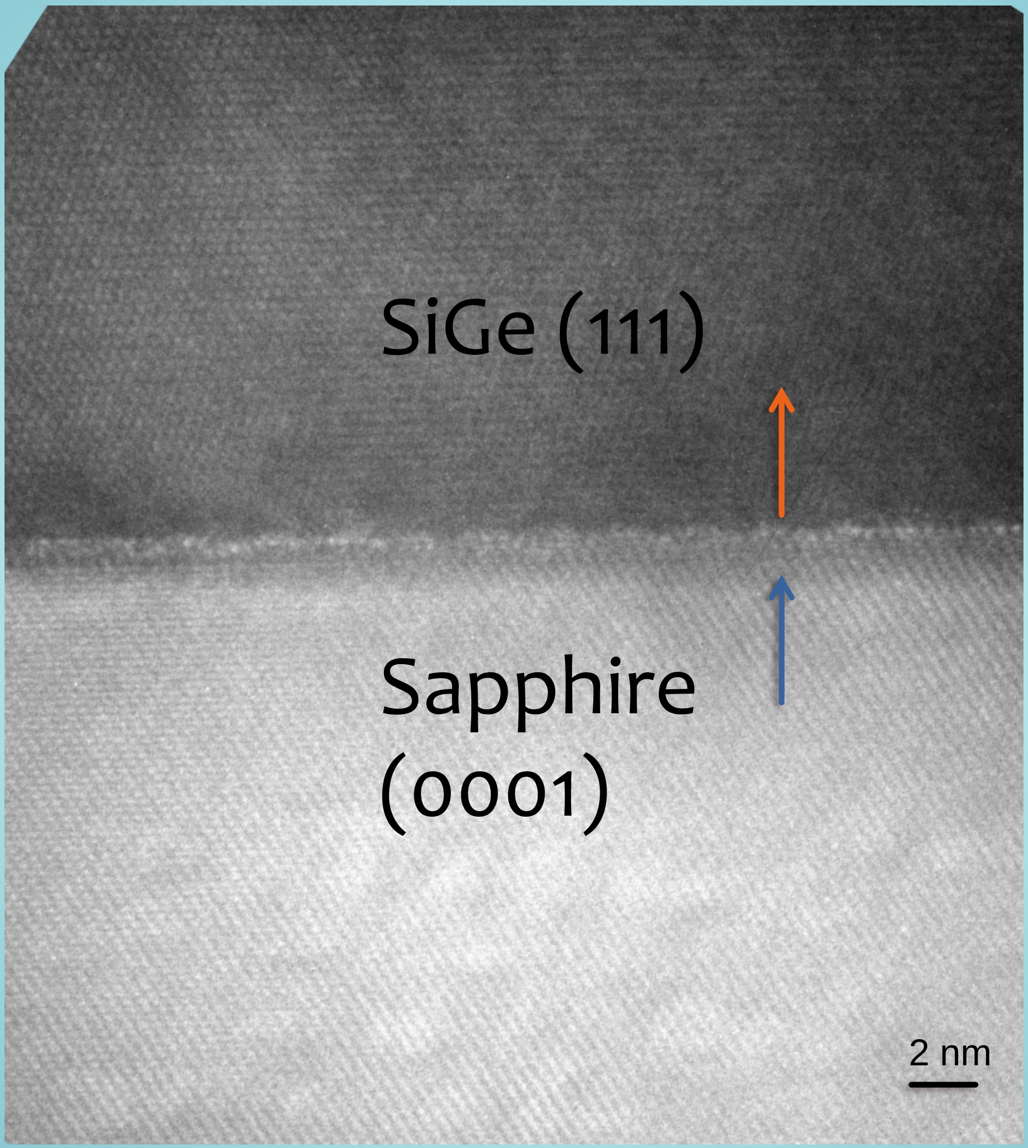


XRD Integral Twin Density Measurement





Single Crystalline SiGe Atomic Layers on Sapphire

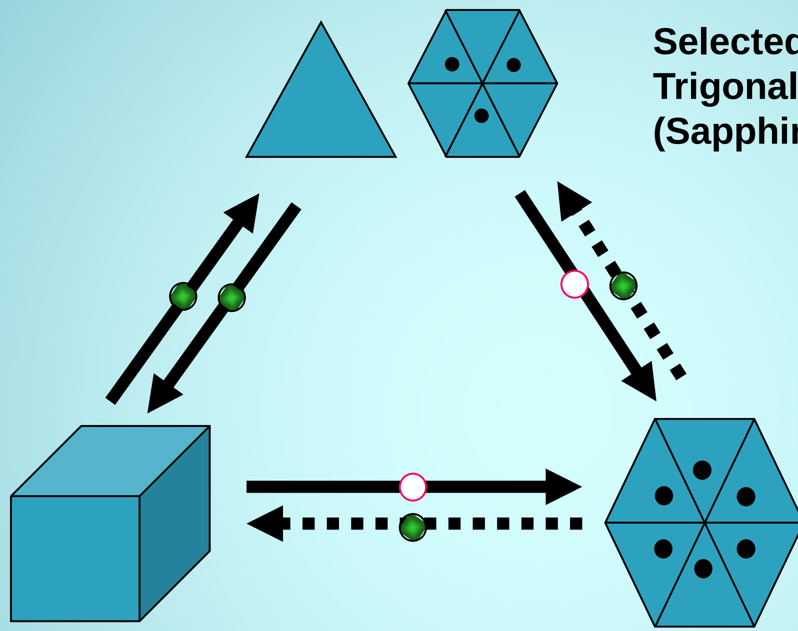


NASA patented XRD methods, materials, and fabrication processes.
(US Patent # 7341883, 7558371, 7769135, 7906358, 8226767 and more.)

Epitaxial Relationship with Three Space Symmetry Groups

Inter-Crystal-Lattice Epitaxial Relation

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



Selected Crystals with Trigonal Space Symmetry (Sapphire and so on)

Crystals with Hexagonal Space Symmetry (GaN, AlN, Wurtzites)

Point Symmetry Group

Trigonal **Hexagonal**

Wurtzites are trigonal in point symmetry group but they belong to hexagonal space symmetry group due to its alternating stacking sequence.

Cubic Crystals
With [111] direction
(Si, Ge, Diamond, GaAs, ZnTe, InP, Zinc-blendes)

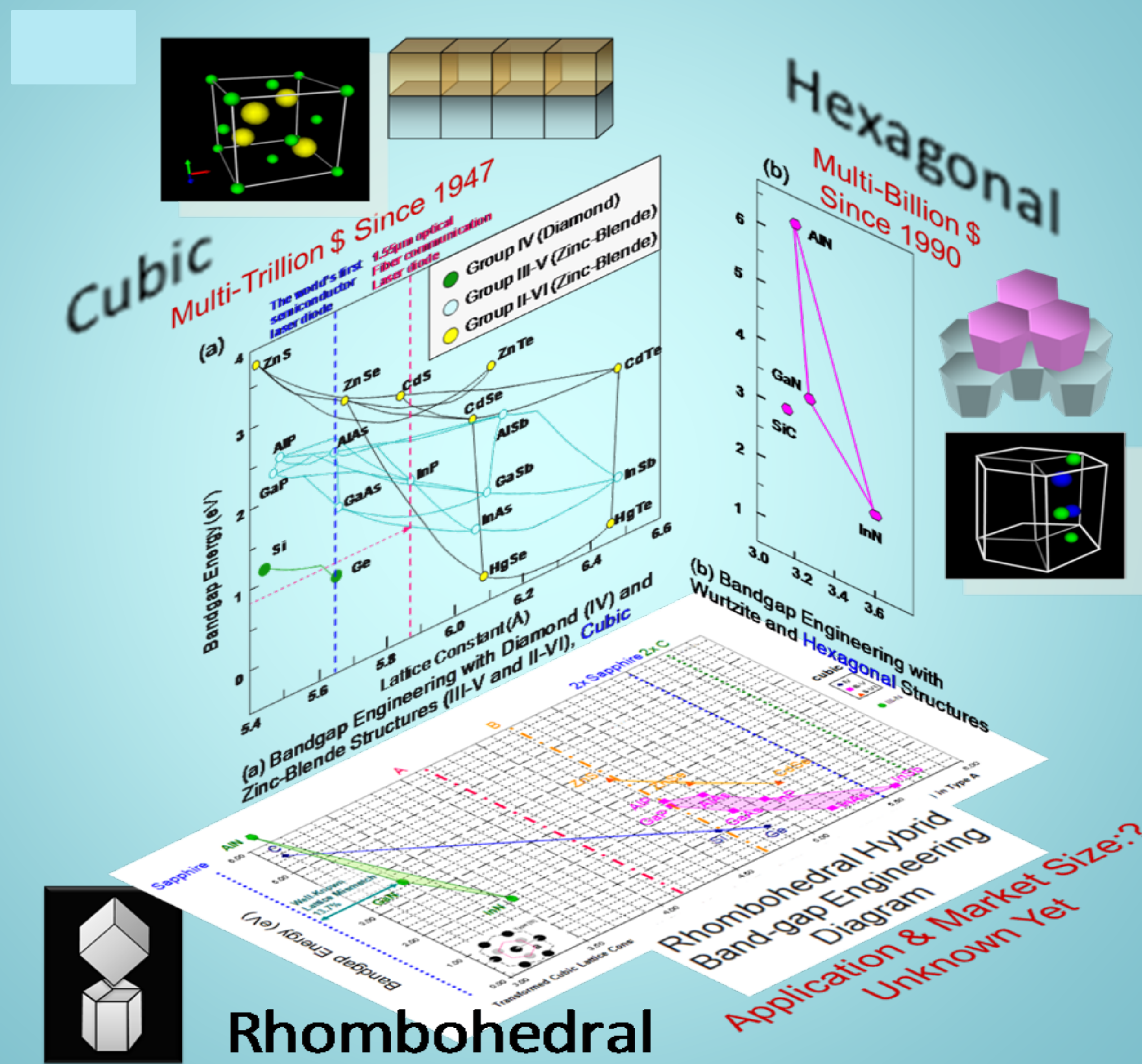
Substrate → Epitaxial Layer : No Double Position Defect

Substrate ⋯→ Epitaxial Layer : Double Position Defect at Stepped Interface

Twin detection XRD works

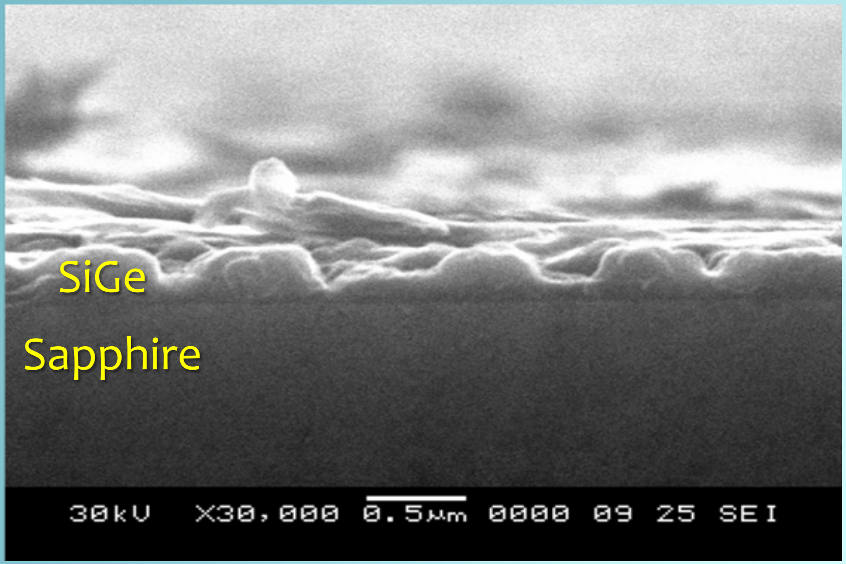
Twin detection XRD does not work

New Rhombohedral Semiconductor Epitaxy

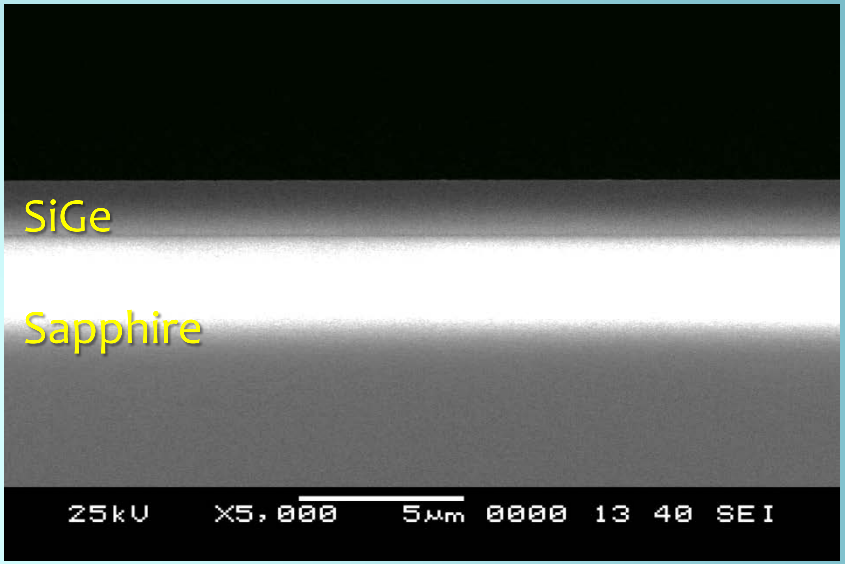


Epitaxial Layer Growth Optimization

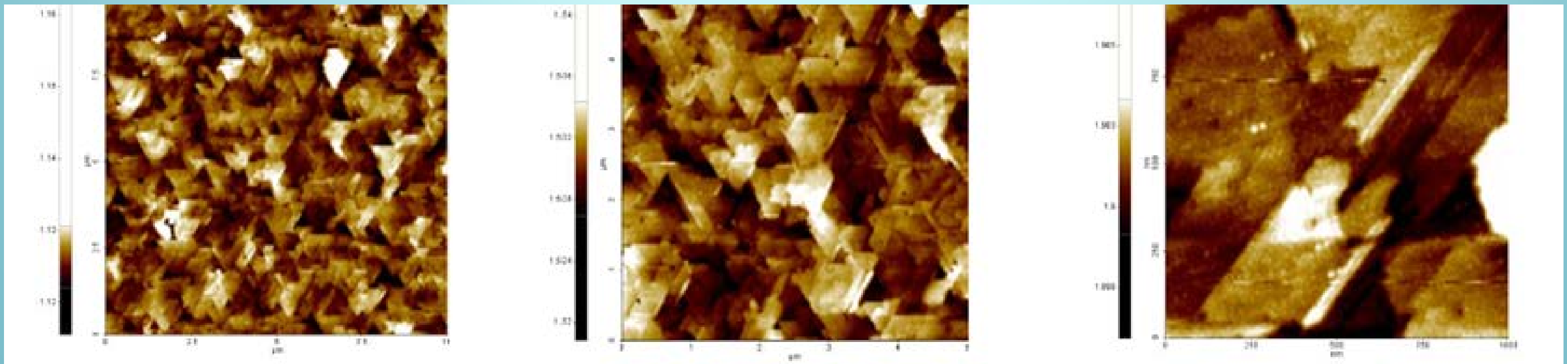
SEM: Unstable island growth



Stable layer-by-layer growth



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

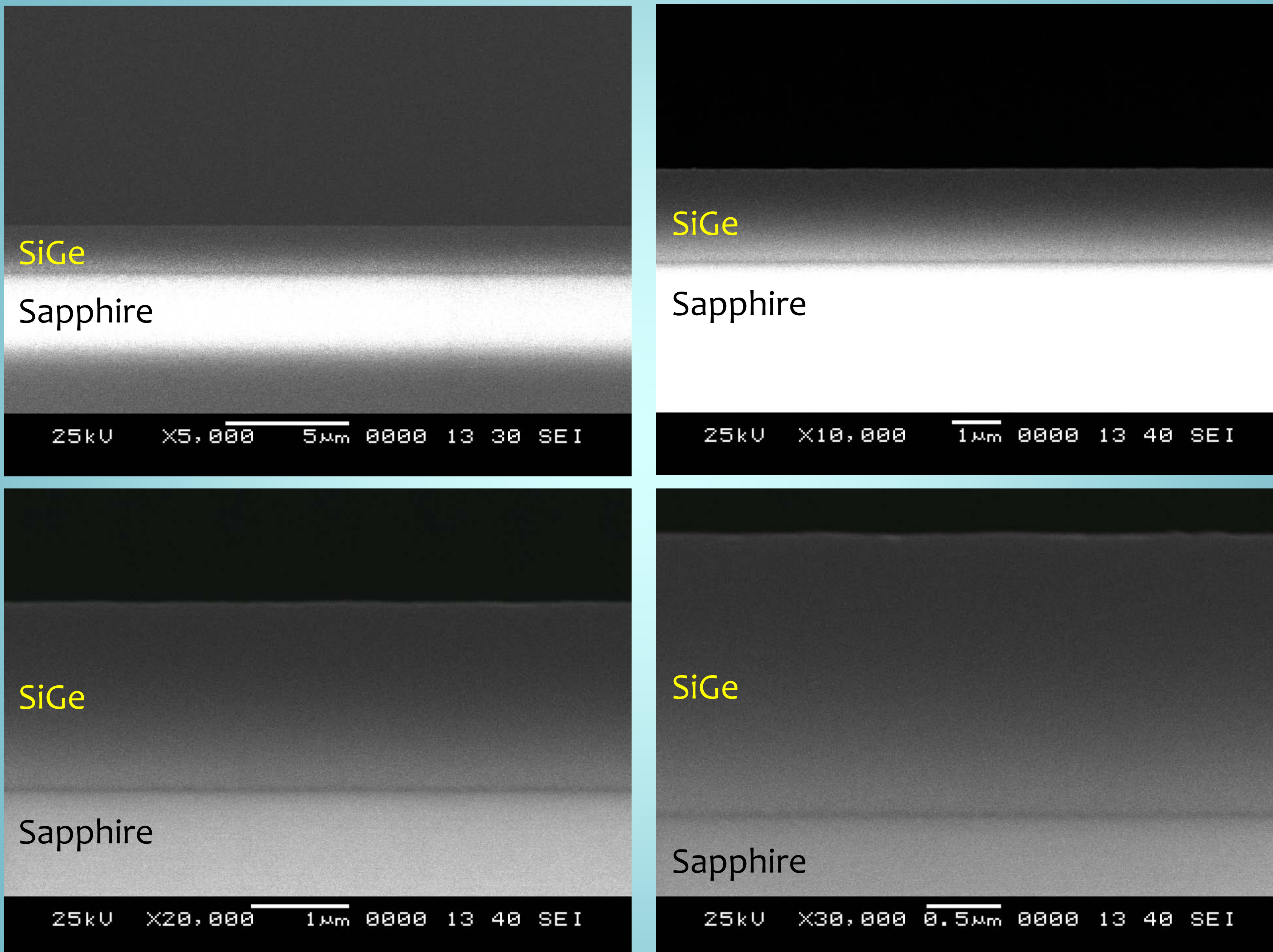


10µm x 10µm Image
RMS Roughness = 2.24nm

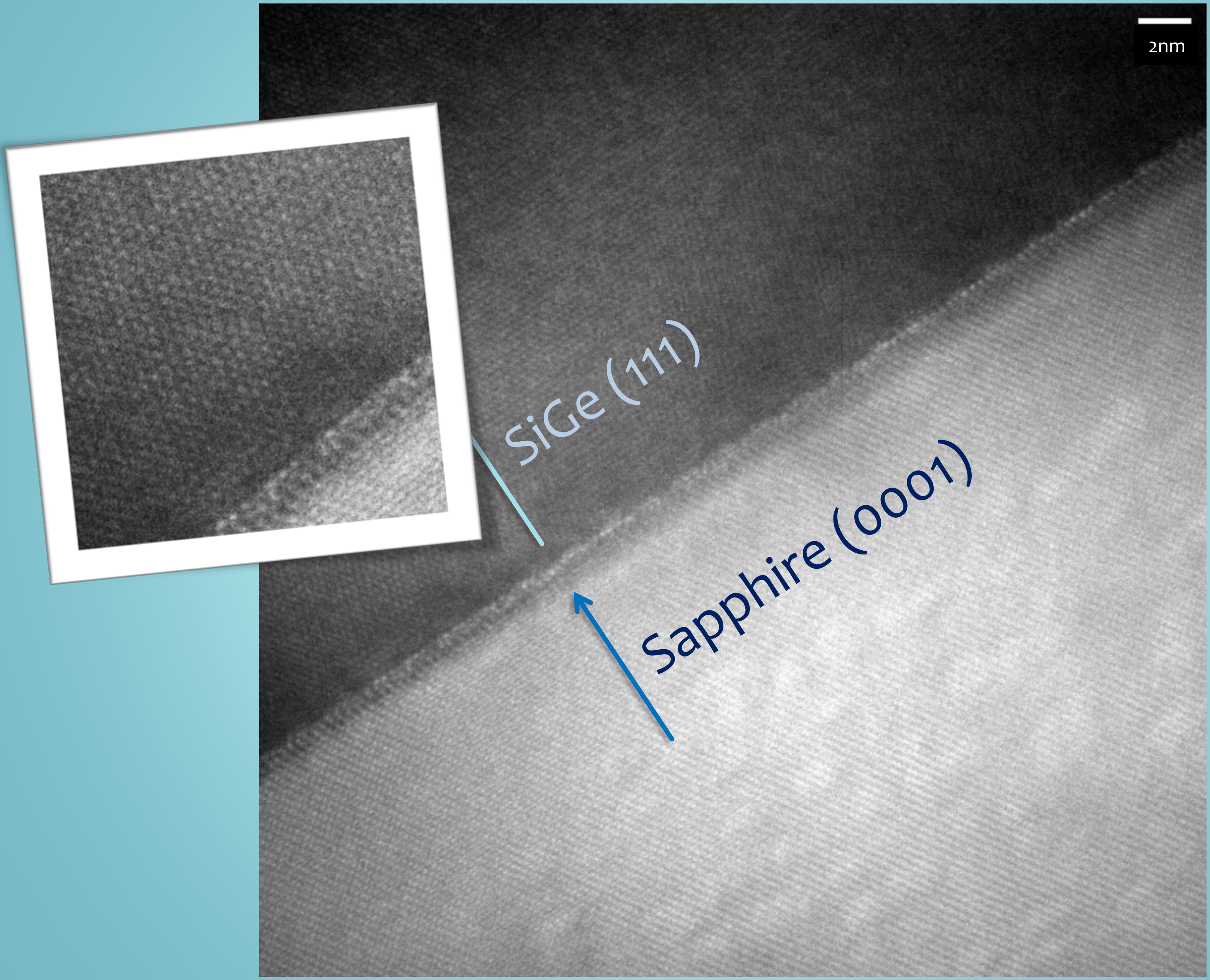
5µm x 5µm Image
RMS Roughness = 1.87nm

1µm x 1µm Image
RMS Roughness = 1.06nm

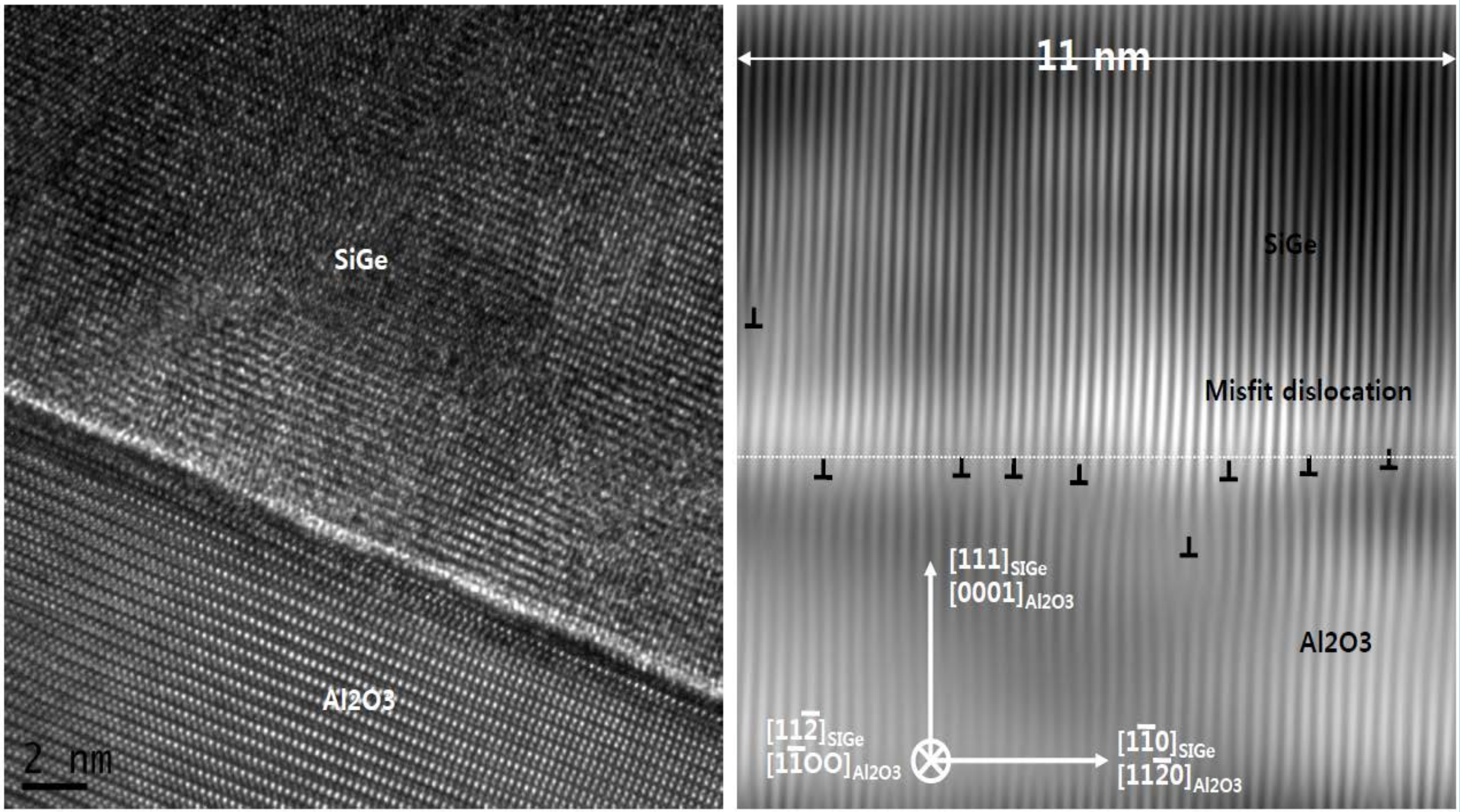
High Resolution Cross-sectional SEM Image of SiGe on c-Sapphire



TEM Image of Rhombohedral-Trigonal Super Structure



Misfit Dislocation – from SK Hynix

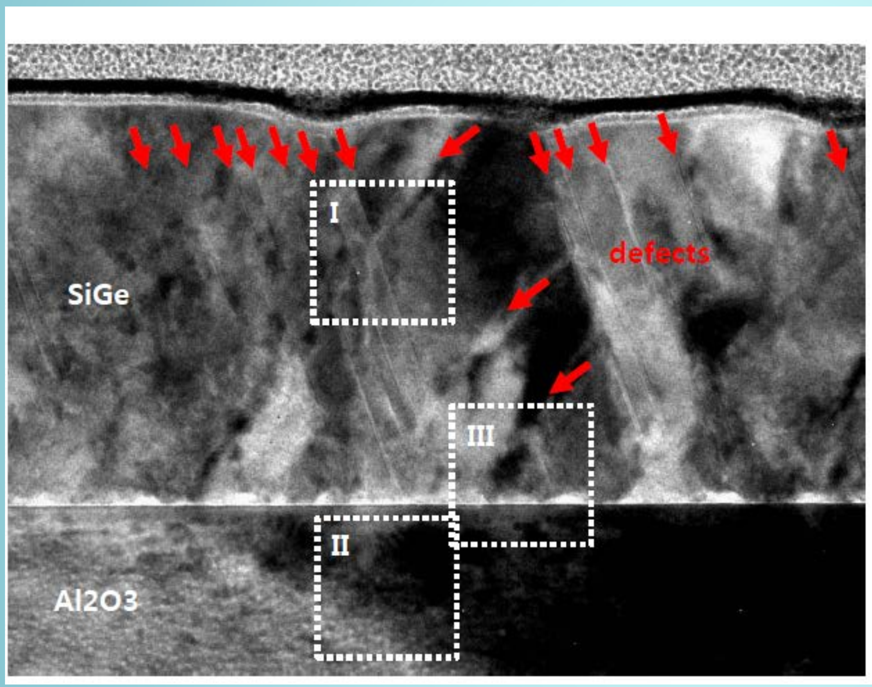


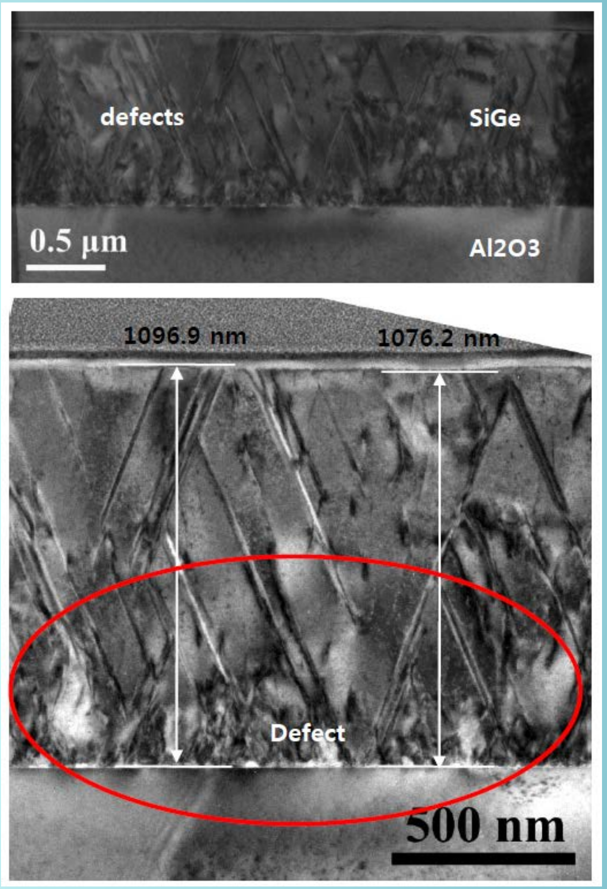
- growth direction: $[111]_{SiGe}$ // $[0001]_{Al2O3}$, $[1\text{-}10]_{SiGe}$ // $[11\text{-}20]_{Al2O3}$

- 9 misfit dislocation in ~11 nm SiGe range (measured)

- Misfit dislocations are confined at Sapphire-SiGe interface only.
- Device does not use Sapphire area. Therefore misfit dislocations do not harm device.

Residual Twin Defects – from SK Hynix

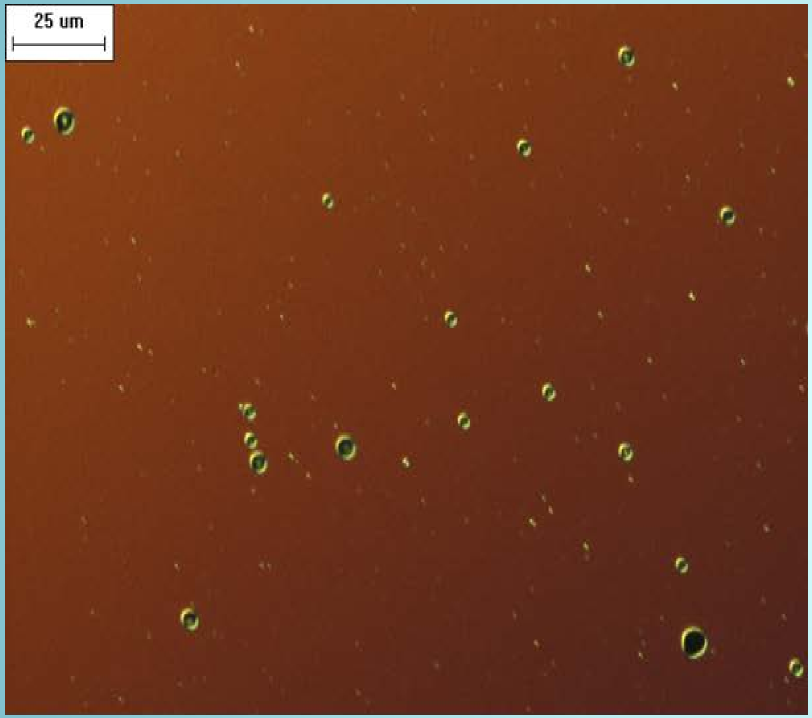




- Sample #SG715 has 0.7% twin and Sample #SG2-007 has 3% twin defects.
- TEM images show that our samples have residual defects, micro-twins and stacking fault columns. These defects can be eliminated with better surface cleaning and preparation and initial nucleation layer control.

Oval Defect Control

Nomarsky Differential Interference Contrast Microscope Images

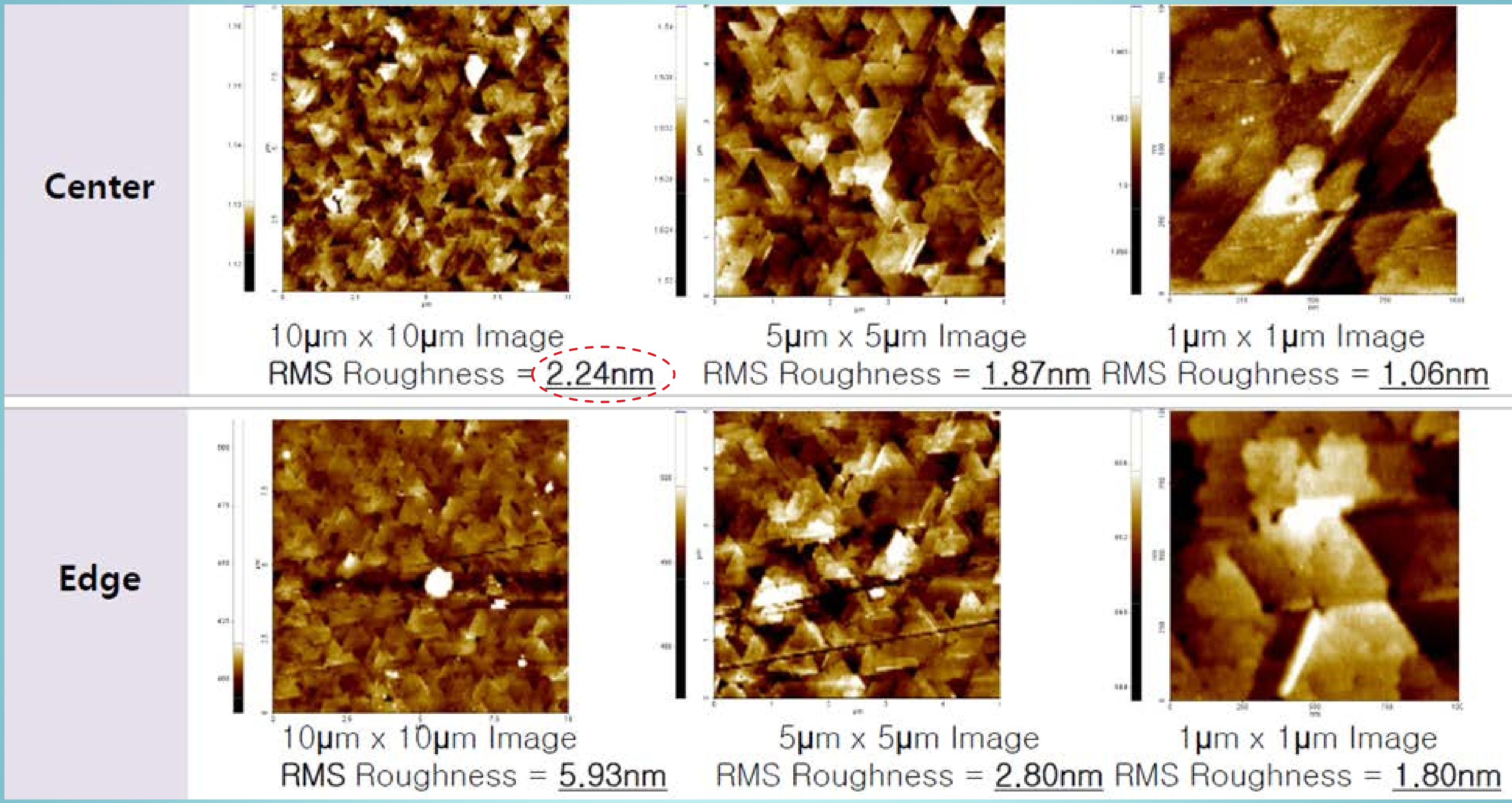


Sample with oval defects (splash)

Good Sample (No Oval Defects)

Oval defects can be eliminated with hot-lip effusion cells and better growth control

AFM Measurement – from SK Hynix

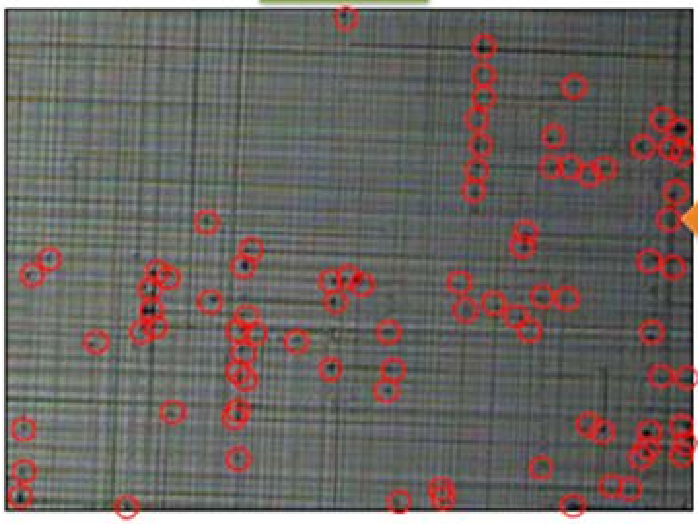


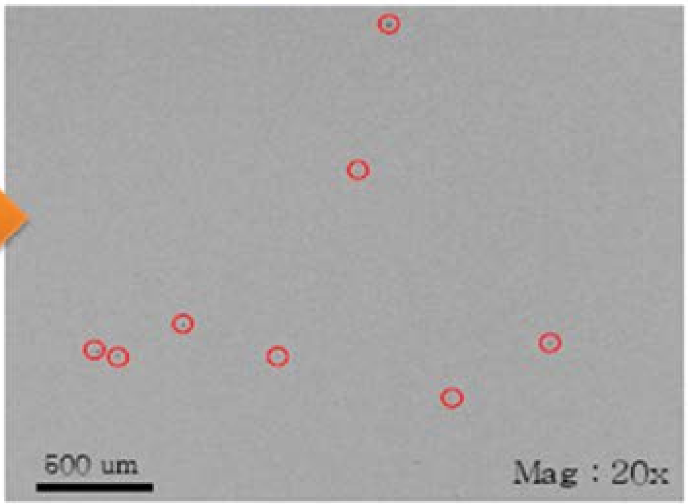
- Best RMS roughness = 2.5 nm
- The World's first epitaxy technology to use triangular crystal planes.
- Bridges between cubic semiconductors and trigonal crystals such as piezo-electric, ferroelectric, and non-linear optical crystals.

Comparison of Etch-Pit Densities

Threading Dislocation Pit Density after Secco Etching

IBM's SiGe	NASA Langley's SiGe
SiGe on Si substrate **Si(100)**	SiGe on sapphire substrate **Sapphire(0001)**
35 % Ge	78 % Ge





IBM's SiGe:

- TDP density : 3.90 X $10^4/cm^2$
- LD density : 1.73 X 10^4/cm
- Cross-hatch pattern

NASA Langley's SiGe:

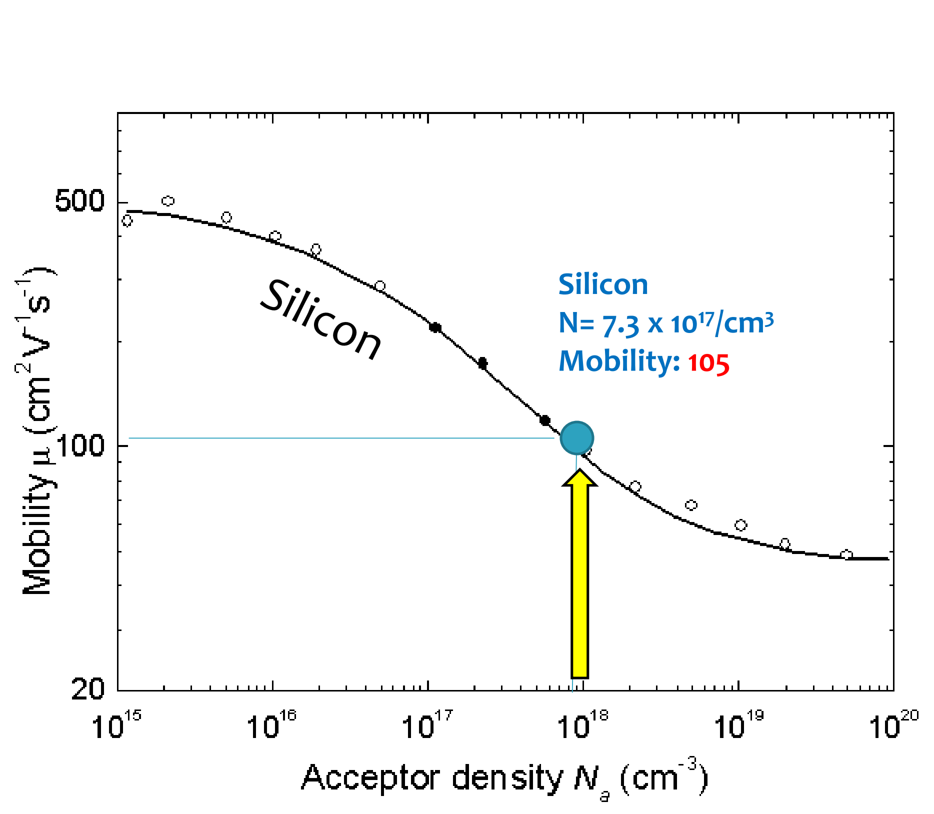
- TDP density : 1.9 X $10^2/cm^2$
- LD density : 0/cm
- No Cross-hatch pattern

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

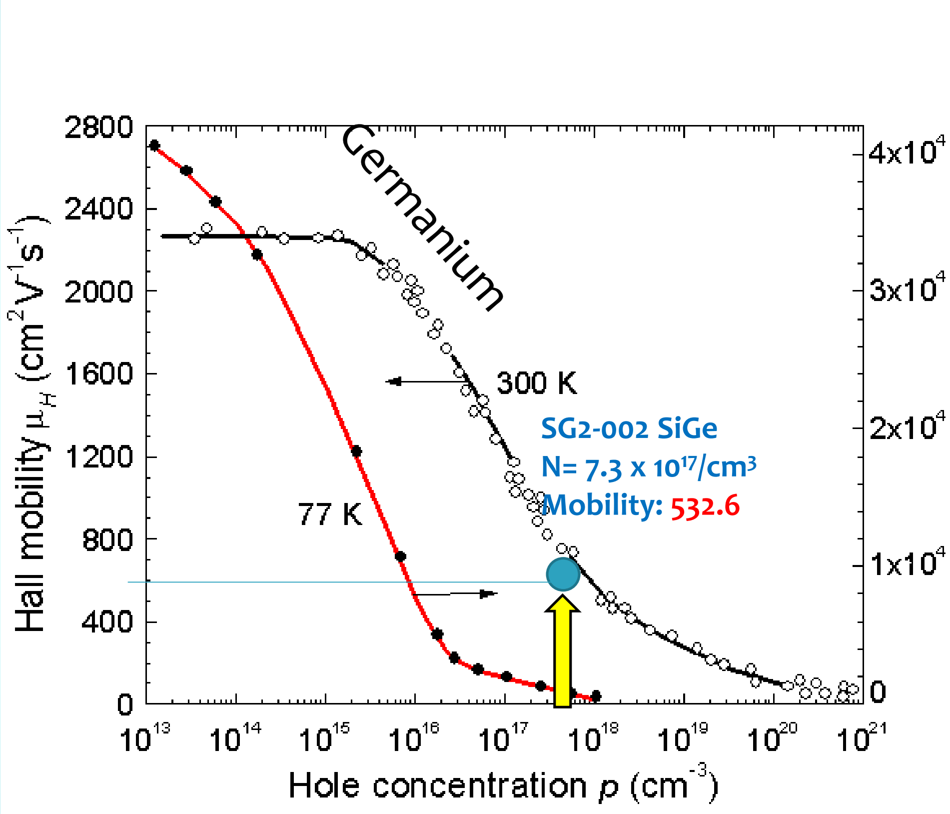
(Etch rate: 25nm/sec)

Hole (p-type) Mobility of SiGe

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



P-type Silicon's Mobility vs. Doping

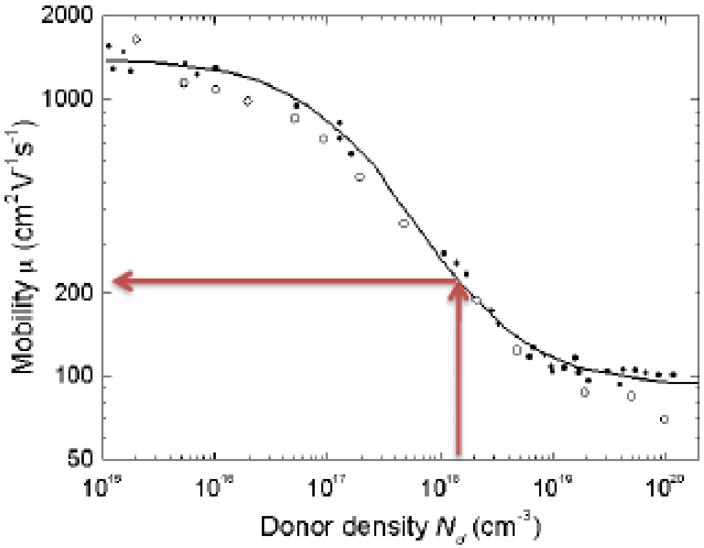


P-type Germanium's Mobility vs. Doping

Electron (n-type) Mobility of SiGe

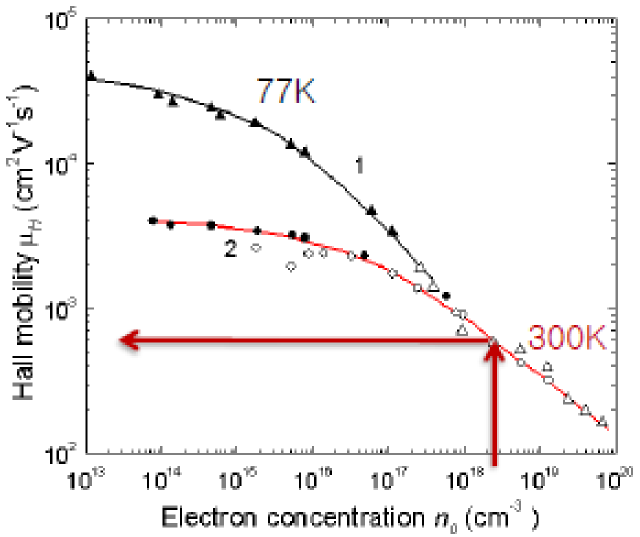
280% Faster Than Silicon (Si=220 vs. SiGe=616)

Standard n−type Silicon



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

Standard n−type Germanium



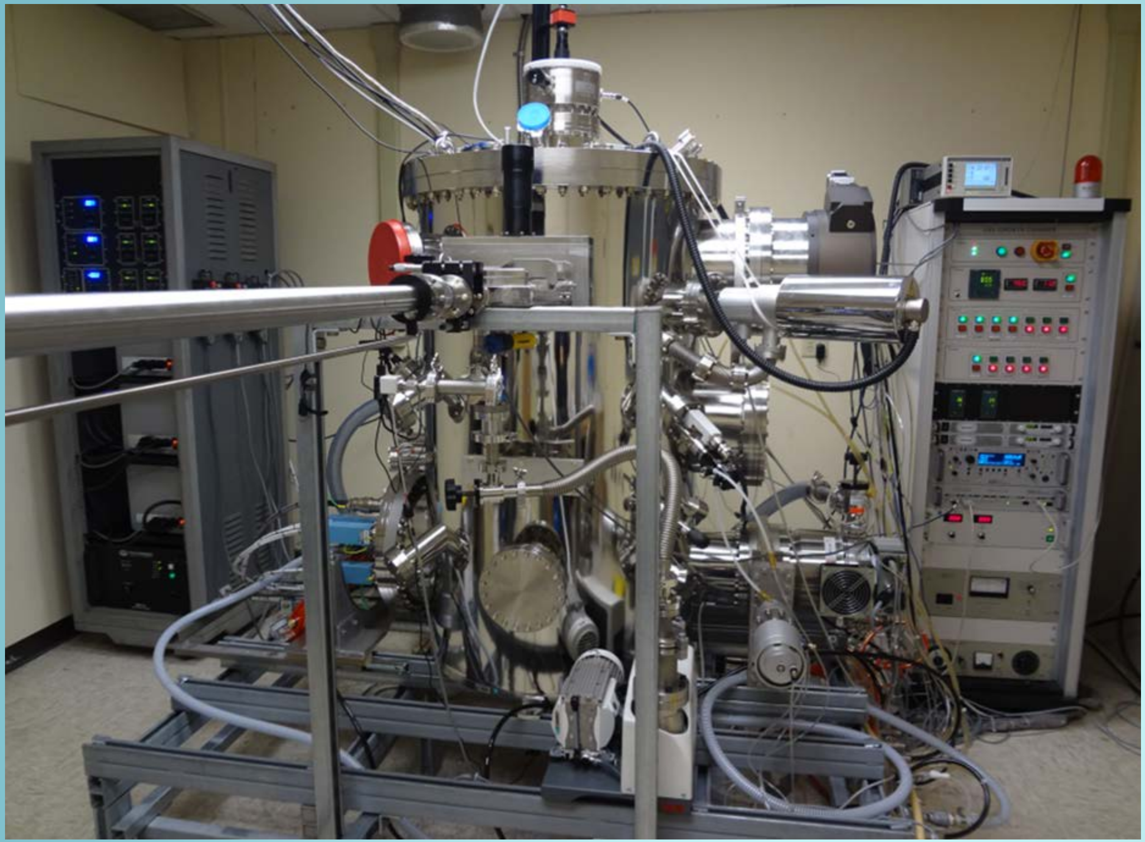
Fistul V. I., M. I. Iglitsyn, and E. M. Omelyanovskii, Sov. Phys. Solid State **4**, 4 (1962) 784-785.

220 $cm^2/V\cdot s$ at $1.5\times10^{18}/cm^3$ doping

780 $cm^2/V\cdot s$ at $1.5\times10^{18}/cm^3$ doping

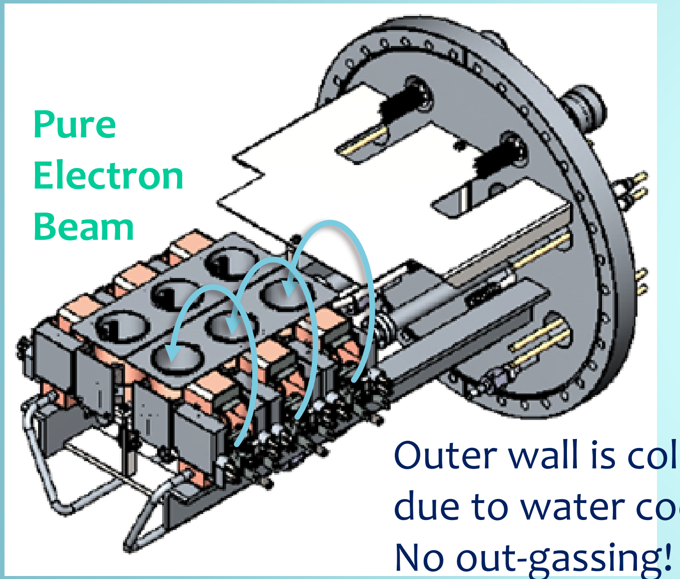
Note: Our Thin Rhombohedral SiGe Sample#2 has **616 $cm^2/V\cdot s$** at $1.5\times10^{18}/cm^3$ doping **which is 2.8 times higher electron mobility** than single crystalline Silicon wafer at the sample doping level. **μ_{SiGe} is 2.8 times higher than μ_{Si}**

Super Hetero Crystal Growth Chamber



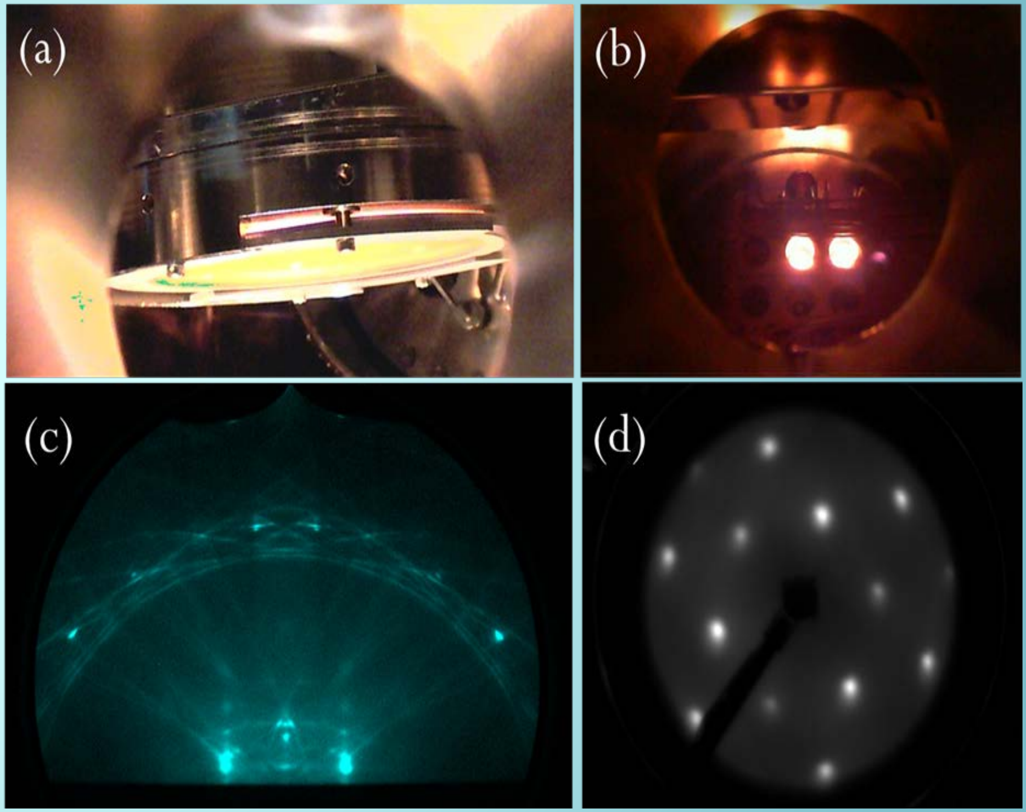
- About $1 Million was invested to build the super hetero-crystal crystal growth chamber.
- Additional financial support was made from Department of Transportation (DoT).
- The system can accept standard 2”-6” wafers with a load-lock.
- The system is ready for full computer control.

Functions of Super Growth Chamber



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

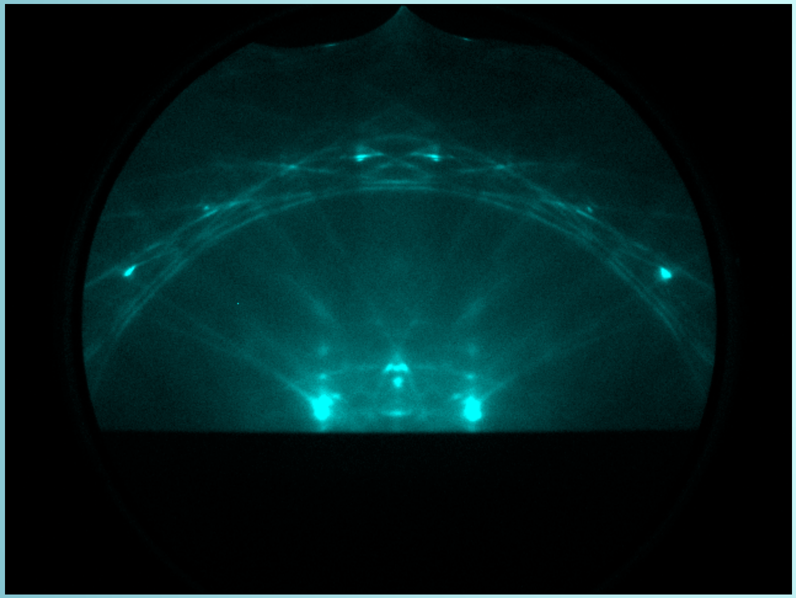
6" Wafer Heater   6-Cell E-Beam Evaporator



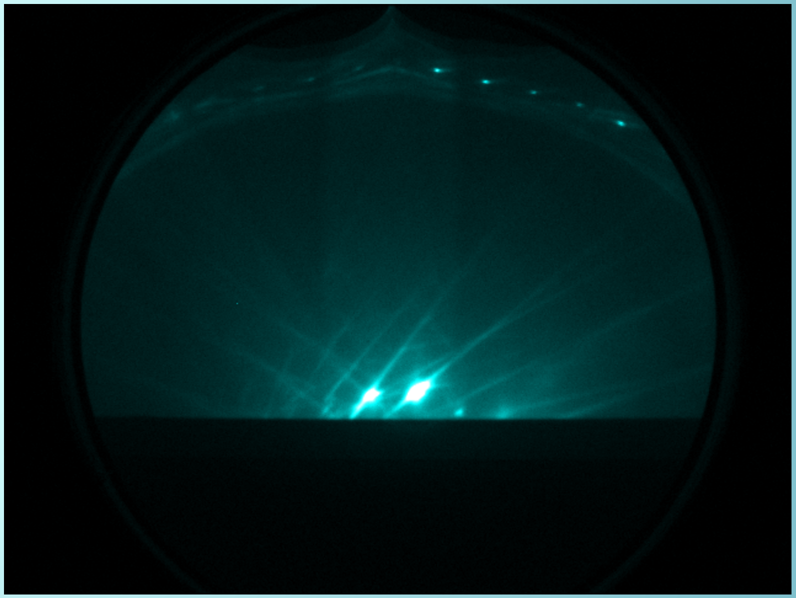
RHEED Monitoring   LEED Monitoring

Atomic Precision In-Situ Growth Monitoring

RHEED Patterns Obtained from Sapphire (0001) Surface

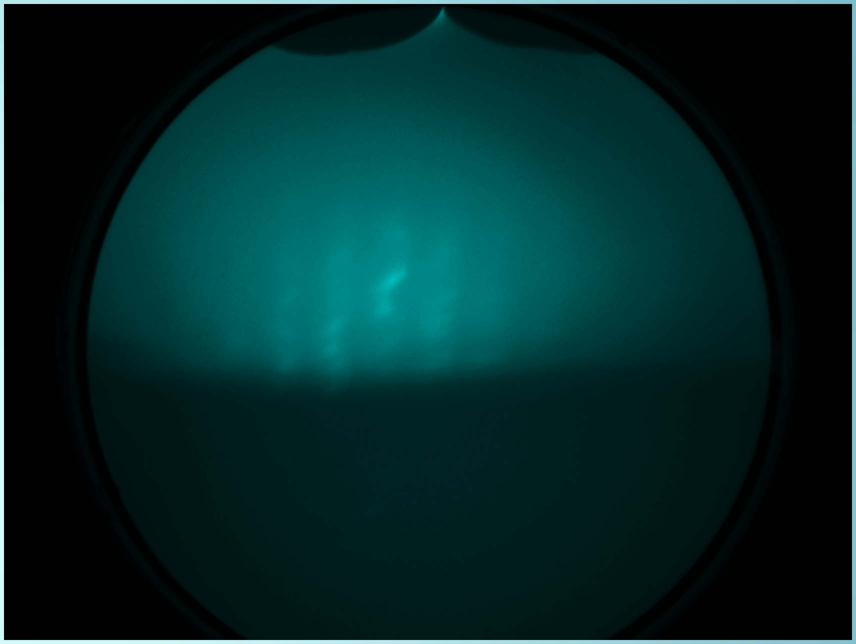


$[2\bar{1}\bar{1}0]$ Direction



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

RHEED Pattern of SiGe Epi-Layer



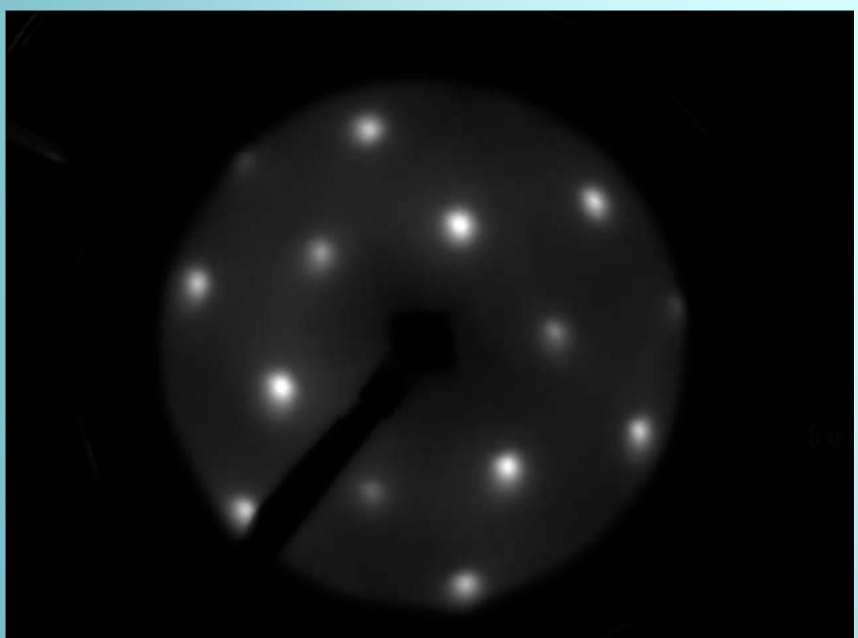
RHEED Pattern of
SiGe Epitaxial Layer

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

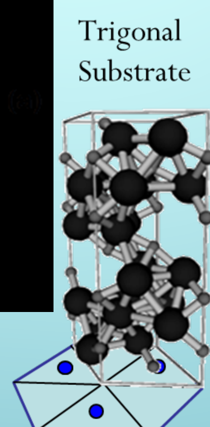
Atomic Precision Substrate Surface Monitoring

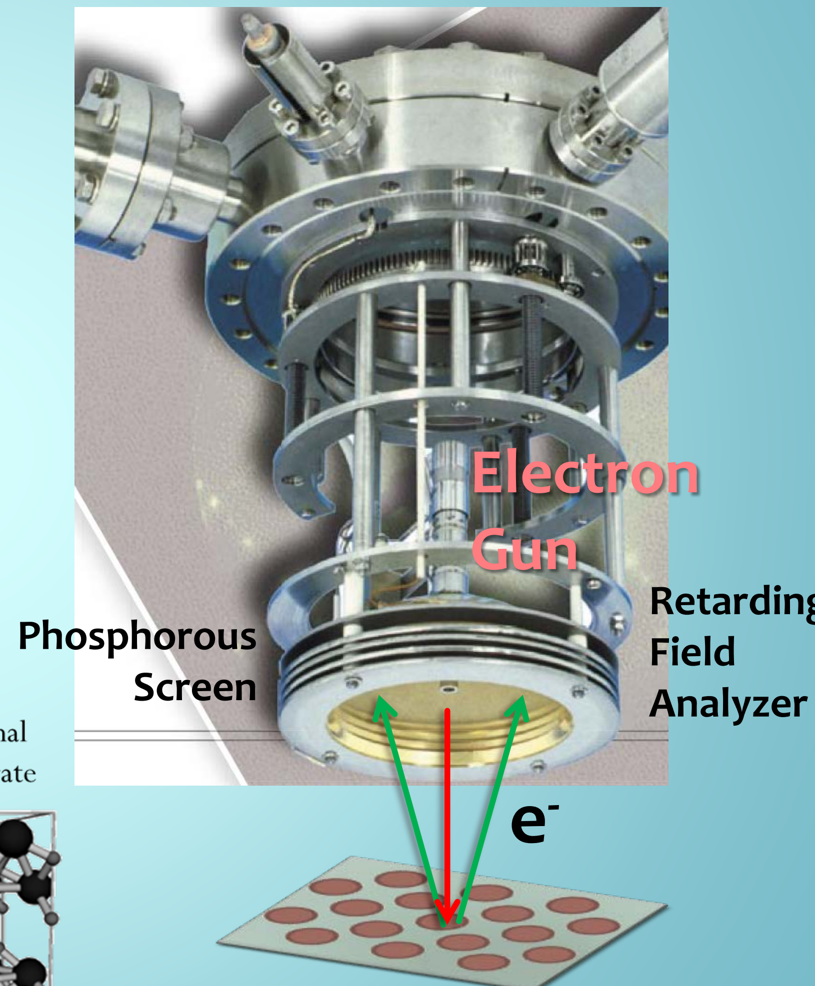
Low Energy Electron Diffraction (LEED)

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



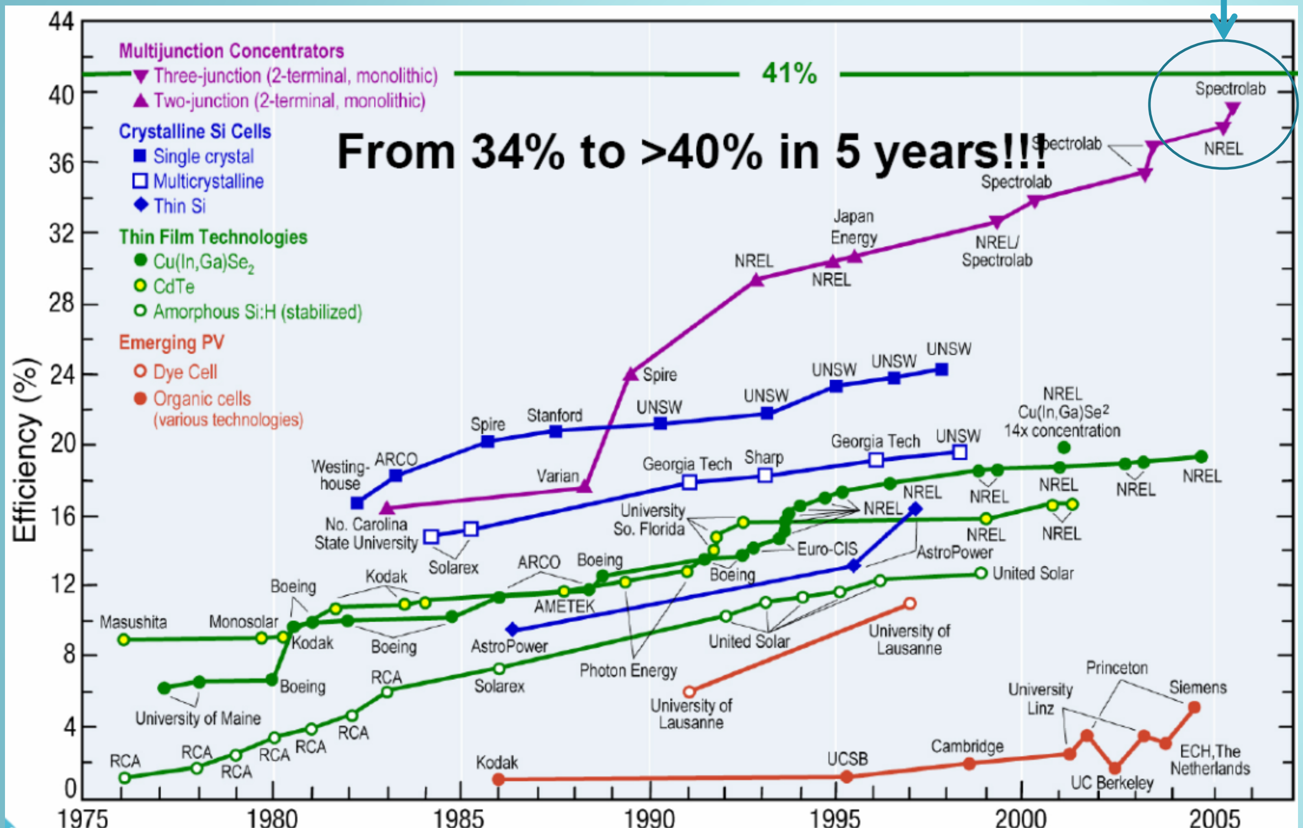
100eV LEED Pattern



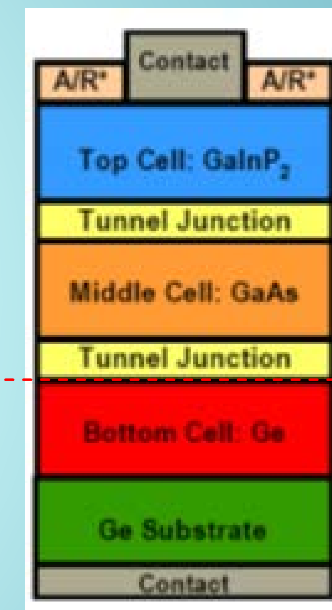


Toward The World's Best Solar Cell

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 1/10th of price.

Summary

- Rhombohedral super-hetero-crystal epitaxy technology was 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 can be fabricated with high reliability (>99.9% single-crystal).
- Technology has been patented: US Patents: #8,257,491. #8,226,767. #7,906,358. #7,769,135. #7,558,371. #7,514,726.
- 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. Quality is being improved with the reduction of residual defects.
- Technology expansion to III-V, III-Nitride and II-VI is underway.