



Defect-engineered $\text{Si}_{1-x}\text{Ge}_x$ Alloy for Thermoelectric Generator

Hyun Jung Kim¹, Yeonjoon Park¹, Sang. H. Choi²

1. National Institute of Aerospace VA USA

2. NASA Langley Research Center, VA USA

ICT/ACT-2016

May 30th 2016

Defect-Engineered SiGe Technology



Materials Facts and Challenges

- The SiGe films are polycrystalline with 90° rotated twin defects due to the bigger atomic size of Ge than that of Si (Lattice Constant: Si = 5.431Å, Ge = 5.658Å) [1]
- High mobility film from high Ge content in single crystal SiGe film [2]
- The thermal conductivity of SiGe lower by phonon-scattering at the stacking fault and twin boundary

NA LaRC discovered single crystal SiGe film on sapphire substrate

- “New Super Hetero Epitaxy Approach” [3]
- Single crystal trigonal SiGe (111) film forms on trigonal sapphire (0001) substrate
- At the 890°C substrate temperature, the continuous SiGe films is formed with twin defect
- Defect-engineered SiGe for Thermoelectric application,
 - Continuous film with high Ge content for high electrical conductivity
 - Twin defect within the film for low thermal conductivity



[1] W. B. Dubbelday, J. Crystal Growth 222, 20 (2001)

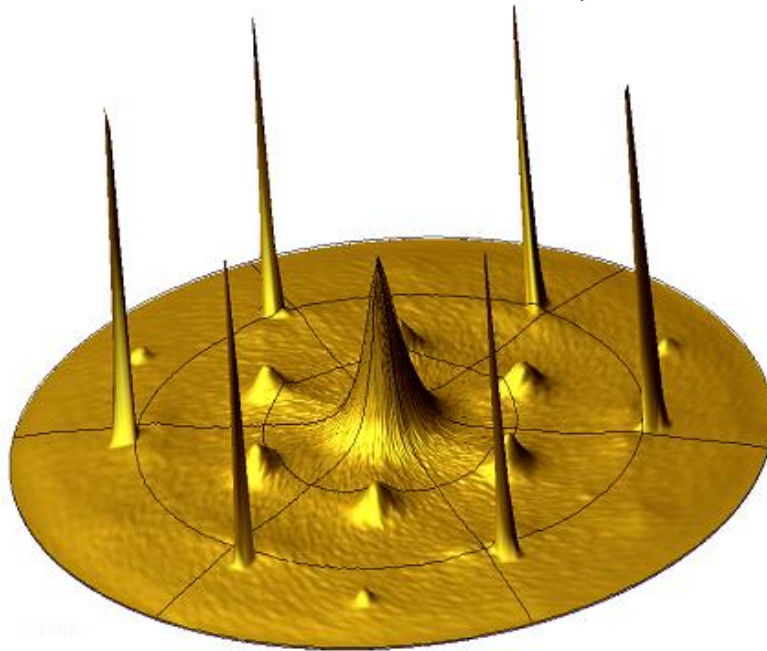
[2] D. L. Smith, Thin film deposition principles and practice, Academic press, New York (1995)

[3] Y. Park, and Sang. H. Choi, Patent application number: PCT / US2008/080411 (2008)

Strategy for Super Hetero Epitaxy



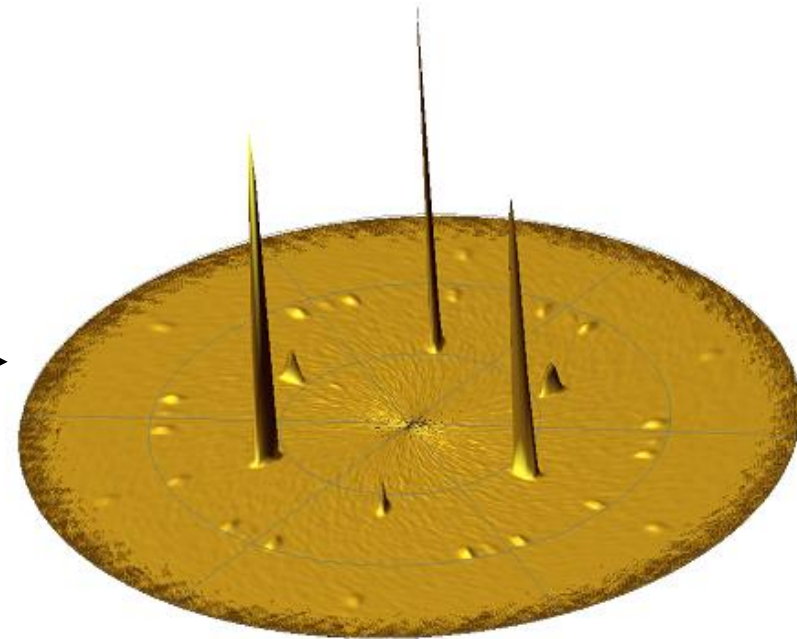
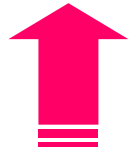
Thermal conductivity



Highly Twinned SiGe Layer

Scatter propagating phonons

Electrical conductivity



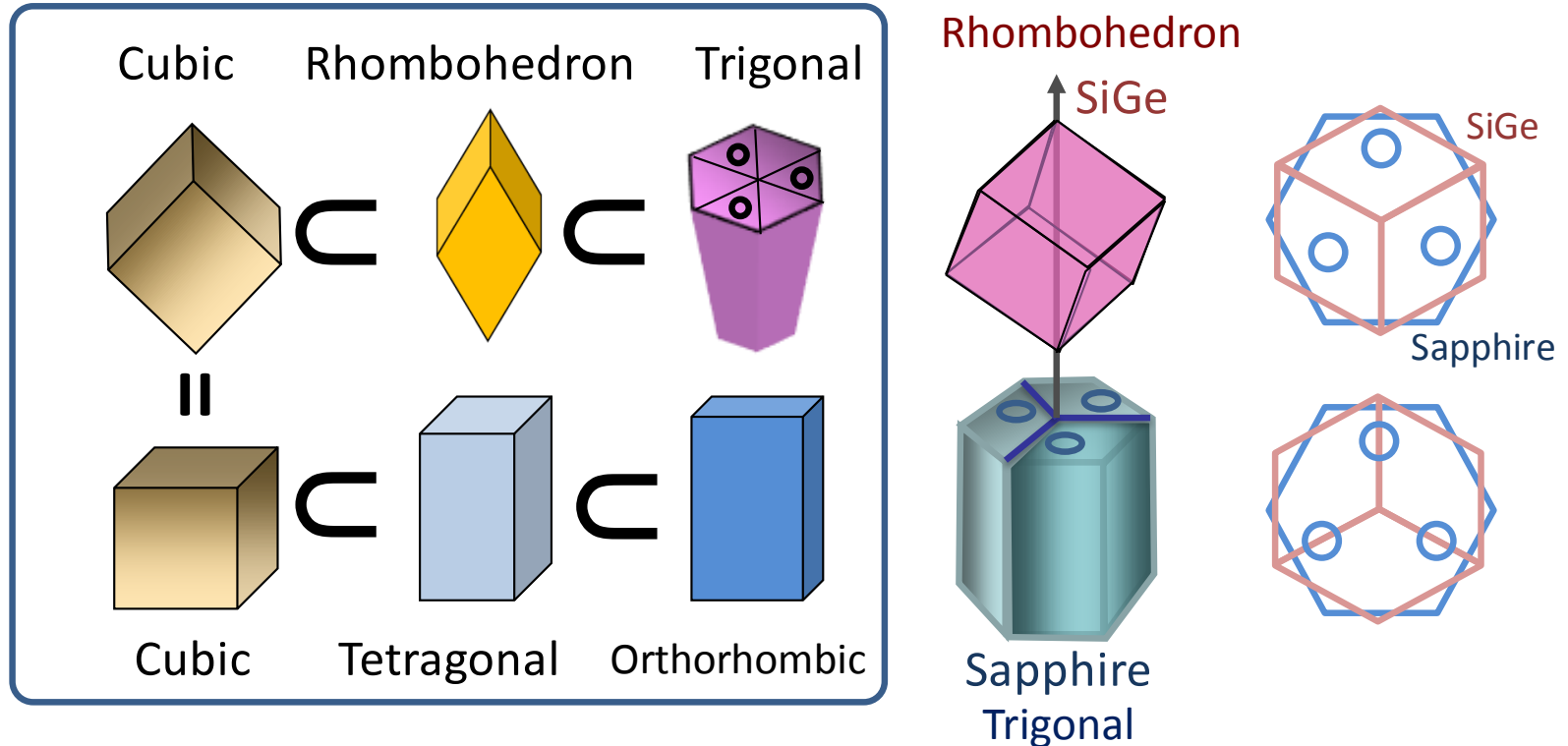
Single-Crystalline SiGe Layer

High charge carrier mobility

Material Design

{220} Pole-figures of [111]-oriented SiGe on Sapphire Substrate

New Super Hetero Epitaxial Approach

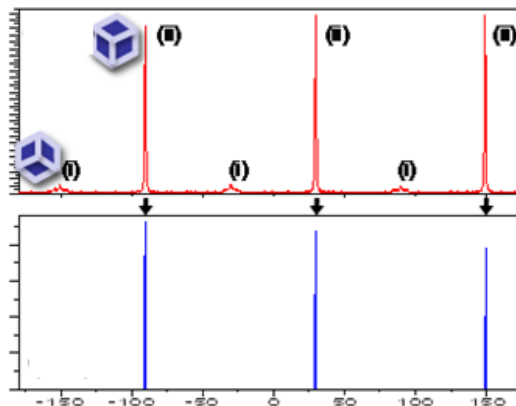
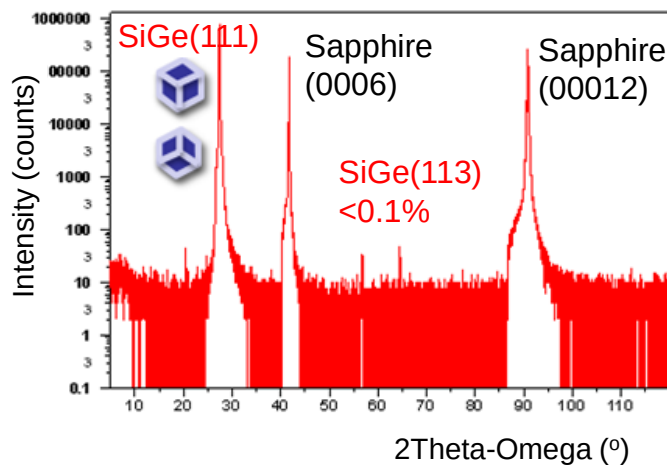


- Cubic crystal belongs to the trigonal crystal group by the symmetry.
- A fundamental cross-structural epitaxy can be established beyond conventional hetero epitaxy, dissimilar materials with the same crystal structure and similar lattice constants.
- This epitaxy is that two crystal structures which are twin to each other can be formed.

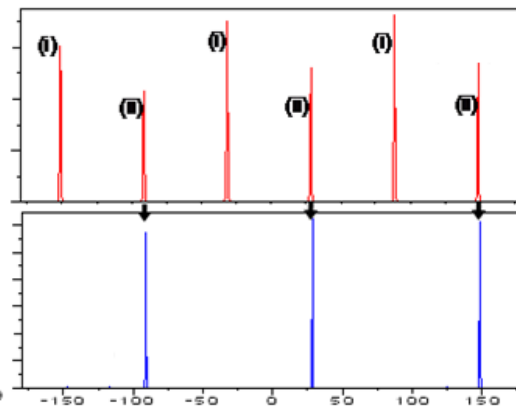
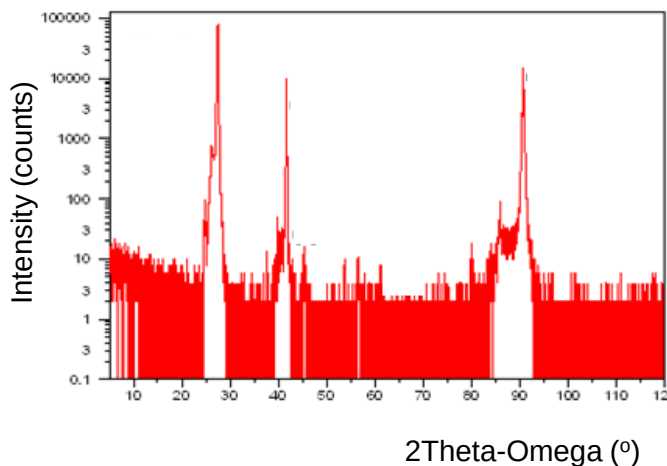
Confirmation of SiGe Orientation



2Theta-Omega Normal Scan Phi-scan of SiGe (440) Identifies Two Crystals



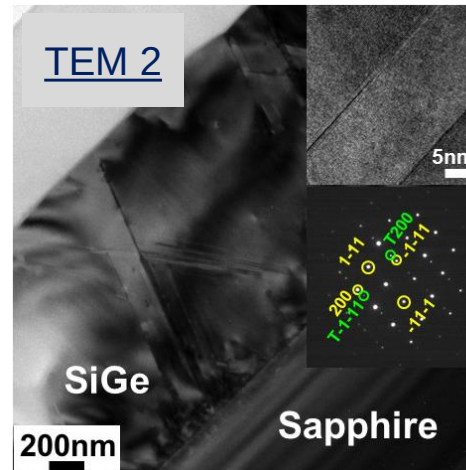
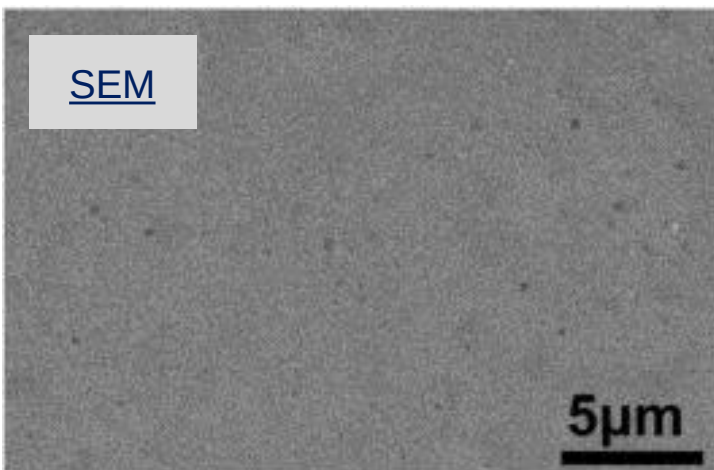
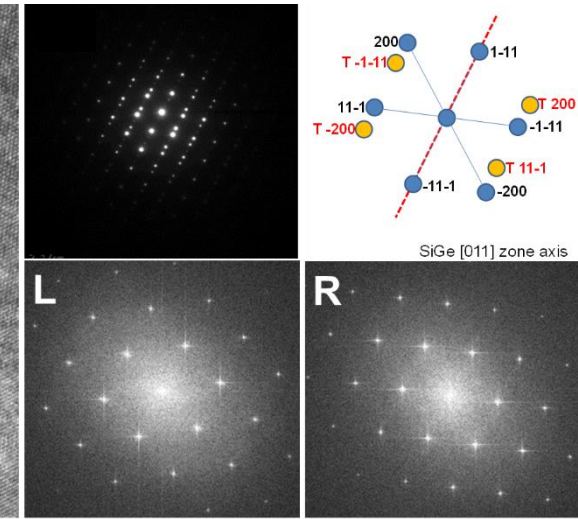
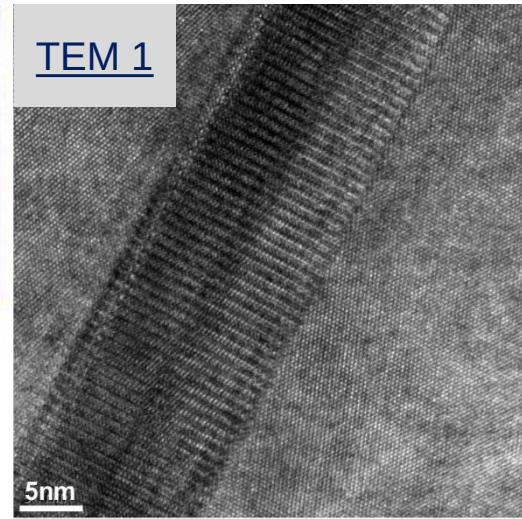
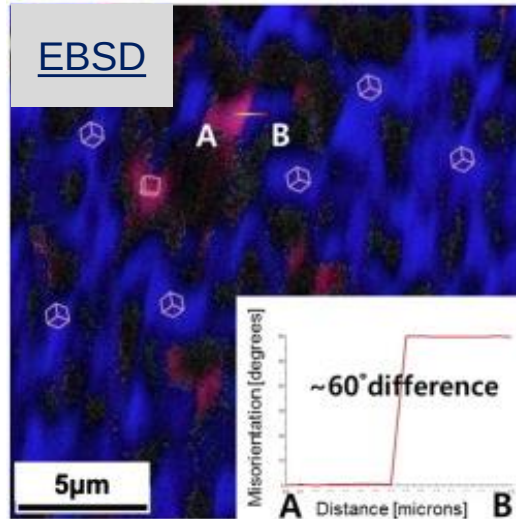
Single 99%: twin 1%



Single 40%: twin 40%

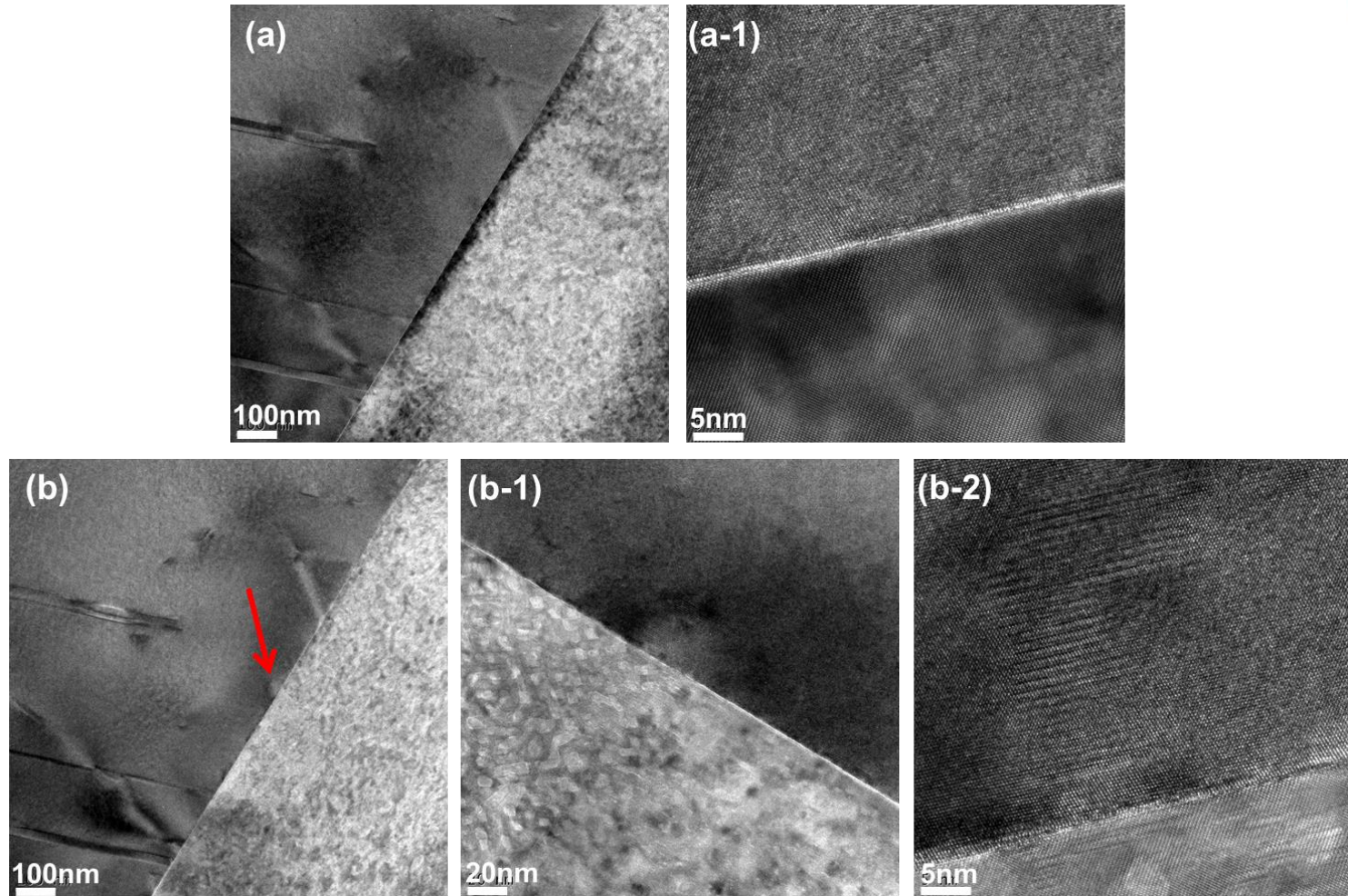
- 2Theta-Omega XRD Scand to measure the integral density and spatial distribution of twin defects in SiGe layer on trigonal sapphire (0001) substrate
- Single (i) and twin (ii) ratio was confirmed from untitled asymmetric phi-scan of SiGe {440} peaks

Continuous SiGe film with 60° twins and stacking faults



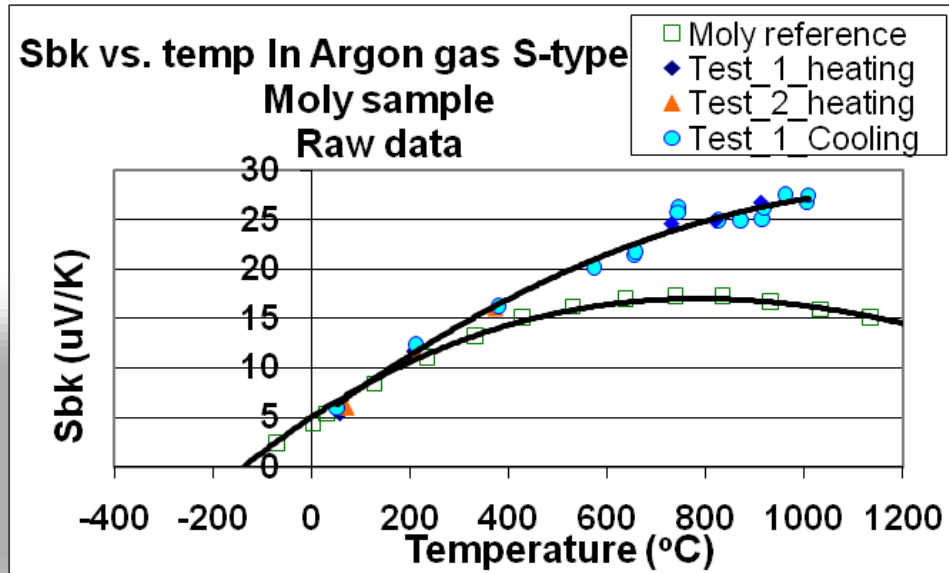
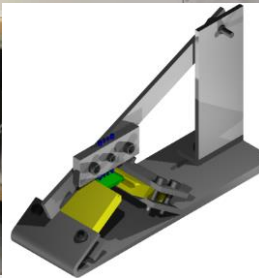
- SEM: Continuous SiGe film morphology
- EBSD and TEM 1: Continuous SiGe film with 60° twin relationship boundary
- TEM 2: Continuous SiGe film with stacking faults

Stacking fault engineer for phonon scattering



- The continuous SiGe film with high σ then control the amount of twins or dislocations through ex-situ E-beam irradiation
- Cross-sectional TEM images of the same site of a SiGe film (a) before and (b) after E-beam irradiation. The stacking faults were formed by the E-beam at the site marked with an arrow.

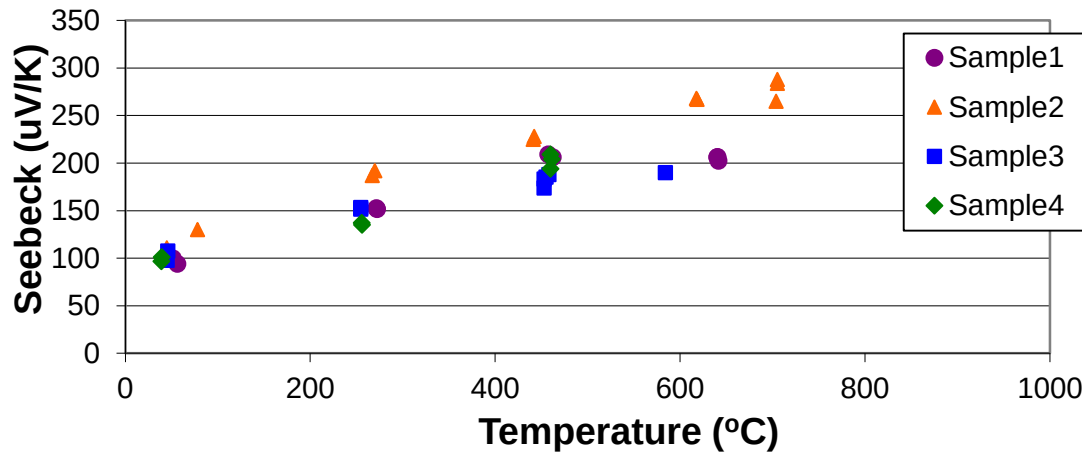
TE Characterization system



- In-house built system with vacuum / temperature control oven, infrared pulsed laser system, LabVIEW graphical user interface
- Measure Seebeck coefficient, electrical conductivity, and thermal diffusivity measurement simultaneously
- Manufacture the sample holder for thin film test
- The correction factor is derived from standard samples test
$$y_{\text{cor}} = -3.945E - 9 \cdot x^3 + 1.1039E - 5 \cdot x^2 + 0.00428 \cdot x - 0.5843$$



Figure of Merit



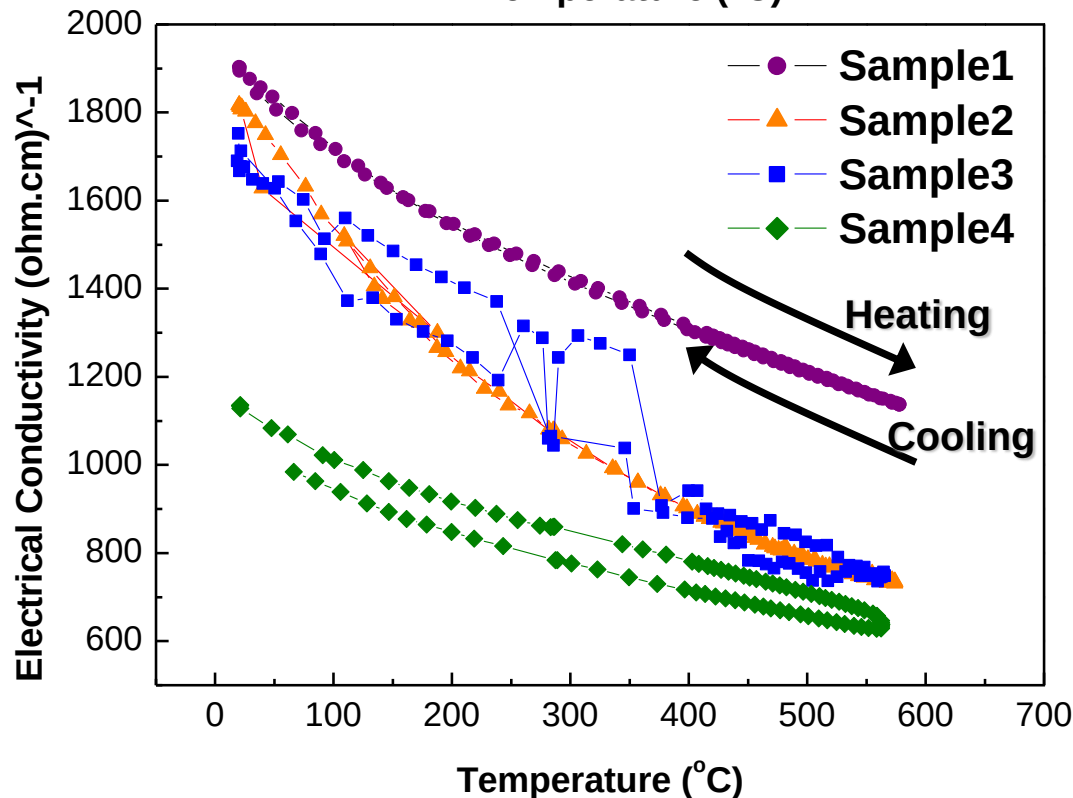
Single ratio : Twin ratio

Sample1 (99:1)

Sample2 (93:7)

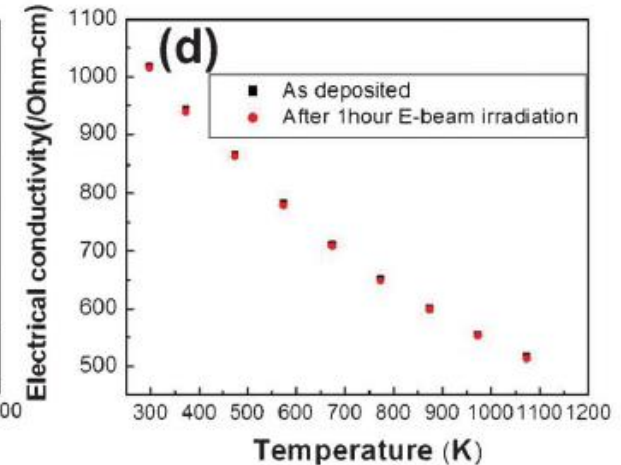
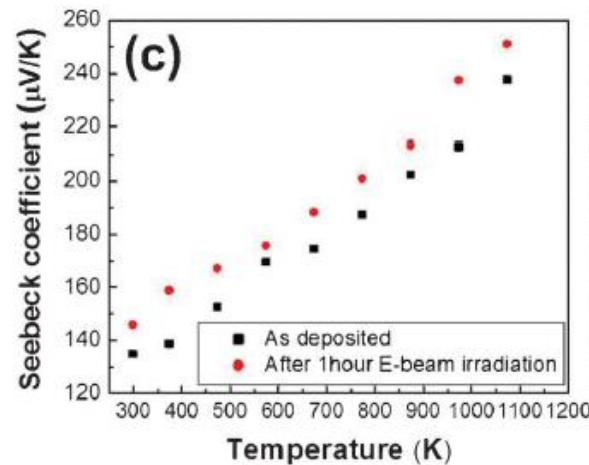
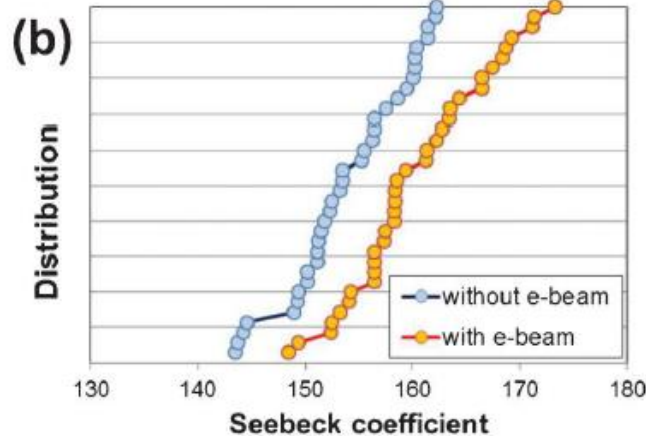
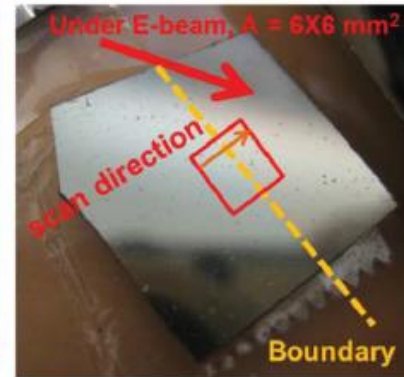
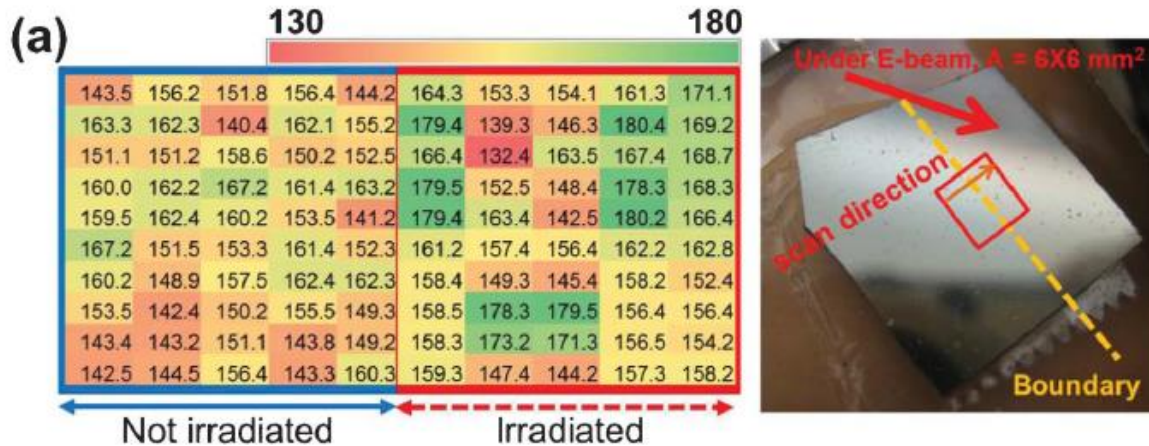
Sample3 (82:18)

Sample4 (60:40)



- Thermal diffusivity is hard to measure because the SiGe layer is grown on the sapphire which has very high thermal conductivity.
- A post-processing to remove the sapphire wafer is required for the evaluation of the characteristics.

Scanning Seebeck coefficient



- (a) Electron beam exposure on a half surface of the SiGe film
- (b) High Seebeck coefficient on the E-beam exposed area
- (c) High Seebeck coefficient from the dislocation scattering with increasing the entropy of randomness \ associated with the charge carrier flow within the system
- (d) The temperature dependency of the electrical conductivity

Summary



Summary

- Defect-Engineered SiGe is beneficial for TE from high σ (high mobility) and low k (phonon scattering)
- The rhombohedral hetero structure epitaxy is established
- A highly [111]- oriented SiGe layer of the c-plane sapphire with twinned phase is fabricated
- The more stacking fault is generated from E-beam irradiation on SiGe film
- A thin film TE measurement system that measure Seebeck coefficient, electrical conductivity, and thermal diffusivity at temperature up to 1000K has been demonstrated
- High electrical conductivity and increased Seebeck coefficient from stacking fault engineered SiGe film
- Thermal diffusivity is challenge to measure because the SiGe layer is grown on the sapphire which has very high thermal conductivity.

Supported

- NASA, DOT-FHWA (Department of Transportation-Federal Highway Administration)