Optical Characterization of Group-IV Semiconductor alloys Using Spectroscopic Ellipsometry and High Resolution X-ray Diffraction

Ph.D. Dissertation Defense

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April 3, 2017

AFOSR: FA9550-13-1-0022

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2009	B.S. (Engineering Physics)	University of Colombo, Sri Lanka
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Publications and Conference Proceedings

- **N. S. Fernando**, T.N. Nunley, A. Ghosh, C.M. Nelson, J. Cooke, A. A. Medina, C. Xu, J. Menendez, J. Kouvetakis, S. Zollner, *Temperature dependence of the interband critical points of bulk Ge and strained Ge on Si*, Appl. Surf. Sci., **XX**, XXXX (2016). (in press)
- Ryan Hickey, **Nalin Fernando**, John Hart, Ramsey Hazbun, Stefan Zollner and James Kolodzey, *Properties of pseudomorphic and relaxed Germanium*$_{1-x}$*Tin*$_x$ *alloys with Tin Contents up to 18.5 Percent grown by MBE,* J. Vac. Sci. Technol. B **35**, 021205 (2017).
- T.N. Nunley, **N.S. Fernando**, N. Samarasingha, J.M. Moya, C.M. Nelson, A.A. Medina, S. Zollner, *Optical constants of germanium and thermally grown germanium dioxide from 0.5 to 6.6 eV via a multi-sample ellipsometry investigation,* J. Vac. Sci. Technol. B **34**, 061205 (2016).
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- C. Xu, **N.S. Fernando**, S. Zollner, J. Kouvetakis, and J. Menéndez, *Observation of Fermi-level singularities in the optical dielectric function of highly doped n-type Ge***,** Phys. Rev. Lett. (submitted November 2016).
- **N.S. Fernando**, R. Hickey, J. Hart, D. Zhang, R. Hazbun, J. Kolodzey, and S. Zollner, *Strain dependence of the band structure and optical properties of pseudomorphic* $Ge_{1-x-y}Si_xSn_y$ *on Ge,* J. Vac. Sci. Technol. B (in preparation).
- **N.S. Fernando**, J. Hart, D. Zhang, R. Hickey, R. Hazbun, J. Kolodzey, and S. Zollner, *Band structure and optical properties of pseudomorphic* $Ge_{1-x-y}Si_xSn_y$ *on Ge*, IEEE Summer Topicals Conference on Emerging Technology for Integrated Photonics, July 2016, Newport Beach, CA.
- T.N. Nunley, **N.S. Fernando**, N. Samarasingha, J.M. Moya, C.M. Nelson, A.A. Medina, S. Zollner, *Precise optical constants of Ge and GeO2 from 0.5 to 6.6 eV***,** IEEE Summer Topicals Conference on Emerging Technology for Integrated Photonics, July 2016, Newport Beach, CA.

Conference Presentation

- N. Fernando, R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodezy, and S. Zollner, Optical properties *of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge (poster),* International Conference on Frontiers of Characterization and Metrology for Nanoelectronics (FCMN), Monterey, CA, 21-23 March , 2017.
- N. Fernando, R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodezy, and S. Zollner, *Effects of composition and strain on band gaps of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge*, AVS 63rd International Symposium, Nashville, TN, 6-11 November 2016.
- N. Fernando, S. Zollner, R. Hickey, J. Hart, D. Zhang, R. Hazbun, and J. Kolodzey, *Band gap engineering of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ alloys on Ge for photonic applications*, APS Four Corners Section Meeting, Las Cruces, NM, 21-22 October 2016.
- N.S. Fernando, J. Hart, D. Zhang, R. Hickey, R. Hazbun, J. Kolodzey, and S. Zollner, *Band structure and optical properties of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge*, IEEE Summer Topicals Conference on Emerging Technology for Integrated Photonics, Newport Beach, CA, 11-13 July 2016.
- N.S. Fernando, R. Hickey, J. Hart, R. Hazbun, D. Zhang, J. Kolodzey, and S. Zollner, *Band structure of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge*, AVS 2016 New Mexico Symposium, Albuquerque, NM, 24 May 2016.
- N. Fernando, J. Moya, S. Zollner, J. Hart, D. Zhang, R. Hickey, R. Hazbun, and J. Kolodzey, *Strain dependence of the band structure and critical points of pseudomorphic $Ge_{1-y}Sn_y$ alloys on Ge*, APS Four Corners Section Meeting, Tempe, AZ,16 October 2015.
- N. Fernando, T. Nunley, S. Zollner, D. Zhang, R. Hickey, J. Kolodzey, *Compositional and strain dependence of the band gaps of pseudomorphic $Ge_{1-y}Sn_y$ alloys on Ge*, AVS 2015 New Mexico Symposium, Albuquerque, NM, 19 May 2015.
- N. Fernando, T.N. Nunley, S. Zollner, S. Xu, J. Menendez, and J. Kouvetakis*, Temperature dependent band gaps of GeSiSn alloys grown on Ge buffered Si substrates*, American Physical Society March meeting, San Antonio, TX, March 2-6, 2015.
- N. Fernando, A. Ghosh, C. Nelson, A. Medina, S. Chi Xu, J. Menendez, J. Kouvetakis, S. Zollner, *Experimental and Theoretical Investigation of Critical Point Energy Shift of Ge Films Grown on Si (100) Substrate due to Strain*, American Physical Society Four Corners Section Meeting, Denver, CO, October 18-19 2013.
- N. Fernando, A. Ghosh, C.M. Nelson, A.A. Medina, S.C. Xu, J. Menendez, J. Kouvetakis, and S. Zollner, *Dynamic Strain Measurements of Ge on Si using Spectroscopic Ellipsometry*, Rio Grande Symposium, Albuquerque, NM, 07 October 2013.
- Nalin Fernando, Tyne Richele Johns, Yue Qi, Chang H. Kim, Abhaya Datye and Boris Kiefer, *Sintering of Pd_n/Pt_n (n=1, 9) Monometallic Clusters on γ-Al_2O_3 (100) Surfaces (poster),* North American Catalysis Society (NAM) meeting, Louisville KY, 2-7 June 2013.
- Nalin Fernando, Tyne Richele Johns, Yue Qi, Chang H. Kim, Abhaya Datye and Boris Kiefer, *A DFT Study of the Interaction of Monometallic Pd_n/Pt_n (n=1, 9) Clusters with γ-Al_2O_3 (100) Surfaces,* American Physical Society March meeting, Baltimore, MD, 18-22 March, 2013.
- Nalin Fernando, Tyne Richele Johns, Yue Qi, Chang H. Kim, Abhaya Datye and Boris Kiefer, *Exploration of Bimetallic Alloys for the Design of Efficient Low Temperature Car Exhaust Catalysts,* Las Cruces Museum of Natural History, Mesilla Valley Mall, NM, June-2012.

Outline

☐ Introduction

- Role of germanium (Ge) in optoelectronic industry
- Band gap engineering of Ge for photonic applications
- $Ge_{1-x-y}Si_xSn_y$ alloys
- Strain, Composition, and temperature dependence

☐ Sample preparation and characterization

- MBE and CVD growth at UD and ASU
- Spectroscopic ellipsometry and high resolution X-ray diffraction
- X-ray reflectivity and atomic force microscopy

☐ Temperature dependent optical properties of Ge

☐ Optical properties of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on Ge

☐ Effects of relaxation of $Ge_{1-y}Sn_y$ on Ge

☐ Conclusion

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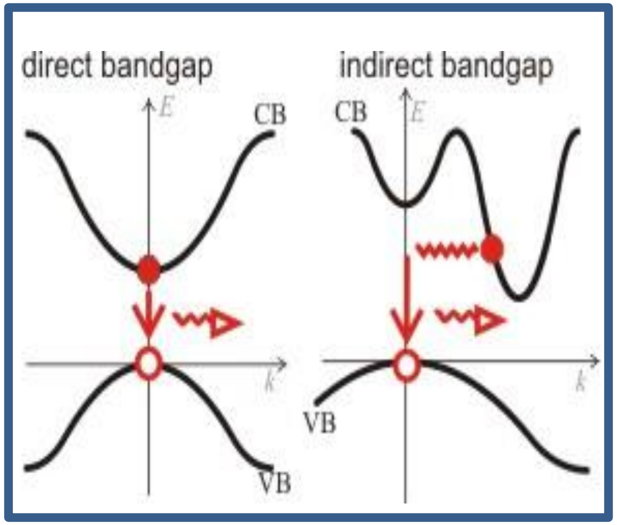
Germanium

- Most thoroughly studied semiconductor.
- Many applications in the field of engineering.
  Eg: High frequency transistors, Solar cells.

- **Ge → indirect band gap material.**

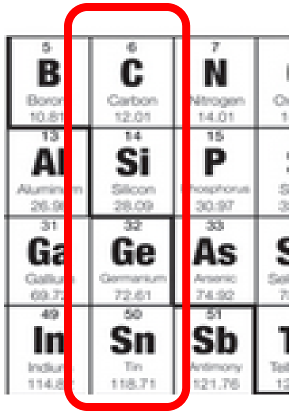


http://www.livescience.com
http://images-of-elements.com
http://nanotech.fzu.cz

- Direct band gap → efficiency of the recombination process is high.
  Used to make photonic devices such as LEDs, semiconductor lasers.
- Indirect band gap → requires an interaction with a phonon or defects.
  Very inefficient.

- **Limited the large scale integration of photonic devices on Si.**

Group-IV alloys for Photonic Devices



- The band structure of Ge is a strong function of strain and alloy composition.
- Ge becomes a direct band gap material at ~2% tensile strain.

Kurdi *et al*., J. Appl. Phys. **107**, 013710 (2010).

- Successful use of group III-V alloys in photonic devices paved the way to think of C-Si-Ge-Sn related alloys.
- C→ Large lattice mismatch (~40%), low solubility (<1%), and perturbation induced in the band structure restricted applications.
- Relaxed $\mathrm{Ge_{1-y}Sn_y}$ alloys become direct at ~6-9% Sn.

He *et al*., Phys. Rev. Lett. **79**, 1937 (1997).
Mathews *et al*., Appl. Phys. Lett. **97**, 221912 (2010).

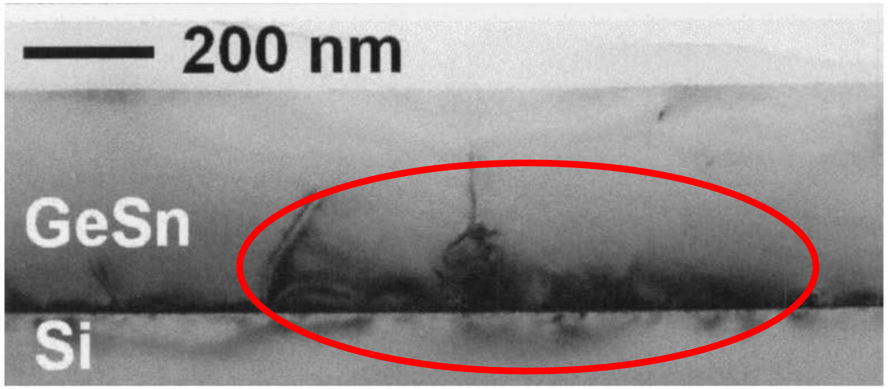
→ Possibility of widespread applications of Ge-Sn based photonic devices

$Ge_{1-y}Sn_y$ Alloys for Photonic Devices

- Lattice parameters: **a_{Sn}=6.489 Å > a_{Ge}=5.657 Å > a_{Si} =5.453 Å**

- Lattice mismatch between the substrate and the epilayer creates a strain

- **Strain is relieved by forming defects and dislocations.**

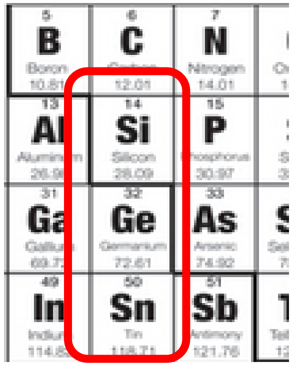


XTEM image of $Ge_{0.94}Sn_{0.06}$ on Si
Bauer *et al*., Appl. Phys. Lett. **81**, 2992 (2002)

- **Act as non radiative recombination centers.**
  → Degrade the performance of the devices.

- **Light emission is too weak for practical applications.**

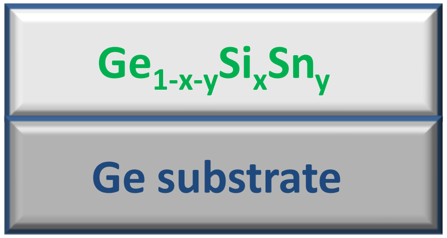
$Ge_{1-y}Si_xSn_y$ Alloys for Photonic Devices



- Incorporation of Si into $Ge_{1-y}Sn_y$ minimizes the lattice mismatch. → **$Ge_{1-x-y}Si_xSn_y$**

  Soref *et al*., J. Appl. Phys. **69**, 539 (1991).

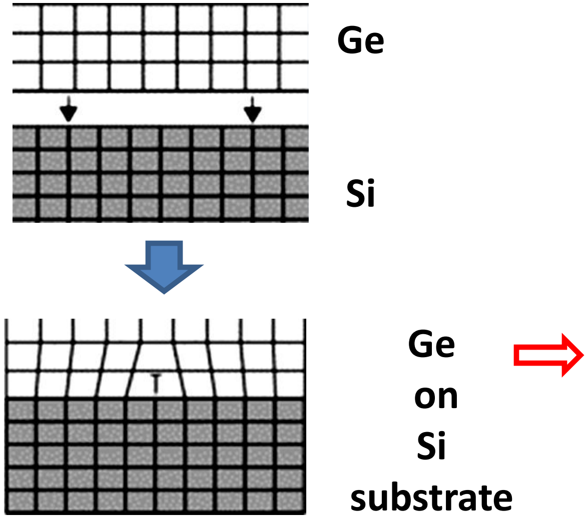
- $Ge_{1-x-y}Si_xSn_y$ allows to decouple lattice parameter and band structure.
- Allows to tune the band gap above and below Ge (0 to1 eV). →Covers a wide range of operating wavelength of devices.
- **Pseudomorphically grown $Ge_{1-x-y}Si_xSn_y$ on Ge** has low defect density and no dislocations.



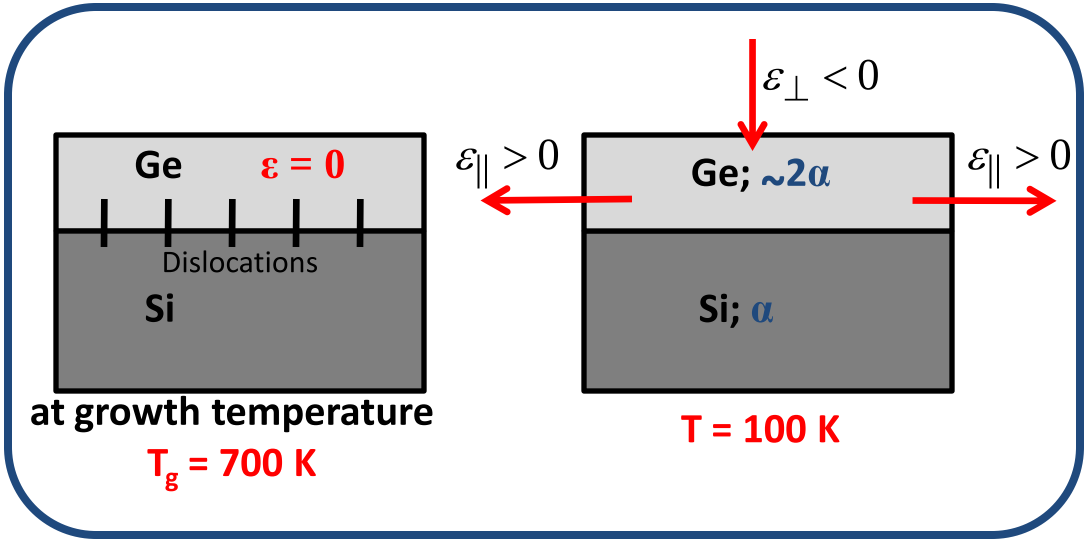
- $Ge_{1-x-y}Si_xSn_y$ may become the first direct band gap material fully integrated on Si technology.
- Temperature, strain and compositional dependence of the optical properties are critical for band gap engineering.

Controlling Strain on Ge

(a) By thermal expansion mismatch

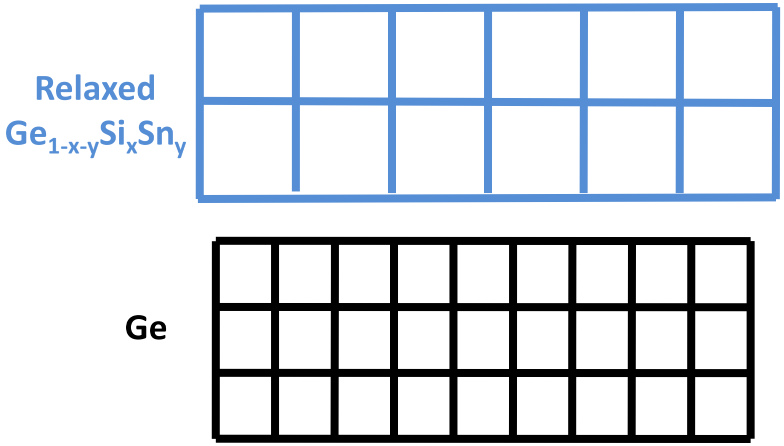


Incommensurate growth
(relaxed at growth temperature)

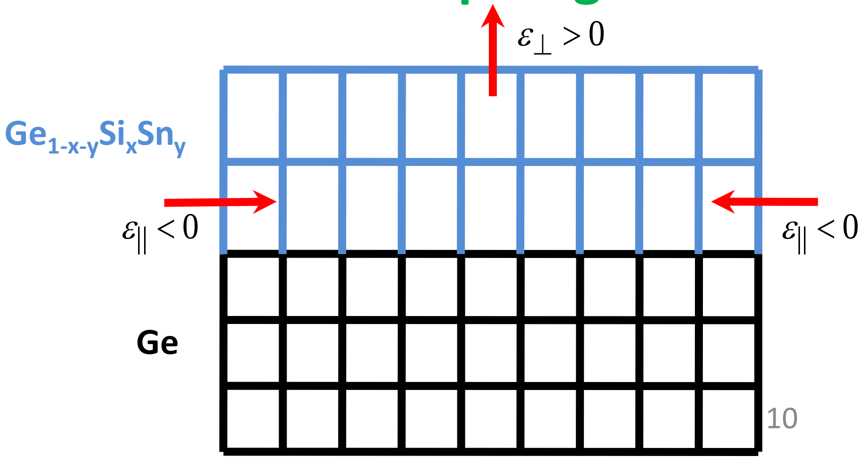


$\varepsilon_{\parallel}$: in−plane strain $\varepsilon_{\perp}$: out−of−plane strain

(b) By lattice mismatch



Pseudomorphic growth



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Sample Preparation

Ge epilayers on Si (Kouvetakis group at Arizona State Uni.)

- Ultrahigh vacuum chemical vapor deposition (UHV-CVD)
- Precursor - tetragermane (Ge_4H_{10})
- Growth temperature 350º C – 400º C
- Growth rate 17 – 30 nm/min
- Annealed in situ at 680º C for 3 min
- Thickness ~ 1500 nm

C. Xu *et al*., Semicond. Sci. Technol. **28**, 105001 (2013).

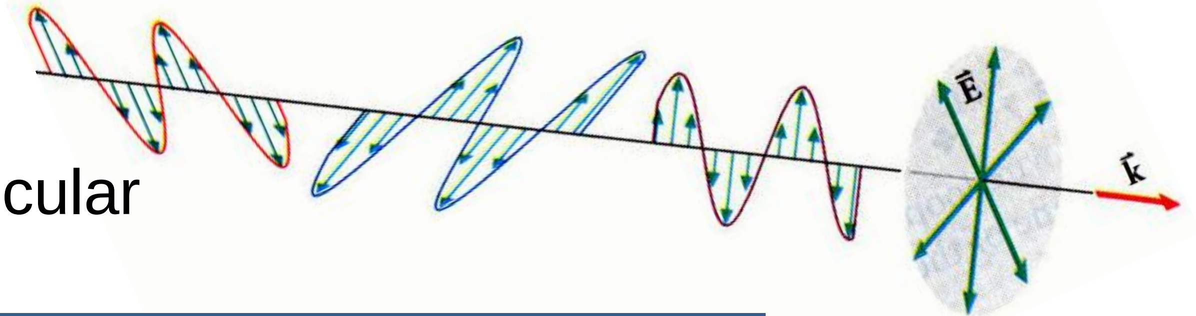
$Ge_{1-y}Sn_y$ on Ge (Kolodzey group at U. of Delaware)

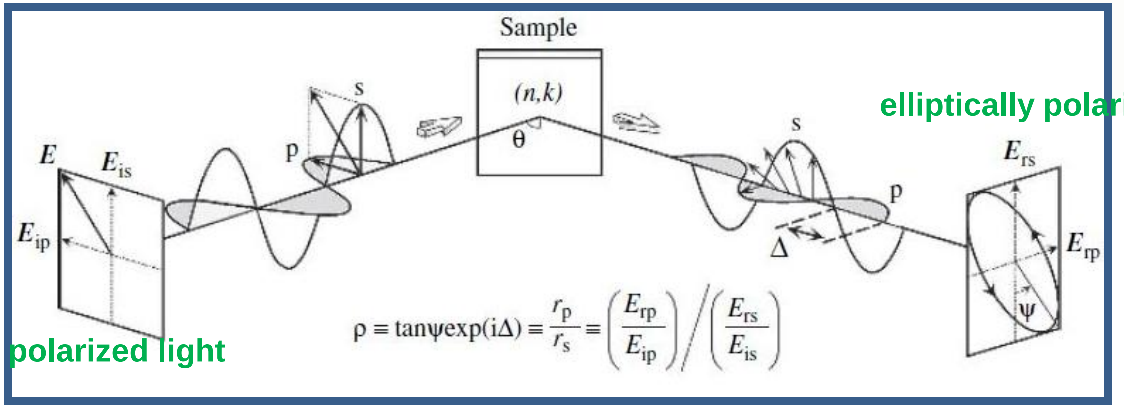
- Molecular beam epitaxy (MBE)
- EPI 620 MBE system with a base pressure of 1.3×10^{-8} Pa
- Growth temperature 150º C – 250º C
- Growth rate 0.6 – 0.7 nm/min
- Thicknesses 45 – 320 nm

R. Hickey and N. Fernando *et al*., J. Vac. Sci. Technol. B **35**, 021205 (2017).

Spectroscopic ellipsometry

- Light wave can be described as superposition of two electric field components
  s and p polarization
  p: parallel, **s**: perpendicular





$$\rho \equiv \tan\psi \exp(i\Delta) \equiv \frac{r_p}{r_s} \equiv \left(\frac{E_{rp}}{E_{ip}}\right) \Big/ \left(\frac{E_{rs}}{E_{is}}\right)$$

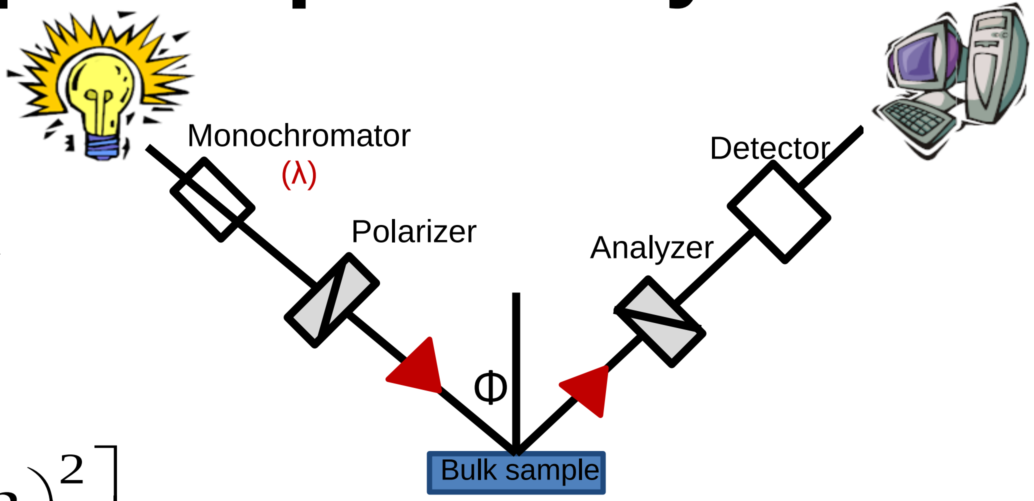
linearly polarized light

elliptically polarized light

- Spectroscopic ellipsometry measures how the polarization state of monochromatic light changes as it is reflected by a surface.

- The change in polarization state is usually expressed as an amplitude **tanψ** and a **phase** Δ (ellipsometric angles).

Spectroscopic ellipsometry



$$\rho = \frac{r_p}{r_s} = \frac{E_{rp}}{E_{ip}} \cdot \frac{E_{is}}{E_{rs}} = \tan\Psi e^{i\Delta}$$

Angle of incidence

$$\langle \tilde{n} \rangle^2 = \sin^2\phi \left[1 + \tan^2 \overset{\uparrow}{\phi} \cdot \left(\frac{1-\rho}{1+\rho} \right)^2 \right]$$

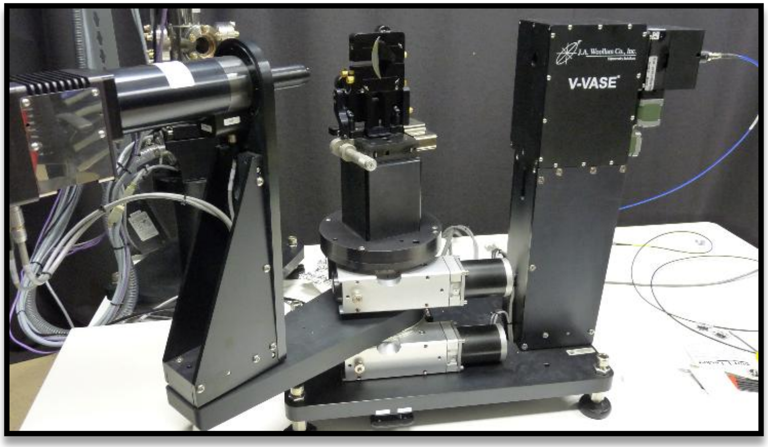
$\tilde{n} = n + ik$ Complex index of refraction

$n, k:$ Optical constants

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

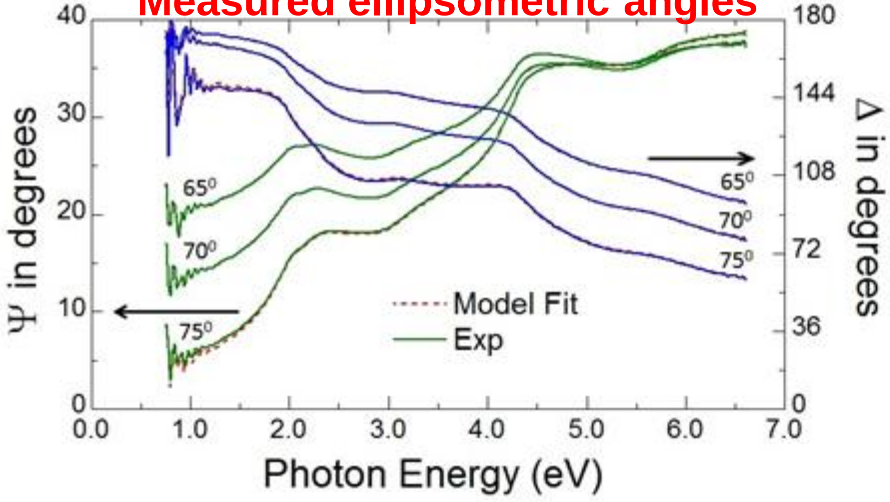


Variable **A**ngle **S**pectroscopic **E**llipsometry (**VASE**)

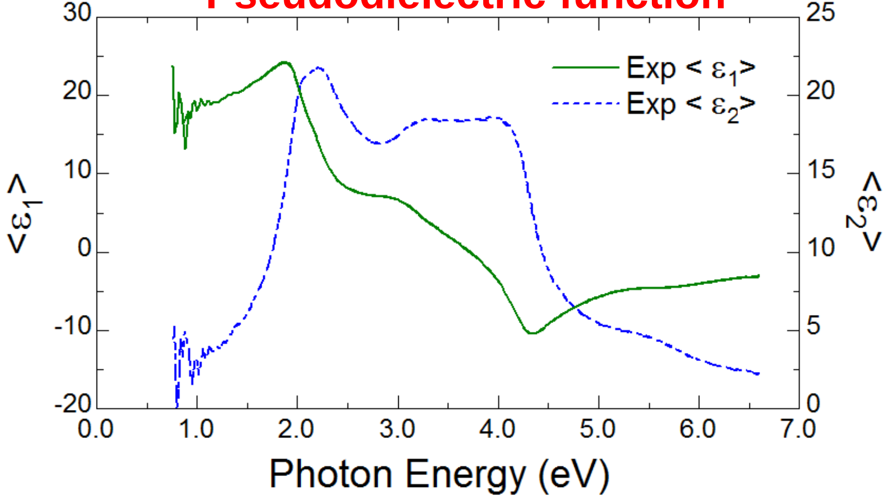
Ellipsometry Data Analysis

$$\langle \tilde{\varepsilon} \rangle = \langle \tilde{n} \rangle^2 = \sin^2\phi \left[1 + \tan^2\phi \cdot \left(\frac{1-\rho}{1+\rho} \right)^2 \right] \quad ; \; \rho = \tan\psi e^{i\Delta}$$

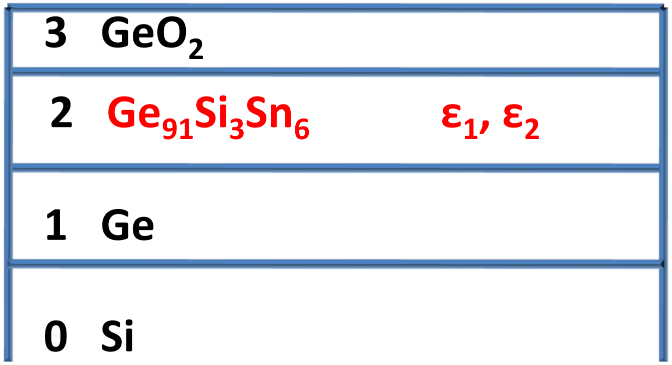
Measured ellipsometric angles



Pseudodielectric function



model fit



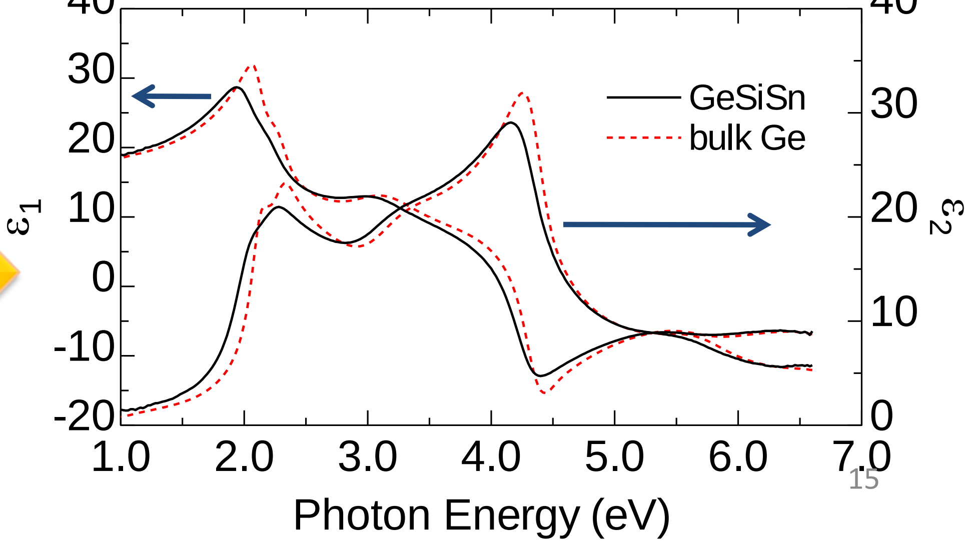
3 **GeO_2**

2 **$Ge_{91}Si_3Sn_6$** **$\varepsilon_1, \varepsilon_2$**

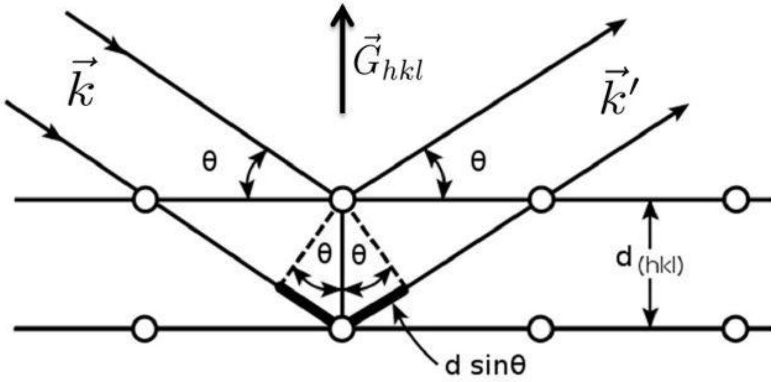
1 **Ge**

0 **Si**

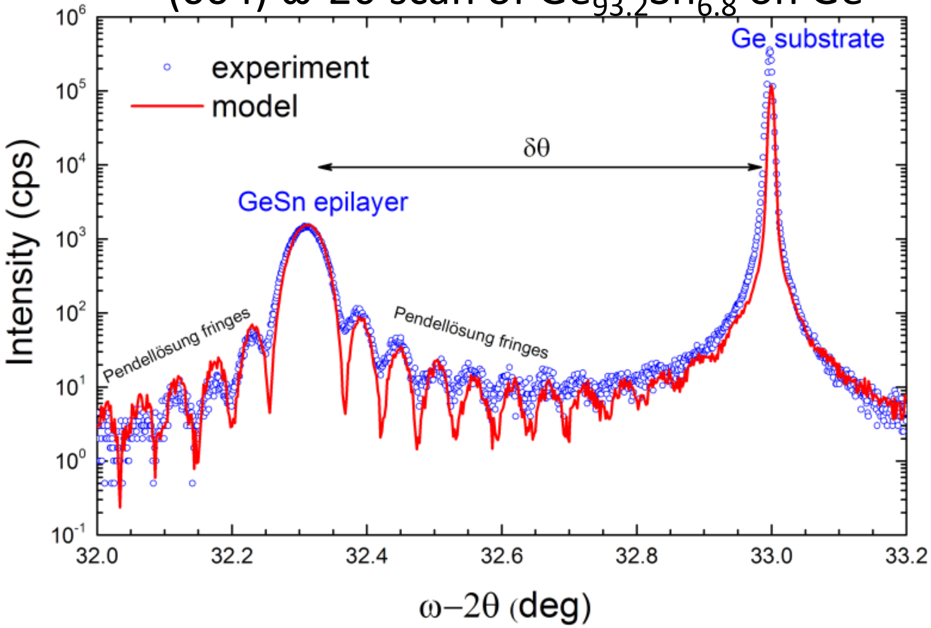
Dielectric function of $Ge_{91}Si_3Sn_6$



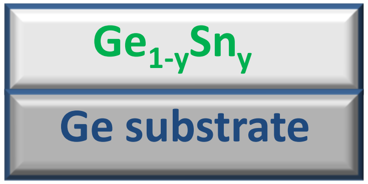
High Resolution X-ray Diffraction



(004) ω-2θ scan of $Ge_{93.2}Sn_{6.8}$ on Ge



An initial plane wave with wave vector k is irradiated on the sample surface at an angle ω (=θ) and the outgoing scattered waves k’ are analyzed under the same angle.



$$2d_{hkl}Sin\theta = n\lambda$$

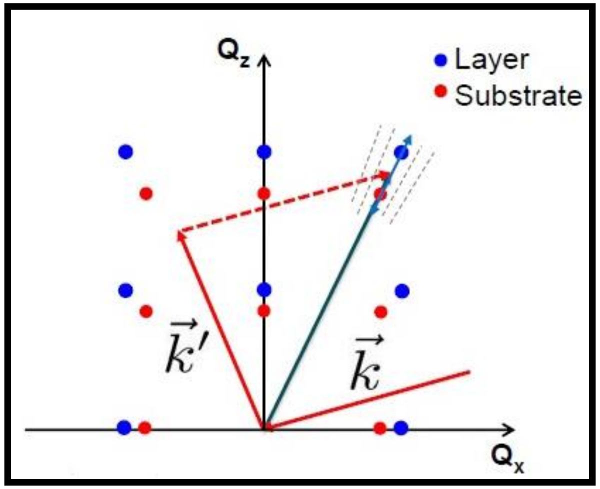
$$where\ \ d_{hkl} = a_{\perp}/\sqrt{h^2+k^2+l^2}$$

Uniform spacing between interference fringes ($\Delta\theta_t$)→ uniform thickness (t)

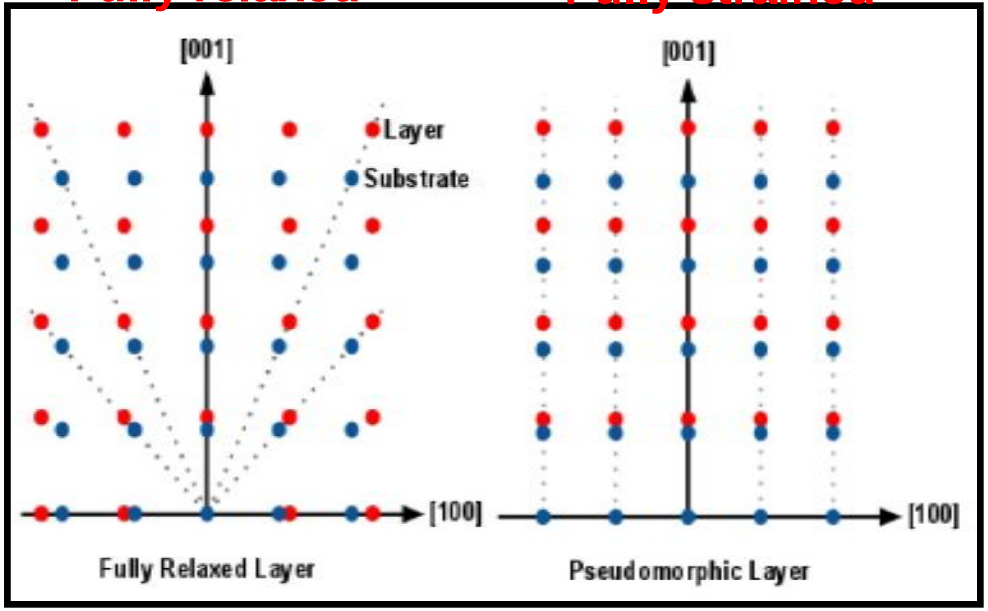
$$t = \frac{0.5\lambda}{\Delta\theta_t \cos\theta}$$

Reciprocal Space Maps (RSMs)

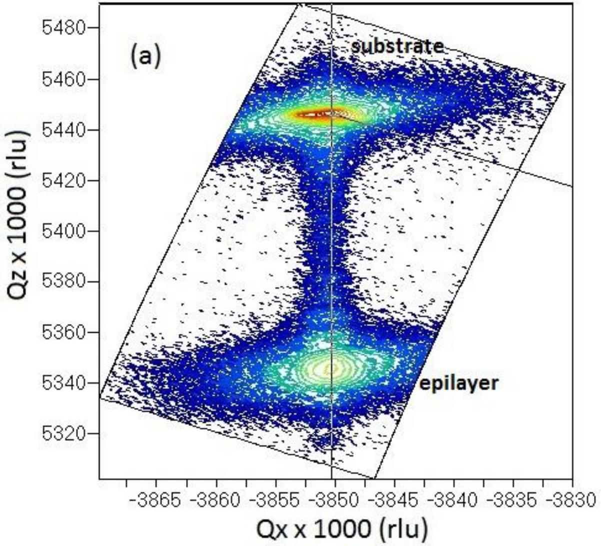
Several ω-2θ scans are performed with stepped ω to cover an area of the Bragg peaks for the epilayer and the substrate



Fully relaxed **Fully strained**



(224) RSM $Ge_{93.2}Sn_{6.8}$ on Ge



Substrate and the layer peak lie on the same reciprocal lattice vectors along the $Q_{\|}$.

→ **Fully strained alloy layer**

$$\varepsilon_{\|} = \frac{a_{\|} - a_{\perp}}{a_{\perp} + 2\frac{C_{12}}{C_{11}} a_{\|}}$$

$$a^{rel}_{Ge_{1-y}Sn_y} = \frac{a_{\|}}{\varepsilon_{\|} + 1}$$

Sn composition $\Rightarrow$ $a^{rel}_{Ge_{1-y}Sn_y} = y a_{Sn} + (1-y) a_{Ge}$

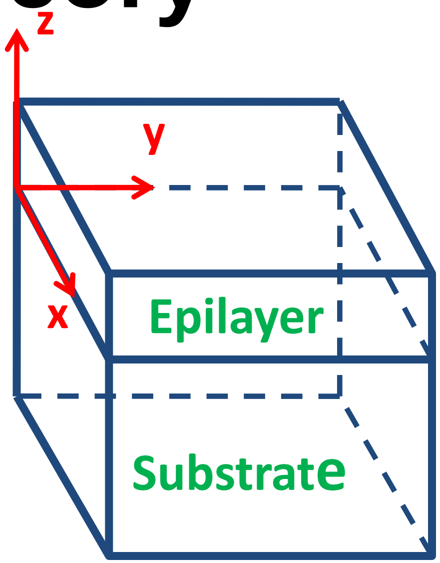
Deformation Potential Theory

- Experimental pressure dependence of the band gaps.
- Strain tensor of a material under biaxial stress:

$$\varepsilon=\begin{bmatrix}\varepsilon_{||} & 0 & 0\\ 0 & \varepsilon_{||} & 0\\ 0 & 0 & \varepsilon_{\perp}\end{bmatrix}=\varepsilon_H\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}+\varepsilon_S\begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{bmatrix}$$

$$\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_{||}$$

$$\varepsilon_{zz}=\varepsilon_{\perp}$$



- Hydrostatic strain: $\varepsilon_H=\dfrac{\varepsilon^{\perp}+2\varepsilon^{||}}{3}$ → Shifts the energy bands

$$\Delta E_H=D\frac{\Delta V}{V}=D\mathrm{Tr}(\varepsilon)=3\mathrm{D}\varepsilon_{\mathrm{H}};$$ D – hydrostatic deformation potential

$$D=\frac{\partial E}{\partial \ln V}=\frac{\partial E}{\partial P}\frac{\partial P}{\partial V}V=B\frac{\partial E}{\partial P};$$ B – bulk modulus

- Shear strain: $\varepsilon_S=\dfrac{\varepsilon^{\perp}-\varepsilon^{||}}{3}$ → Splits the bands by removing degeneracies

$$\Delta E_S=U\hat{n}[\varepsilon-\frac{1}{3}\mathrm{Tr}(\varepsilon)]\hat{n}=U\varepsilon_S\hat{n}\begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{bmatrix}\hat{n}$$

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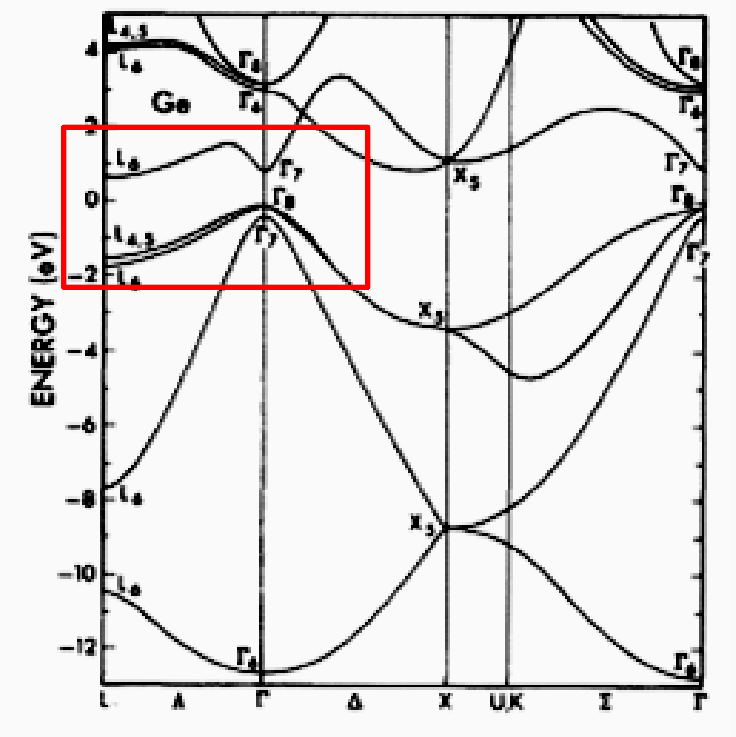
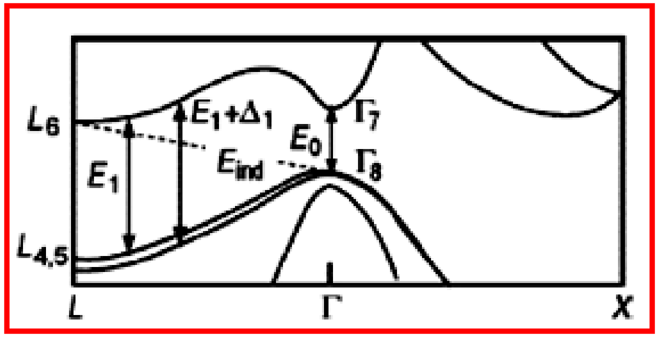
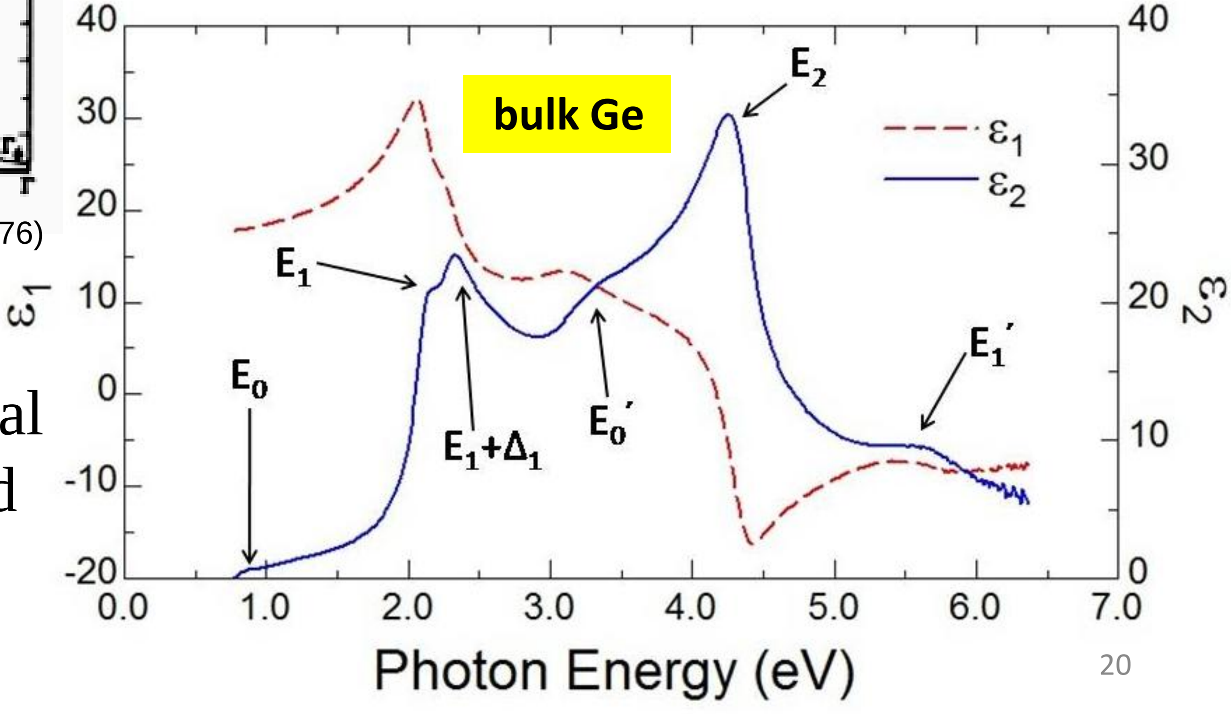
Ge Band Structure: E_1, $E_1+\Delta_1$ Critical Points



Chelikowsky *et al*., Phys. Rev. B **14**, 556 (1976)





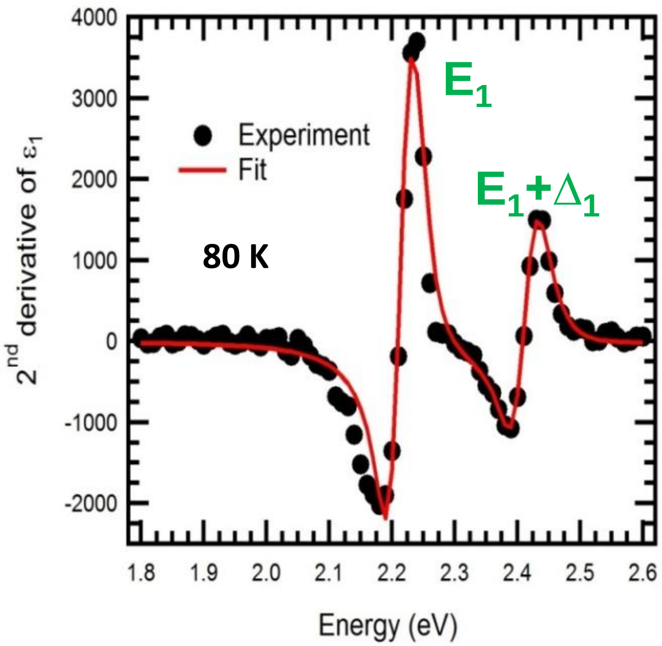
- T dependence of optical constants directly related to the T dependence of band states.

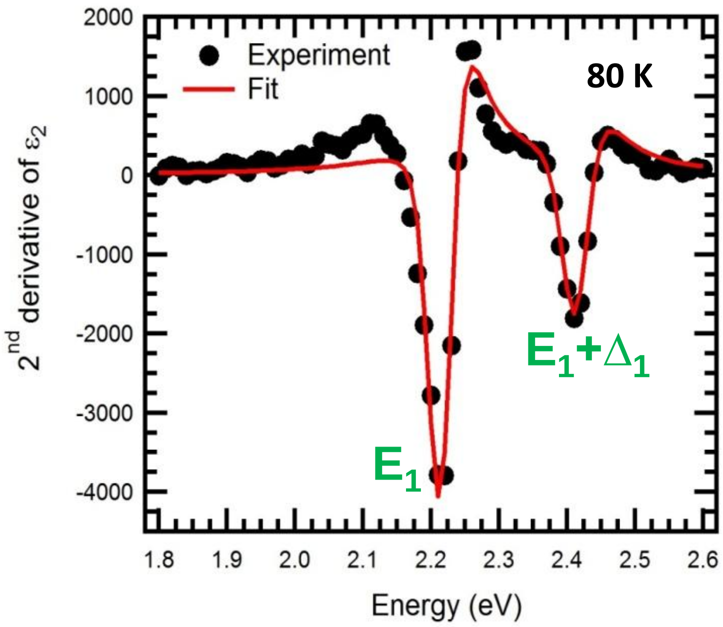
2^{nd} Derivative Analysis of ε_1 and ε_2 Near E_1 and $E_1+\Delta_1$

- Result from transitions in the Λ direction of the BZ {111}.
- E_1, $E_1+\Delta_1$: 2D critical points → $\boxed{\varepsilon \sim C - A\ln(\mathrm{E} - \hbar\omega - i\Gamma)\,\mathrm{e}^{i\varphi}}$

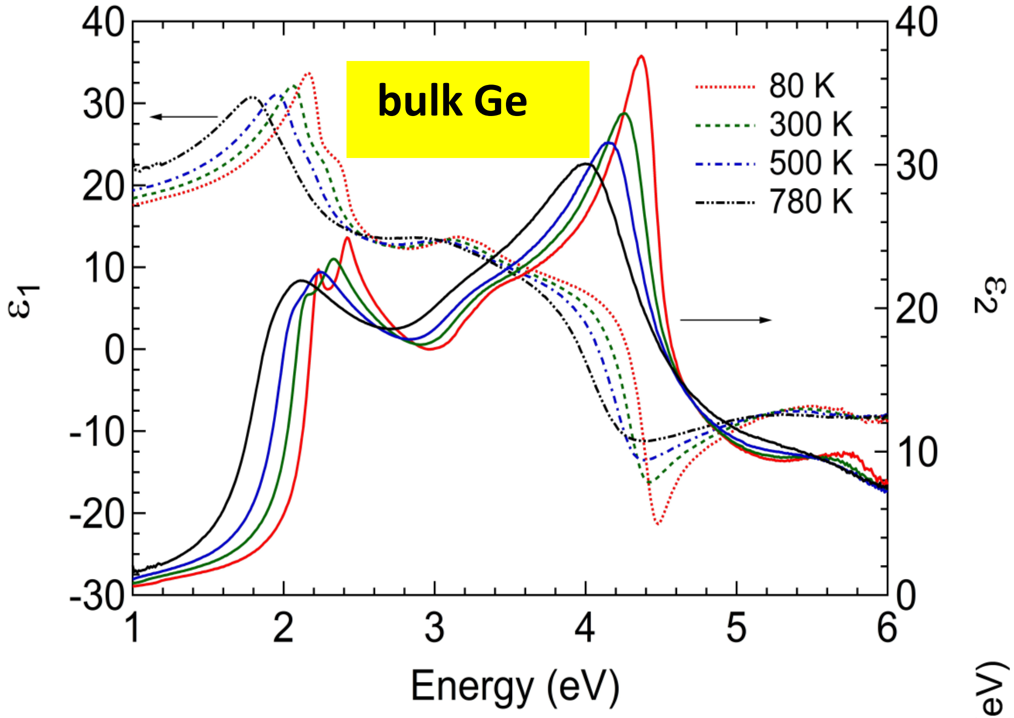
L. Viña *et al*., Phys. Rev. B **30**, 1979 (1984)

- Analysis of $d^2\varepsilon/dE^2$ → CP parameters; E- energy, A- amplitude, Γ- broadening, φ- phase

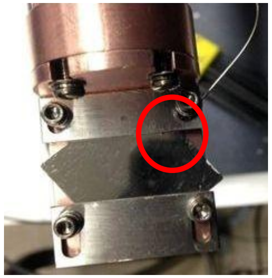




Temperature Dependent Optical Properties



- Red shifted and broadened dielectric function with increasing T.



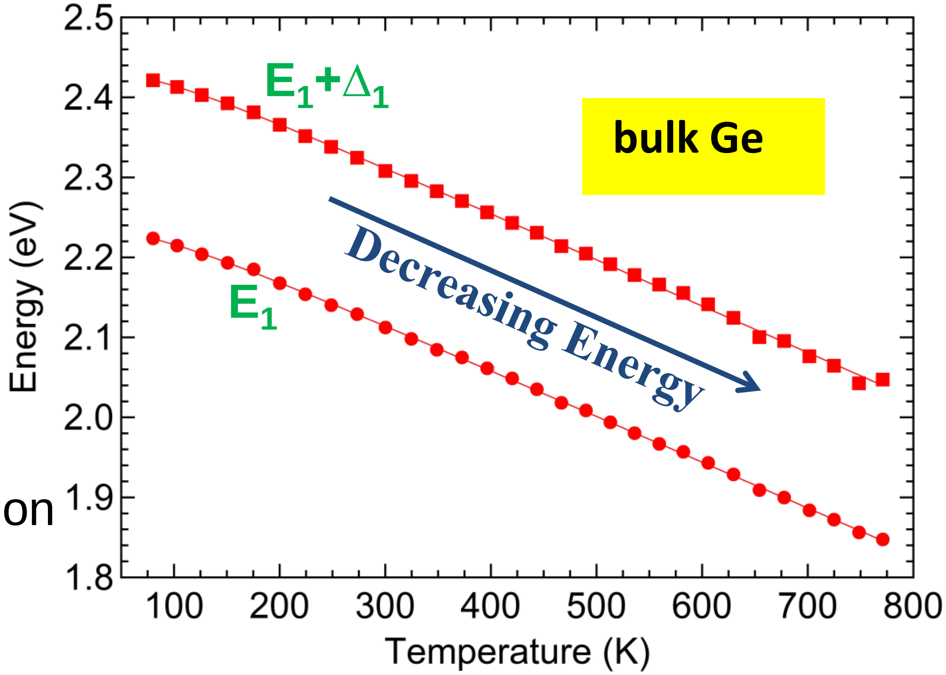
- Thermal expansion of the crystal:

$$\Delta E_{th}(T) = D\int_0^T \alpha(T')\,dT'$$

D- deformation potential, α- thermal expansion

- Electron-phonon interaction:

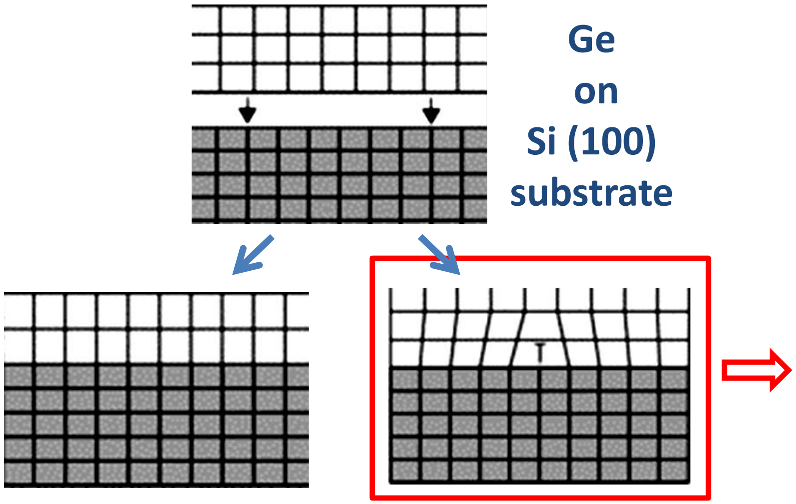
$$E_{\text{e-ph}}(T) = a' - b'\left[1 + 2/\left(e^{\theta'_B/T} - 1\right)\right]$$



$$E_{\text{total}}(T) = a - b\left[1 + 2/\left(e^{\theta_B/T} - 1\right)\right]$$

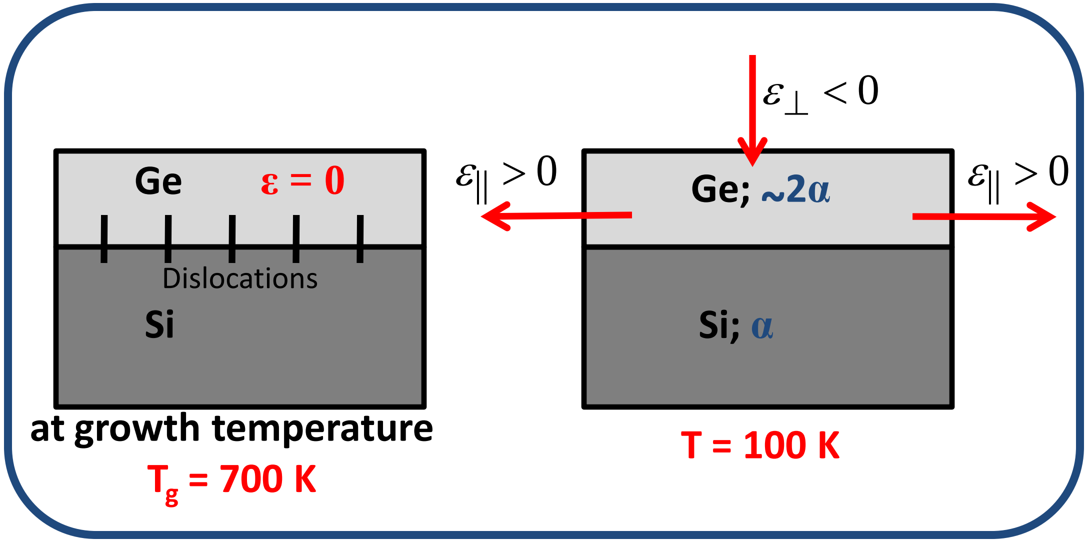
Vina *et al*., Phys. Rev. B **30**, 1979 (1984)

Ge Films on Si(100) Substrate



Commensurate growth (Pseudomorphic)

Incommensurate growth (relaxed at growth temperature)



$\varepsilon_\parallel$ in-plane strain

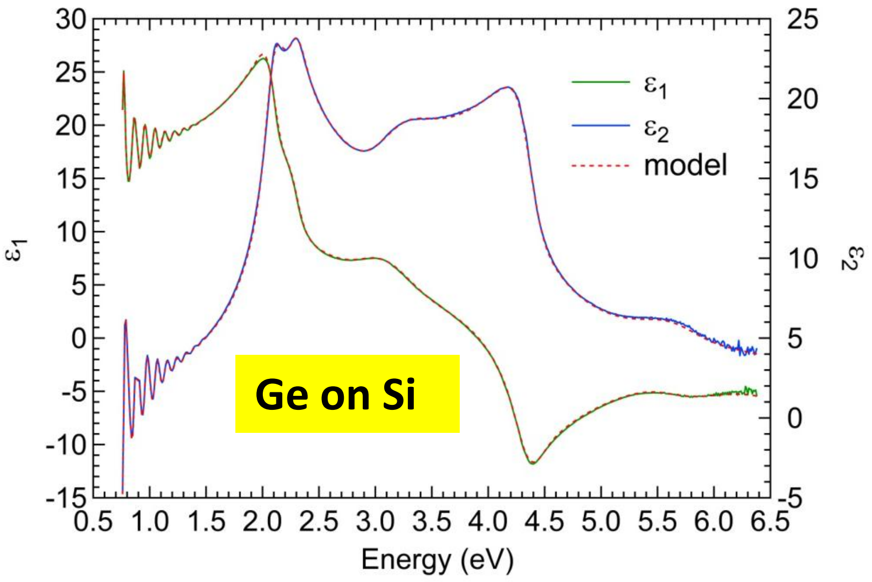
$\varepsilon_\perp$ out of plane strain

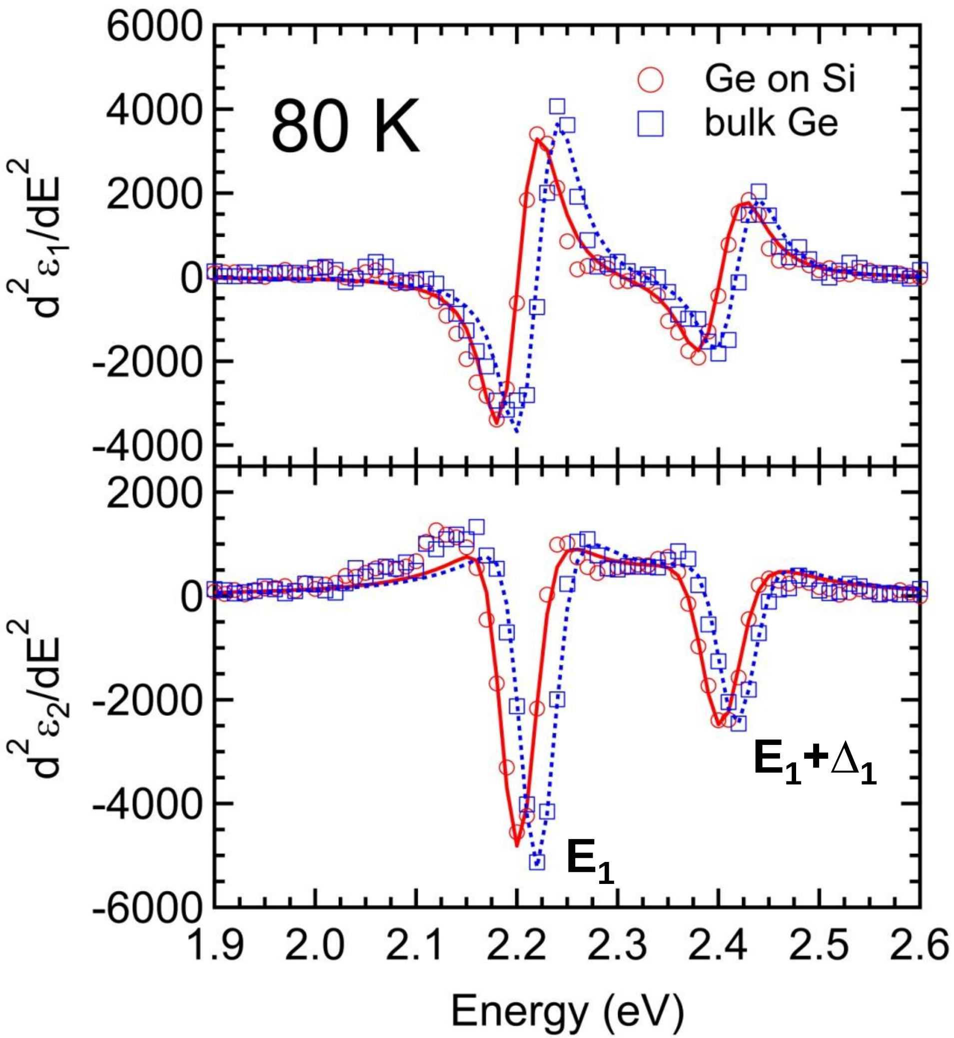
At 300 (K)	Thermal expansion coefficient α_L (K^{-1})	Lattice parameter (Å)
Ge	5.80×10^{-6}	5.6579
Si	2.56×10^{-6}	5.4310

Roucka *et al*., Phys. Rev. B **81,** 245214 (2010)

- **α_{Ge} ~$2\alpha_{Si}$: Thermal expansivity mismatch.**
- Biaxial stress upon cooling:
  →**Develop strain (ε) upon cooling**.
  →Affect the film's electronic and optical properties.
  → **Shifts E_1 and E_1+Δ_1 critical point energies**.

Temperature Dependent Dielectric Function

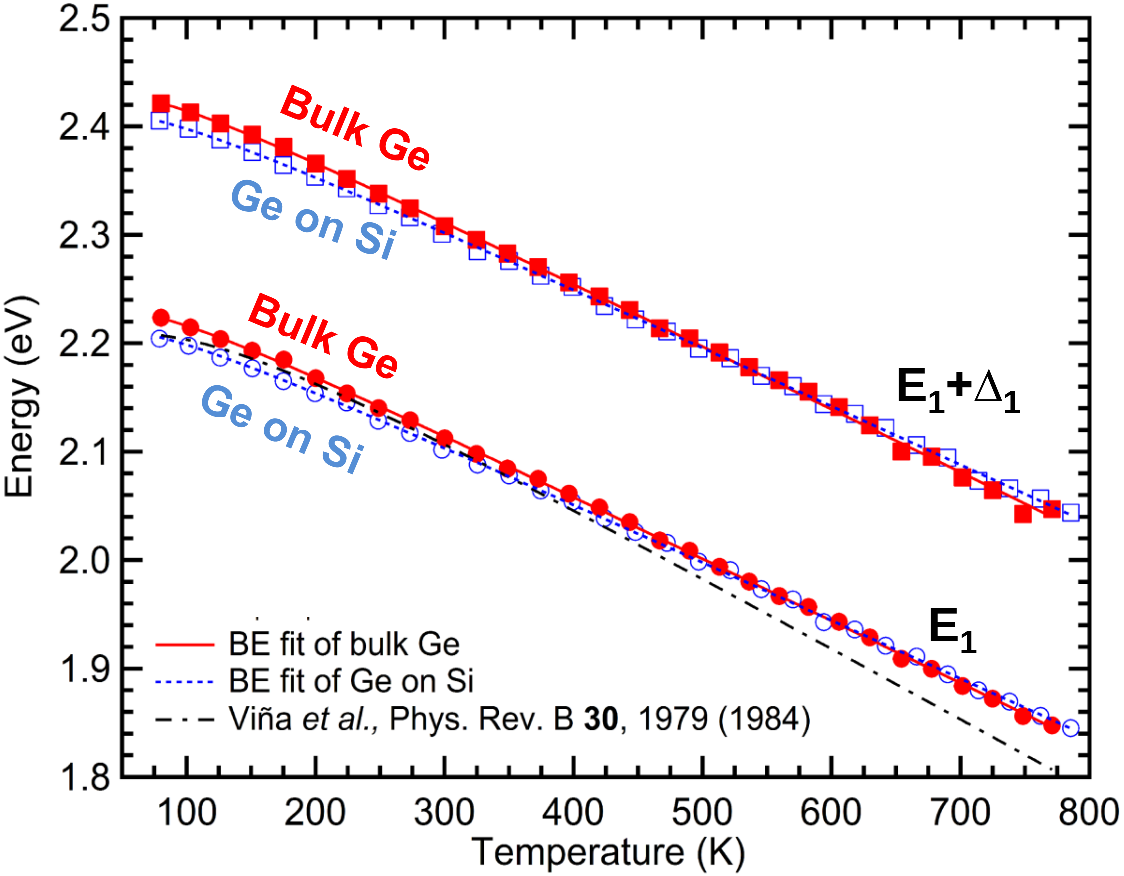


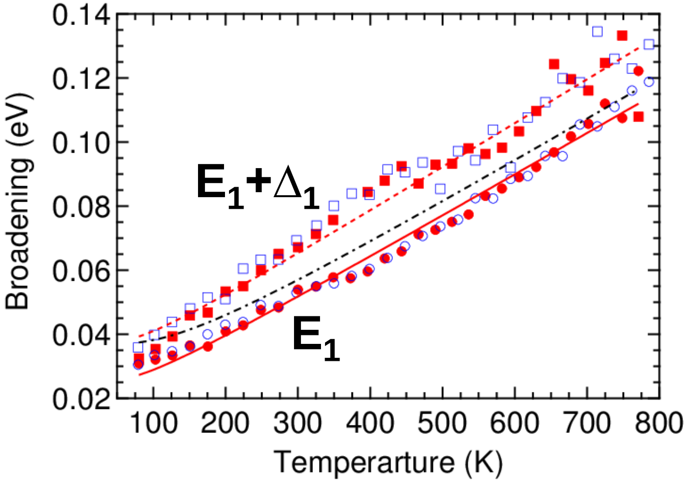


Bulk Ge and Ge on Si have different critical point energies.

Bulk Ge critical points are at higher energies due to strain.

Temperature Dependence of the CP





- **Strain generated due to the thermal expansivity mismatch shifts critical point to lower energies.**
- **Energy shift has increased upon cooling to lower temperatures.**

Model for Thermal Expansivity of Ge and Si

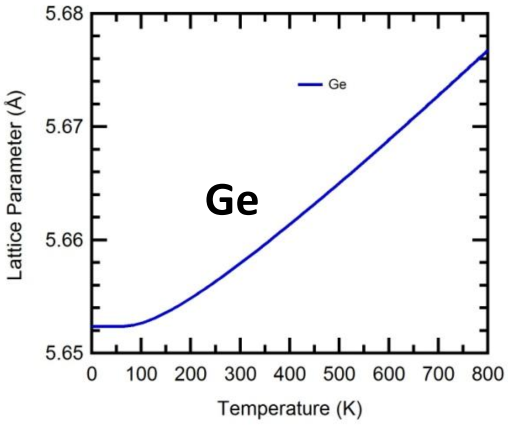
$$\alpha_{\nu}(T)=3\sum_{i=1}^{4}X_i\,\frac{(\theta_i/T)^2\exp(\theta_i/T)}{[\exp(\theta_i/T)-1]^2}$$

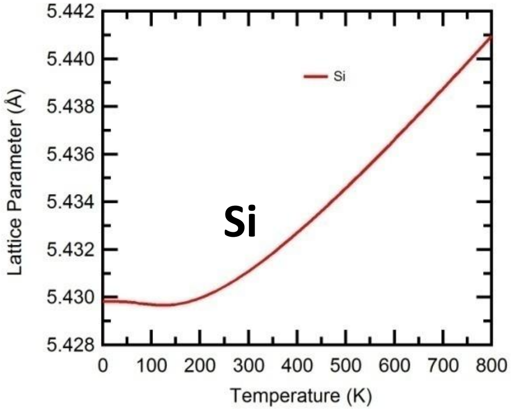
$$a(T)=a(T_0)+\int_{T_o}^{T}\alpha(T)dT$$

Reeber *et al*., Mater. Chem. Phys. **46**, 259 (1996)

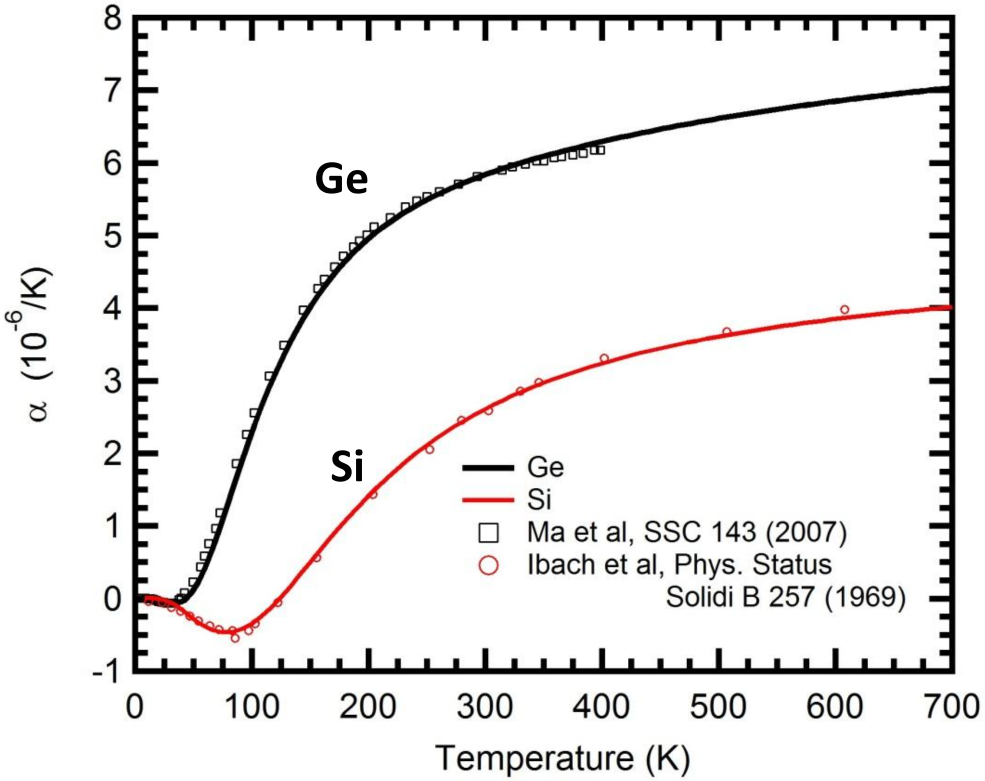
$$\varepsilon_{||}(T)=\int_{T_1}^{T_g}[\alpha_{Ge}(T)-\alpha_{Si}(T)]dT$$

α_v - Thermal expansion coefficient (volume), Θ_i, X_i- Fitting parameters
α - Linear thermal expansion coefficient , a - Lattice parameter





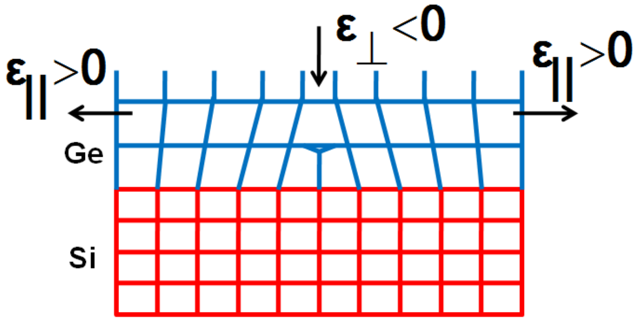
Cannon *et al*., Appl. Phys. Lett. **84,** 906 (2004)



XRD measurement: Strain of Ge on Si (100)

$$\varepsilon_{||}(T) = \int_{T_1}^{T_g} [\alpha_{Ge}(T) - \alpha_{Si}(T)]dT$$

Cannon *et al*., Appl. Phys. Lett. **84**, 906 (2004)

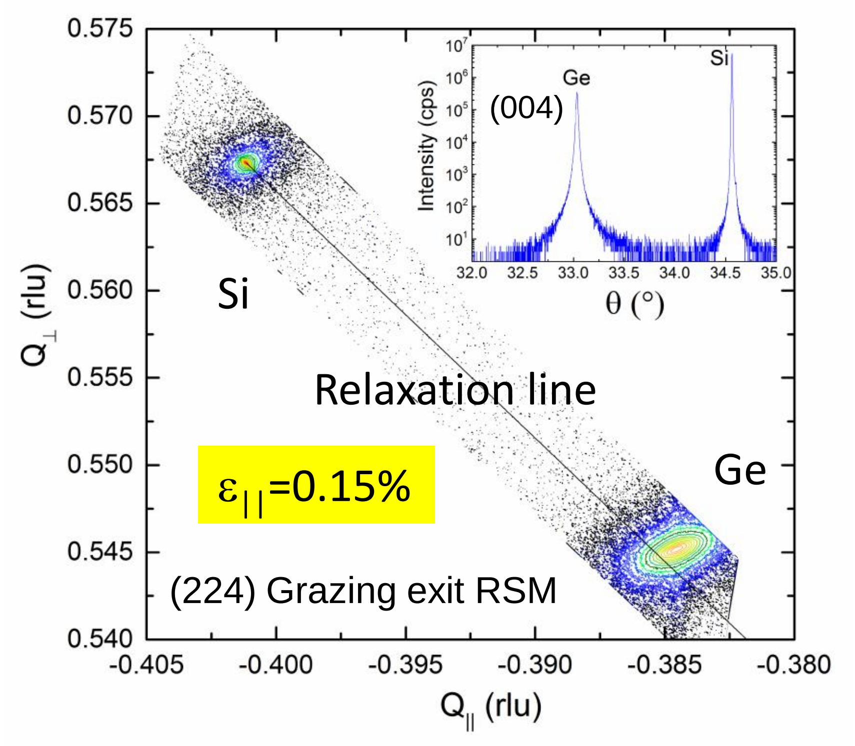


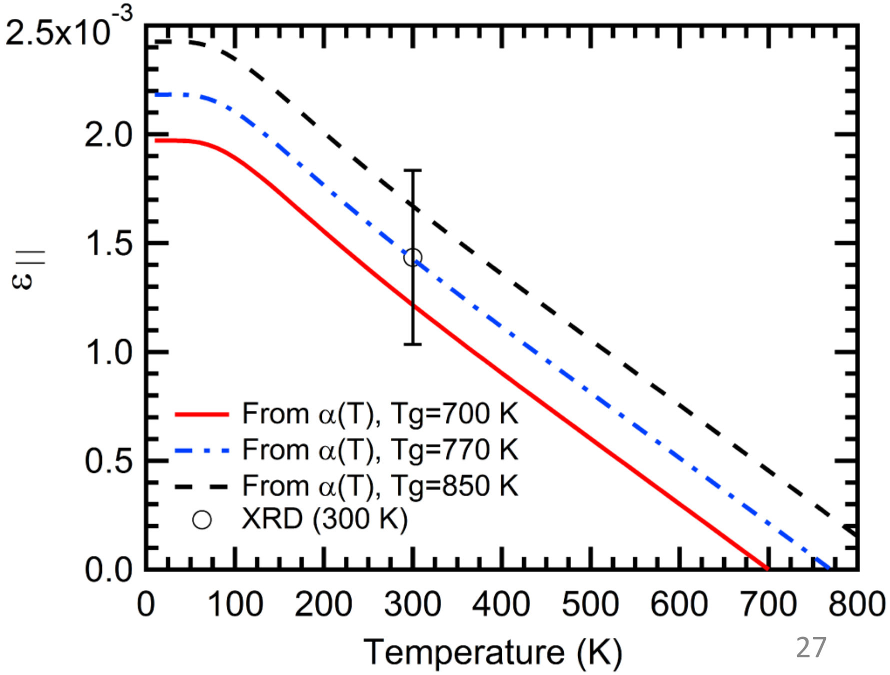
$$\varepsilon_{\perp}(T) = -2\frac{C_{12}}{C_{11}}(T)\varepsilon_{||}(T)$$

C_{11}, C_{12} – elastic constants of Ge

$$\frac{C_{12}}{C_{11}}(T) = 0.37492 - 3.6891*10^{-6}T$$

Roucka *et al*., Phys. Rev. B **81**, 245214 (2010)





Energy Shift: Bulk Ge minus Ge on Si

$$E_1^S(T) = E_1^0(T) + \Delta E_H(T) + \frac{\Delta_1}{2} - \sqrt{\frac{\Delta_1^2}{4} + (\Delta E_S(T))^2} \quad ;$$

$$\Delta E_H(T) = \sqrt{3} D_1^1 \varepsilon_H(T)$$

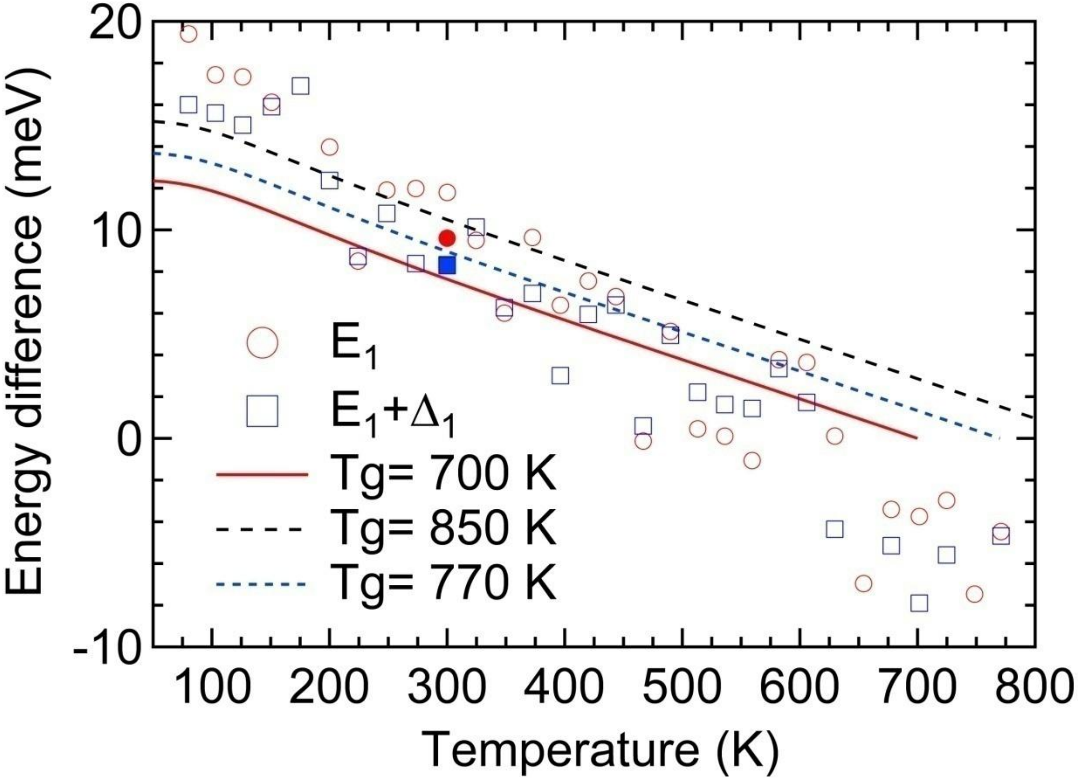
$$(E_1 + \Delta_1)^S(T) = (E_1 + \Delta_1)^0(T) + \Delta E_H(T) - \frac{\Delta_1}{2} + \sqrt{\frac{\Delta_1^2}{4} + (\Delta E_S(T))^2}$$

$$\Delta E_S(T) = \sqrt{3} D_3^3 \varepsilon_S(T)$$

$$\varepsilon_H = \frac{\varepsilon^\perp + 2\varepsilon^\parallel}{3}$$

$$\varepsilon_S = \frac{\varepsilon^\perp - \varepsilon^\parallel}{3}$$

Meera Chandrasekhar's Ph.D. thesis: Chandrasekhar & Pollak, PRB 15 (1977)



Predicted energy shift is in reasonably good agreement with the observed energy shifts of E_1 and $E_1+\Delta_1$.

Temperature Dependent Energy Shift

$$E\left(T\right)=a-b\left[1+\frac{2}{\left(e^{\theta_B/T}-1\right)}\right]$$

Bose-Einstein fit:
$k\theta_B$ is an effective intervalley phonon energy.

$$\Delta E_{th}\left(T\right)=3D_1^1\int_0^T\alpha\left(T'\right)dT'$$

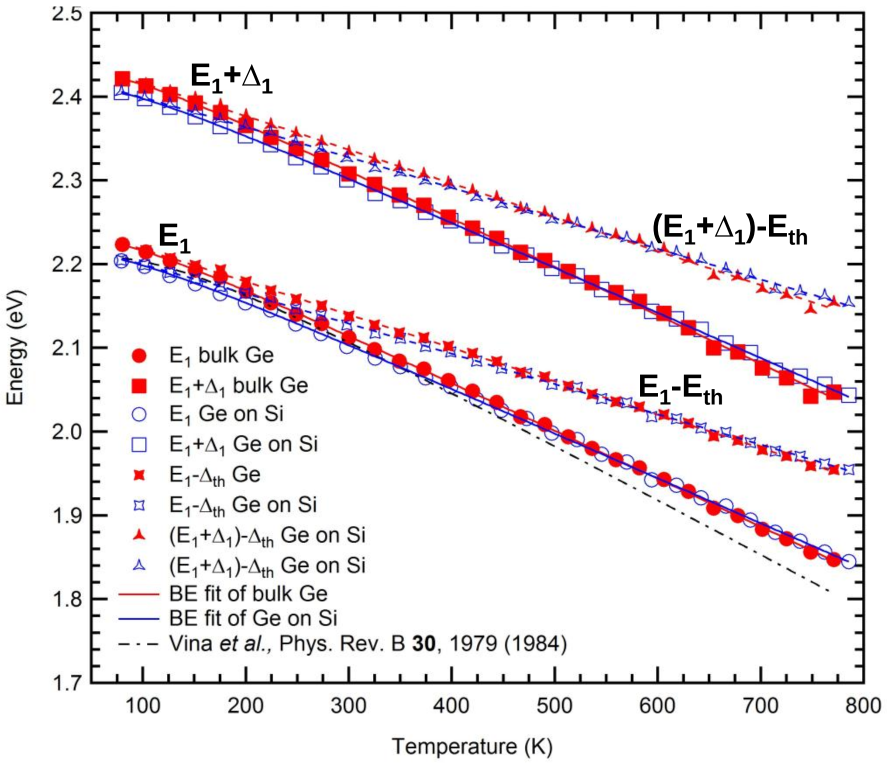
Contribution from thermal expansion.

$$E\left(T\right)-\Delta E_{th}\left(T\right)=a'-b'\left[1+\frac{2}{\left(e^{\theta'_B/T}-1\right)}\right]$$

True electron-phonon contribution.

Bulk Ge	a (eV)	b (eV)	θ_B (K)
E_1	2.295±0.002	0.063±0.004	218±14
$E_1+\Delta_1$	2.494±0.002	0.0640±0.0004	218 (f)
E_1[8]	2.33±0.03	0.12±0.04	360±120
Ge on Si			
E_1	2.273±0.001	0.0591±0.0002	218 (f)
$E_1+\Delta_1$	2.472±0.001	0.0595±0.0002	218 (f)

Bulk Ge	a' (eV)	b′ (eV)	θ'_B (K)
$E_1-\Delta E_{th}$	2.261±0.002	0.019±0.008	95±40
$(E_1+\Delta_1)-\Delta E_{th}$	2.460±0.002	0.0193±0.0002	95 (f)
Ge on Si			
$E_1-\Delta E_{th}$	2.2386±0.0008	0.0172±0.0008	95 (f)
$(E_1+\Delta_1)-\Delta E_{th}$	2.438±0.001	0.0174±0.0001	95 (f)



Theory:
P. Lautenschlager *et al.*, PRB **31**, 1985

N.S. Fernando *et al*., Appl. Surf. Sci. (2016) in press.

Summary I

- We determined the temperature-dependent energies of the **E_1 and $E_1+\Delta_1$ critical points** of Ge on Si.
- Strain is generated due to the **thermal expansivity mismatch** (between Ge epilayer and Si substrates). This strain **shifts the E_1 and $E_1+\Delta_1$ CP to lower energies.**
- **Pseudo-quasi-harmonic model** (Reeber, 1996) was used to derive theoretical strain generated on Ge film on Si due to the thermal expansivity mismatch. Theoretically predicted E_1 and $E_1+\Delta_1$ CP energy shifts are **in excellent agreement with the ellipsometry results.**

☐ Introduction

- Role of germanium (Ge) in optoelectronic industry
- Band gap engineering of Ge for photonic applications
- $Ge_{1-x-y}Si_xSn_y$ alloys
- Strain, Composition, and temperature dependence

☐ Sample preparation and characterization

- MBE and CVD growth at UD and ASU
- Spectroscopic ellipsometry and high resolution X-ray diffraction
- X-ray reflectivity and atomic force microscopy

☐ Temperature dependent optical properties of Ge

☐ Optical properties of $Ge_{1-x-y}Si_xSn_y$ on Ge

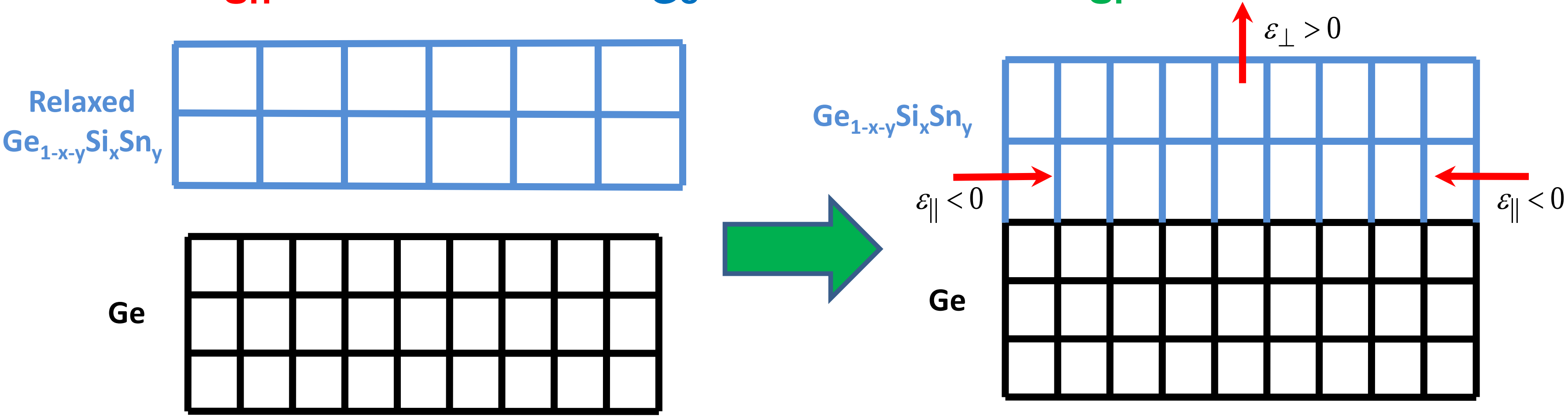
☐ Effects of relaxation of $Ge_{1-x-y}Si_xSn_y$ on Ge

☐ Conclusion

Pseudomorphic $\mathrm{Ge_{1\text{-}x\text{-}y}Si_xSn_y}$ Alloys on Ge

$$\boxed{a^{rel}_{Ge_{1-x-y}Si_xSn_y} = xa_{Si} + ya_{Sn} + (1-x-y)a_{Ge} + b_{GeSn}y(1-x-y) + b_{GeSi}x(1-x-y) + b_{SiSn}xy}$$

a_{Sn} = 6.489 Å > a_{Ge} = 5.657 Å > a_{Si} = 5.453 Å



In-plane strain:

$$\boxed{\varepsilon^{\parallel} = \frac{a_{Ge} - a^{rel}_{Ge_{1-x-y}Si_xSn_y}}{a^{rel}_{Ge_{1-x-y}Si_xSn_y}}}$$

Out-of-plane strain:

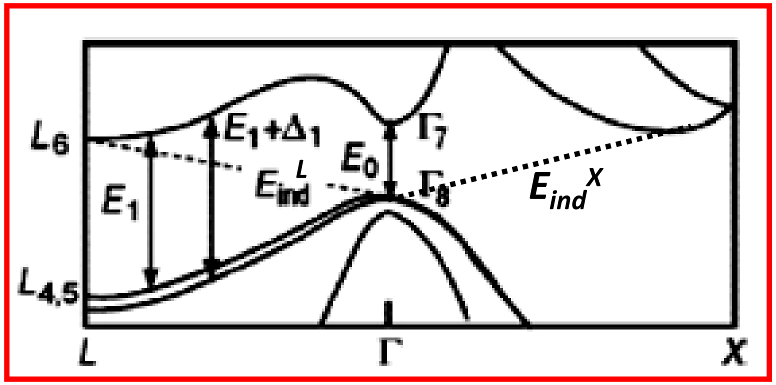
$$\boxed{\varepsilon^{\perp} = -2\frac{C_{12}}{C_{11}}\varepsilon^{\parallel}}$$

$$\left[\frac{C_{12}}{C_{11}}\right]^{Ge_{1-x-y}Si_xSn_y} = \frac{C_{12}^{Ge_{1-x-y}Si_xSn_y}}{C_{11}^{Ge_{1-x-y}Si_xSn_y}}$$

$$C_{mn}^{Ge_{1-x-y}Si_xSn_y} = xC_{mn}^{Si} + yC_{mn}^{Sn} + (1-x-y)C_{mn}^{Ge}$$

Kouvetakis *et al*., Annu. Rev. Mater. Res. **36**, 497 (2006)

Strain and Compositional Dependence of Band Gaps



Bauer *et al.*, Solid State Commun. 127, **355** (2003)

Hydrostatic strain $\varepsilon_H = \dfrac{\varepsilon^{\perp} + 2\varepsilon^{\parallel}}{3}$

Shear strain $\varepsilon_S = \dfrac{\varepsilon^{\perp} - \varepsilon^{\parallel}}{3}$

a_v

$\left(\Xi_d + \frac{1}{3}\Xi_d + a_v\right)^X$

$\left(\Xi_d + \frac{1}{3}\Xi_d + a_v\right)^L$

Ξ_d^{Δ}

b

Strained conduction band

$$E_c^{\Gamma} = E^{rel}_{dir,\Gamma} + 3a_v\varepsilon_H$$

$$E_c^{L} = E^{rel}_{ind,L} + 3\left(\Xi_d + \frac{1}{3}\Xi_d + a_v\right)^L \varepsilon_H$$

$$E_c^{X4} = E^{rel}_{ind,X} + 3\left(\Xi_d + \frac{1}{3}\Xi_d + a_v\right)^X \varepsilon_H - \varepsilon_S\Xi_d^{\Delta}$$

$$E_c^{X2} = E^{rel}_{ind,X} + 3\left(\Xi_d + \frac{1}{3}\Xi_d + a_v\right)^X \varepsilon_H + 2\varepsilon_S\Xi_d^{\Delta}$$

Strained valence band

$$E^{\Gamma}_{v_1} = -\frac{\Delta_0}{2} + \frac{3}{2}b\varepsilon_S + \frac{1}{2}\sqrt{\Delta_0^2 + 6\Delta_0 b\varepsilon_S + (9b\varepsilon_S)^2}$$

$$E^{\Gamma}_{v_2} = -3b\varepsilon_S$$

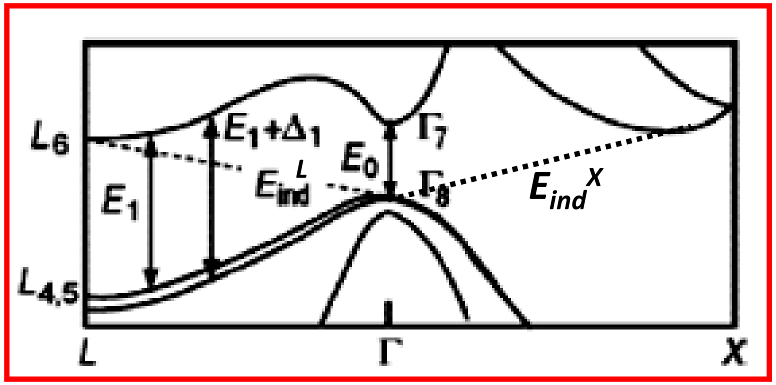
$$E^{\Gamma}_{v_3} = -\frac{\Delta_0}{2} + \frac{3}{2}b\varepsilon_S - \frac{1}{2}\sqrt{\Delta_0^2 + 6\Delta_0 b\varepsilon_S + (9b\varepsilon_S)^2}$$

S. T. Pantelides and S. Zollner, Silicon-Germanium Carbon Alloys Growth, Properties and Applications (Taylor & Francis, New York, NY, 2002)

Kurdi *et al*., Appl. Phys. **107,** 013710 (2010)

Beeler *et al*., IEEE J. Photovolt. **2,** 434 (2012)

E_1 Critical Point Energy



Bauer *et al.*, Solid State Commun. **127,** 355 (2003)

$$E_1^s(x,y) = E_1^0(x,y) + \Delta E_H(x,y) + \frac{\Delta_1(x,y)}{2} - \sqrt{\frac{\Delta_1^2(x,y)}{4} + \Delta E_s^2(x,y)}$$

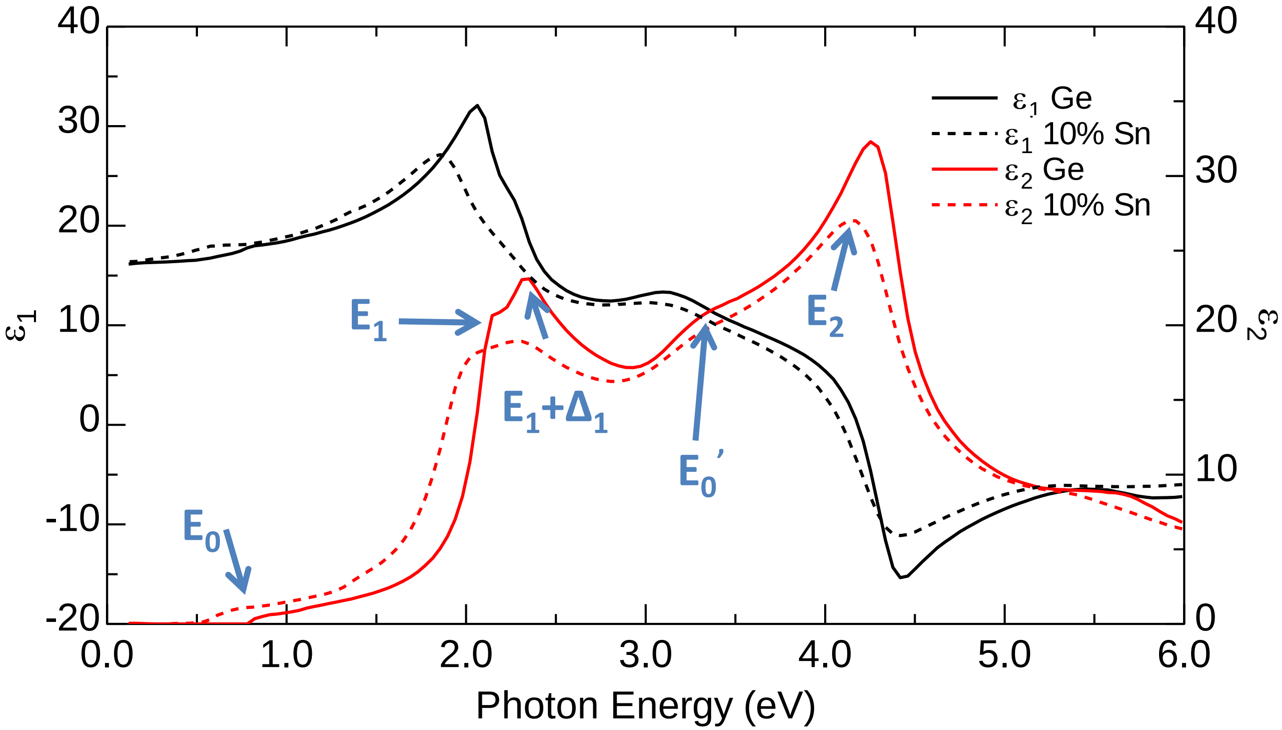
$$\Delta E_H(x,y) = \sqrt{3}D_1^1\varepsilon_H \qquad \Delta E_S(x,y) = \sqrt{6}D_3^3\varepsilon_S$$

$$\varepsilon_H = \frac{\varepsilon^{\perp} + 2\varepsilon^{\parallel}}{3} \qquad \varepsilon_S = \frac{\varepsilon^{\perp} - \varepsilon^{\parallel}}{3}$$

V. R. D'Costa *et al.*, J. Appl. Phys. **116,** 053520 (2014)

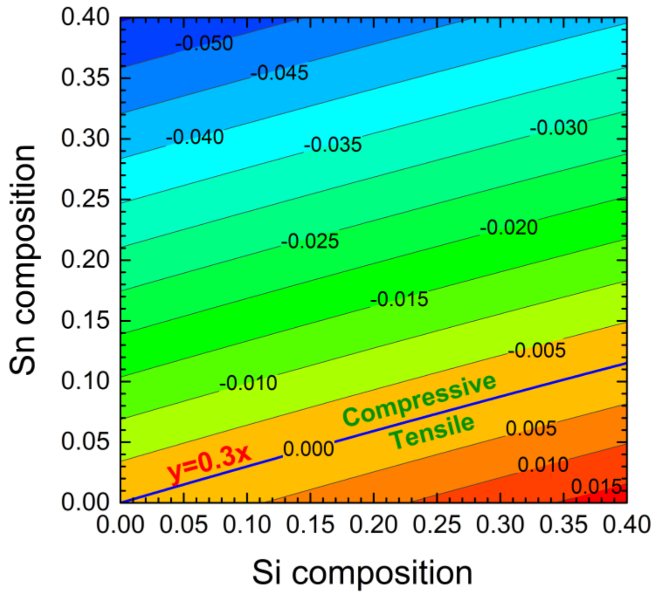
Beeler *et al.*, IEEE J. Photovolt. **2,** 434 (2012)

Kurdi *et al.*, Appl. Phys. **107,** 013710 (2010)

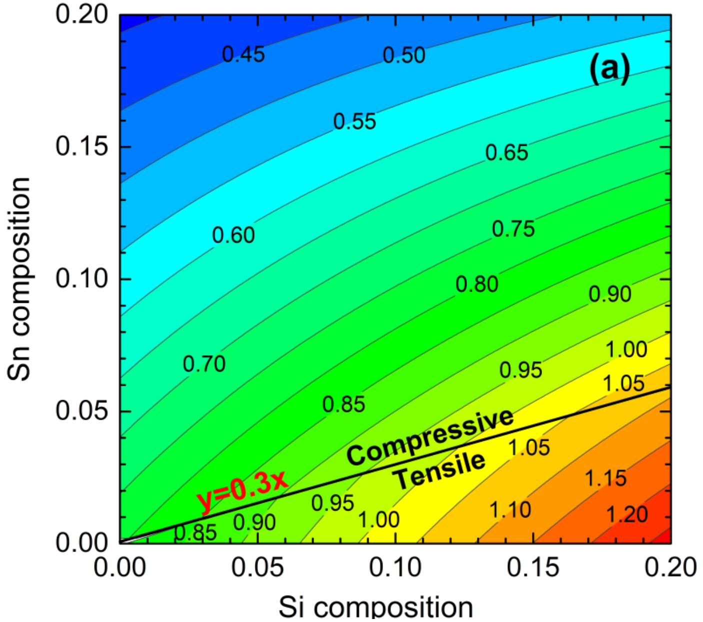


Pseudomorphic $\mathrm{Ge_{1-x-y}Si_xSn_y}$ Alloys on Ge

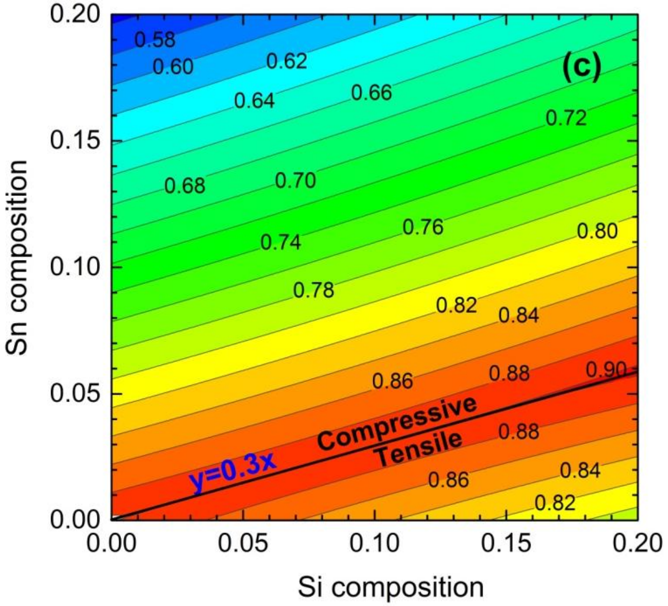
In-plane strain $\varepsilon_{||}$



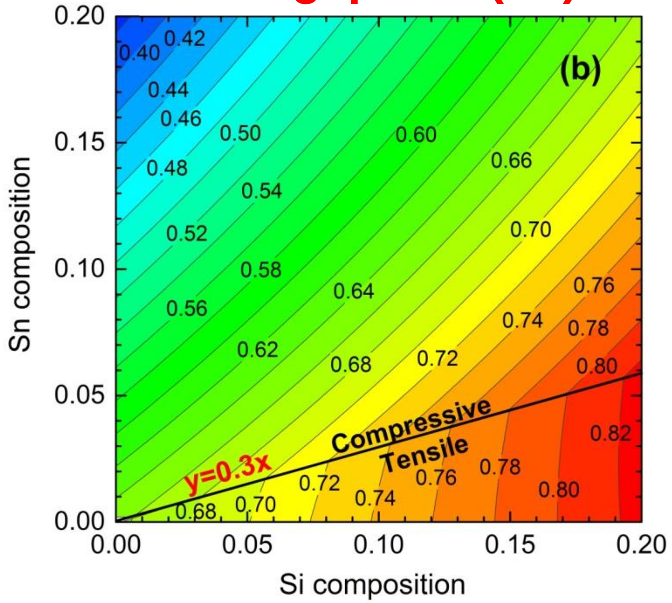
Band gap at Γ (eV)



Band gap at Δ (eV)

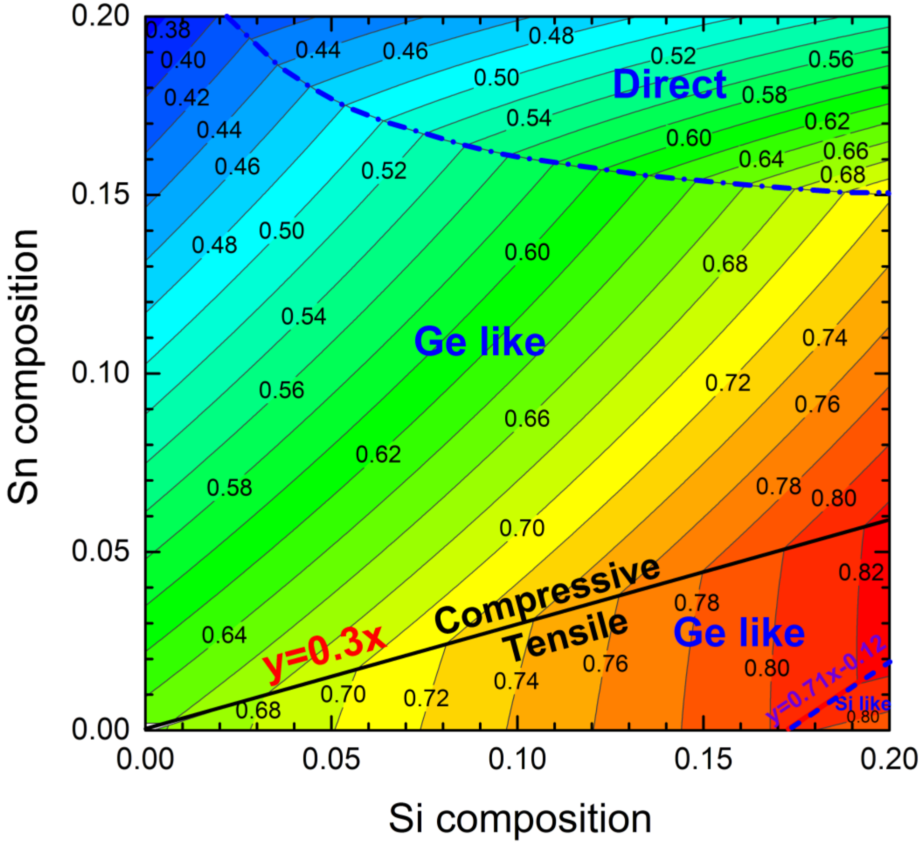


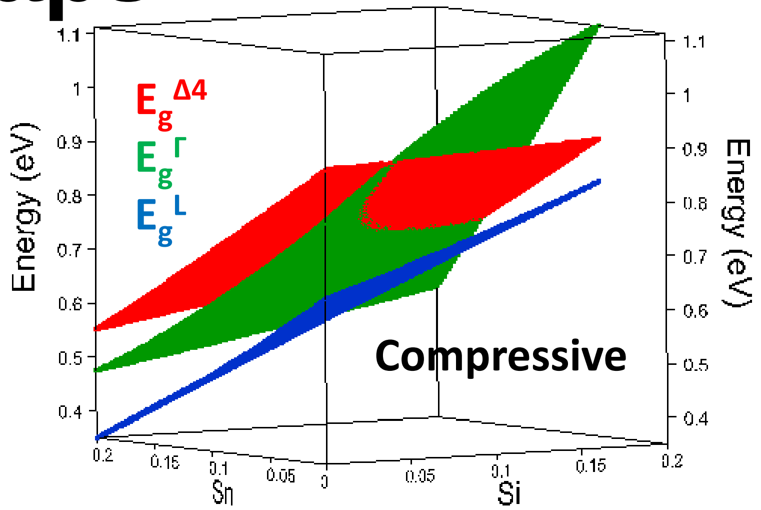
Band gap at L (eV)

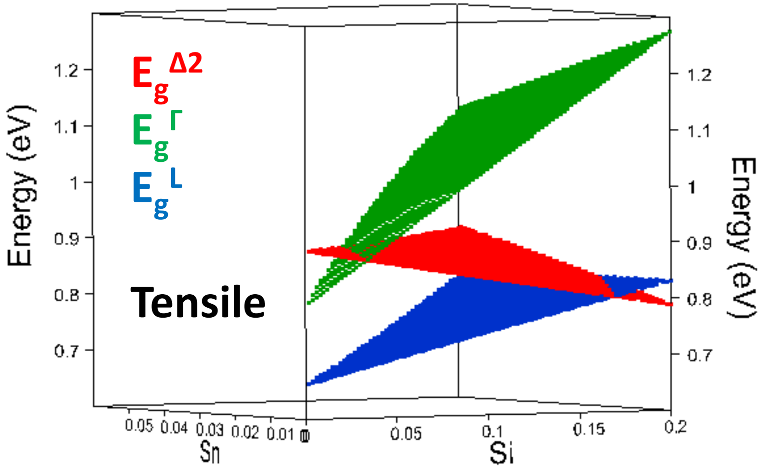


Strain and Compositional Dependence of Band Gaps

Smallest band gap (eV)



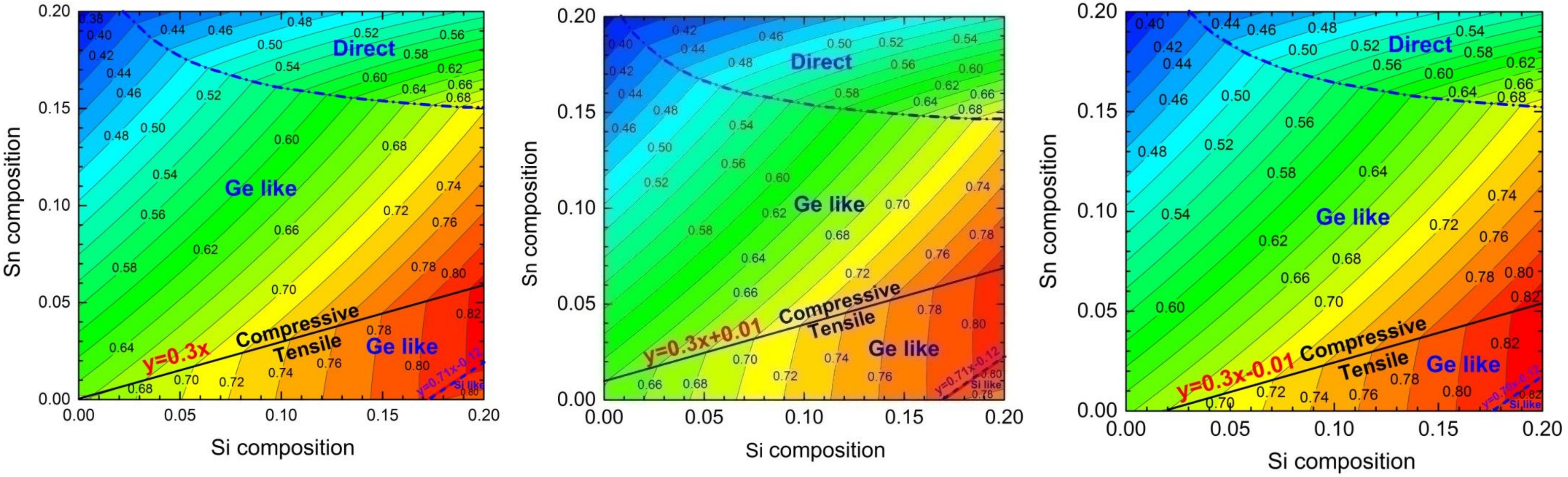




Pseudomorphic Ge$_{1-x-y}$Si$_x$Sn$_y$ alloys become direct for **Sn >15-20%**

Effects of Substrate on Indirect-Direct Transition

Compositional dependence of the lowest band gap of pseudomorphic $Ge_{1-x-y}Si_xSn_y$ on different substrates:

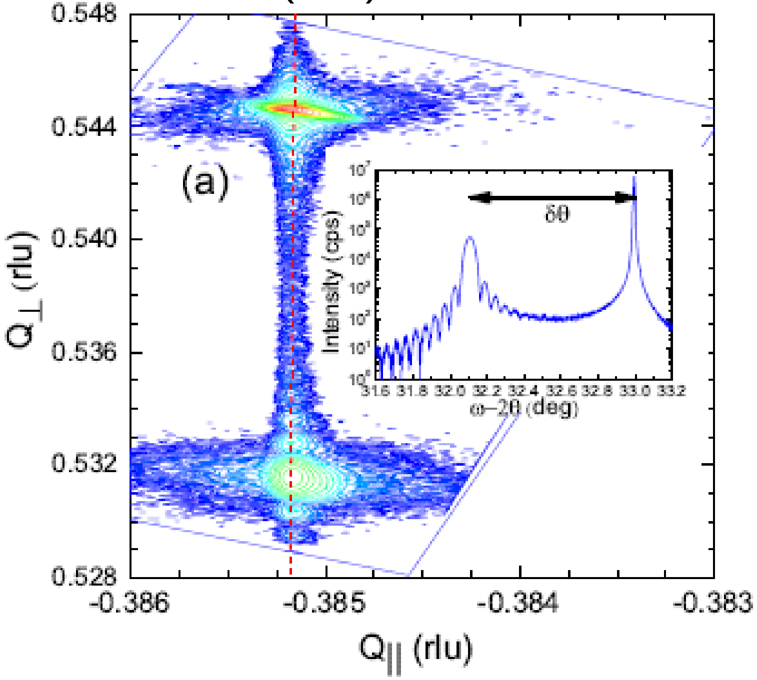


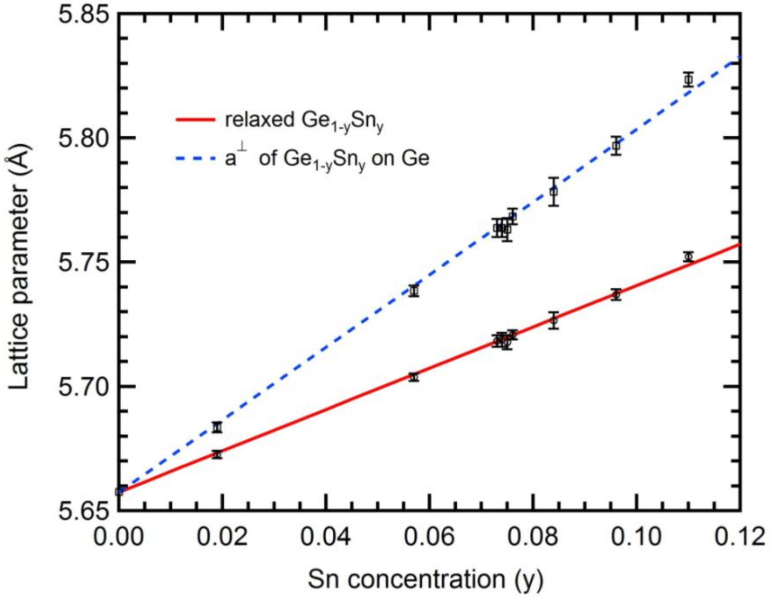
(a) On bulk Ge **(b) Ge buffered Si** **(c) GaAs**

- Increasing the growth temperature of the Ge buffer layer reduces the compressive strain → reduces the x (Si) and y (Sn) for the indirect to direct crossover, but not significantly.

Lattice parameter and Strain of $Ge_{1-y}Sn_y$ Alloys on Ge by MBE

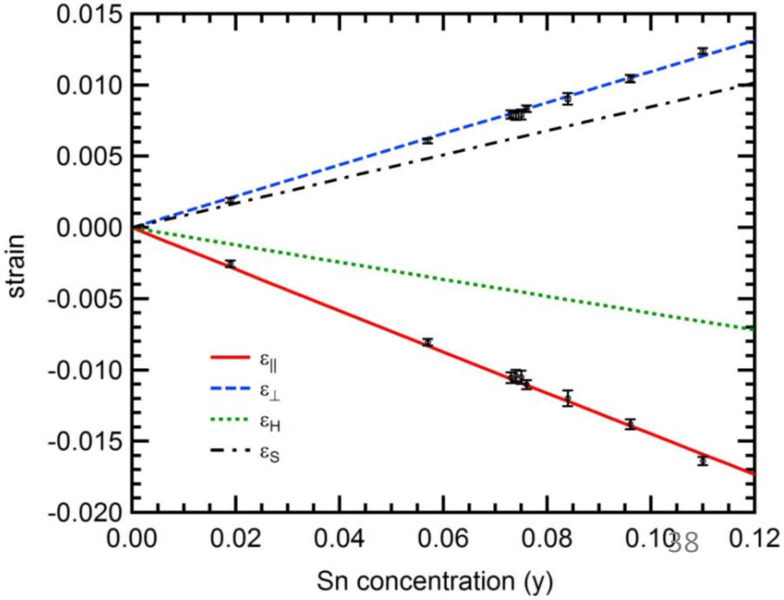
(224) RSM



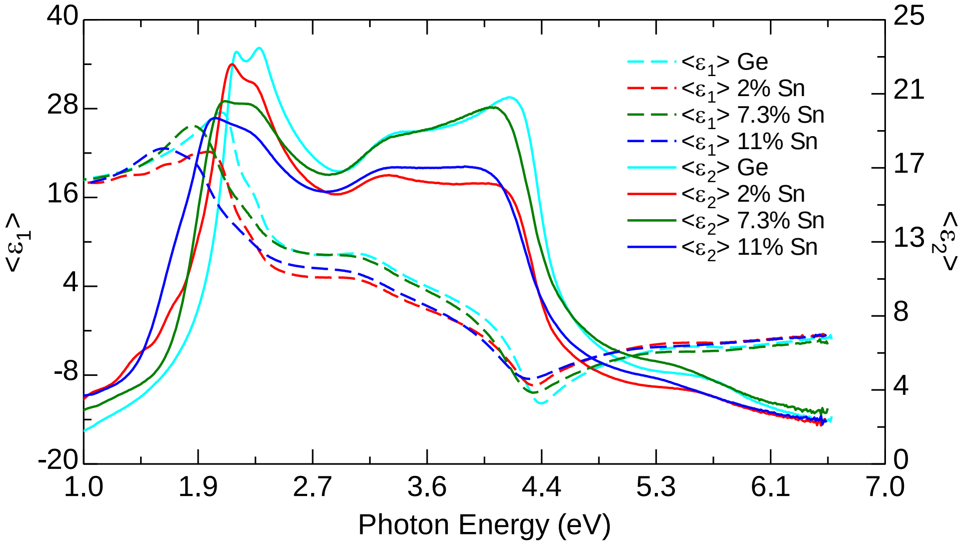


Hydrostatic strain:
$$\boxed{\varepsilon_H = \frac{\varepsilon^\perp + 2\varepsilon^{||}}{3}}$$

Shear strain:
$$\boxed{\varepsilon_S = \frac{\varepsilon^\perp - \varepsilon^{||}}{3}}$$



Optical Constants of $Ge_{1-y}Sn_y$ Alloys



Measured pseudodielectric function

2	**GeO_2**	**40 Å**
1	**$Ge_{1-y}Sn_y$**	**1046 Å**
0	**Ge**	**1 mm**

Parametric model fit and then point-by-point fit to obtain the dielectric function of the alloy.

- E_1, $E_1+\Delta_1$: 2D critical points

$$\boxed{\varepsilon \sim C - A\ln(E-\omega-i\Gamma)\,e^{i\varphi}}$$

Viña *et al*., Phys. Rev. B **30**, 1979 (1984)

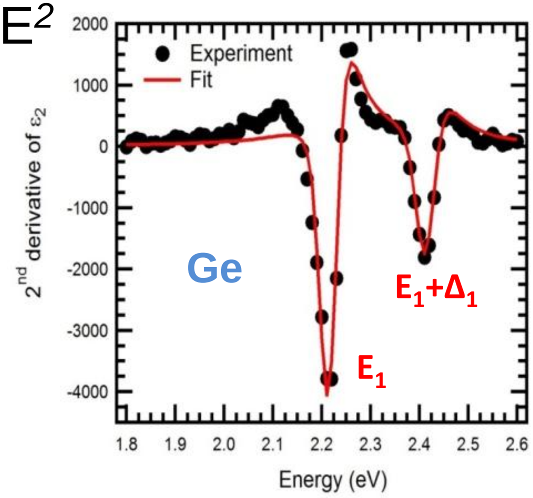
- Analysis of $d^2\varepsilon/dE^2$ →CP parameters;

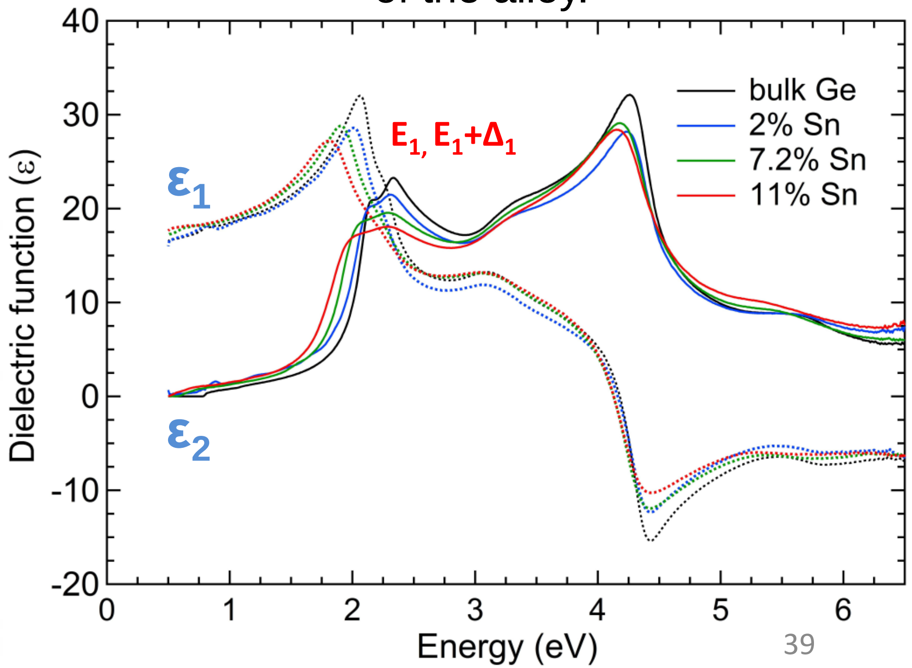
E- CP energy

A- amplitude

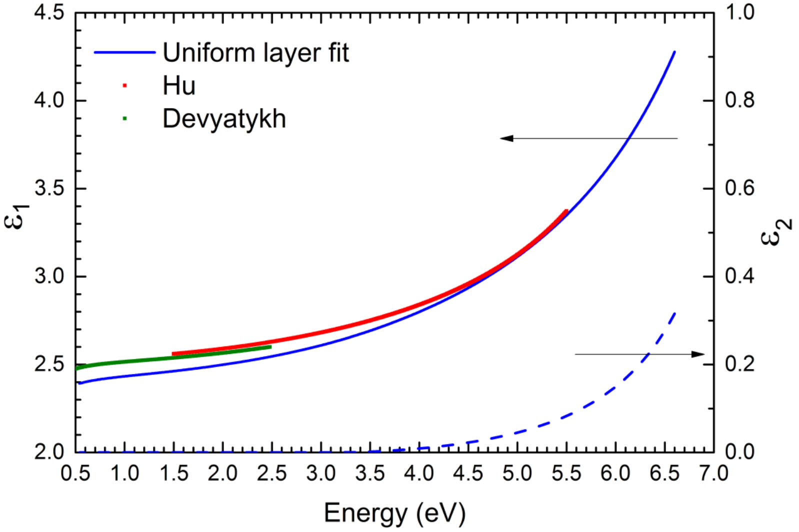
Γ- broadening

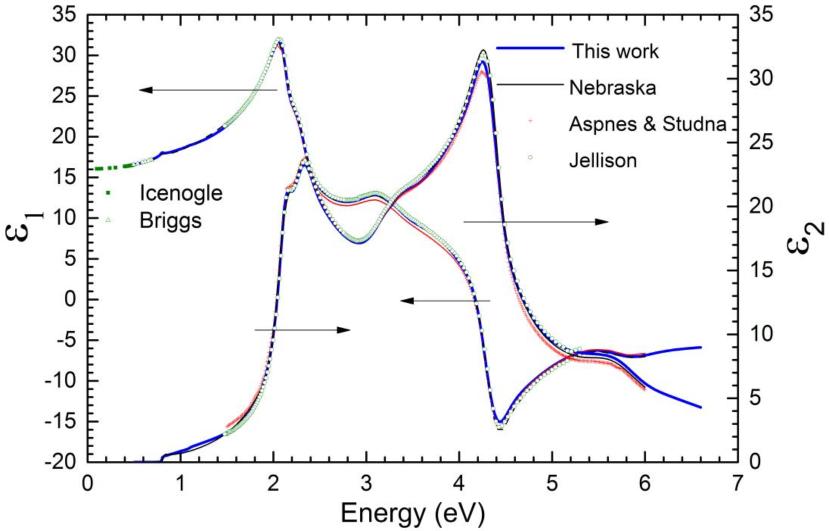
φ- phase



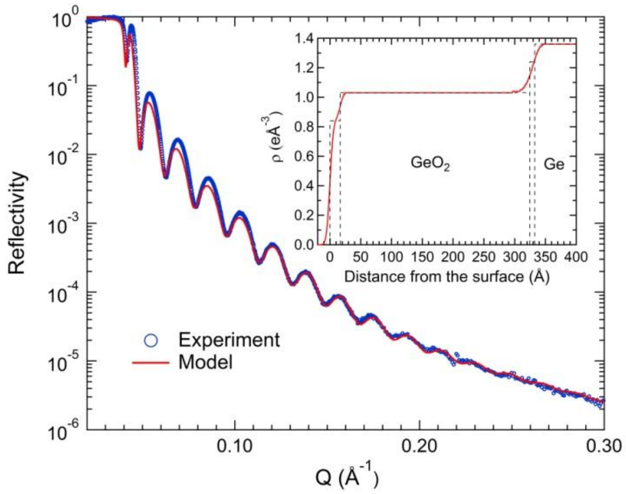


Optical Constants of Ge and GeO_2





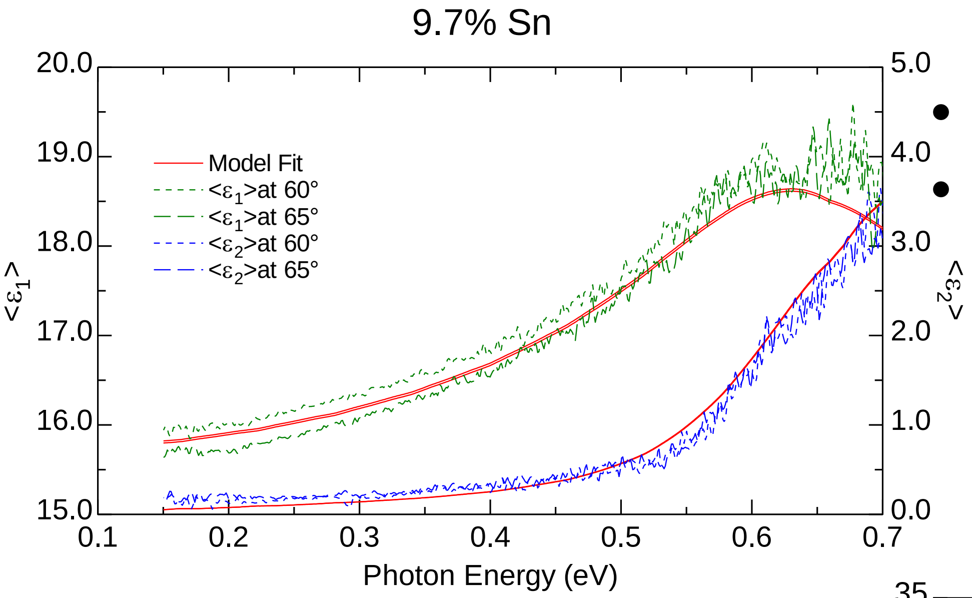
- Thermally grown GeO_2 by annealing Ge wafers in pure O_2.



N. Nunley and N. Fernando *et al.*, J. Vac. Sci. Technol. B **34**, 061205 (2016).

Accurate optical constants for Ge substrate and GeO_2 layer are obtained by multisample analysis of ellipsometry data.

Direct band gap of Ge$_{1-y}$Sn$_y$ Alloys



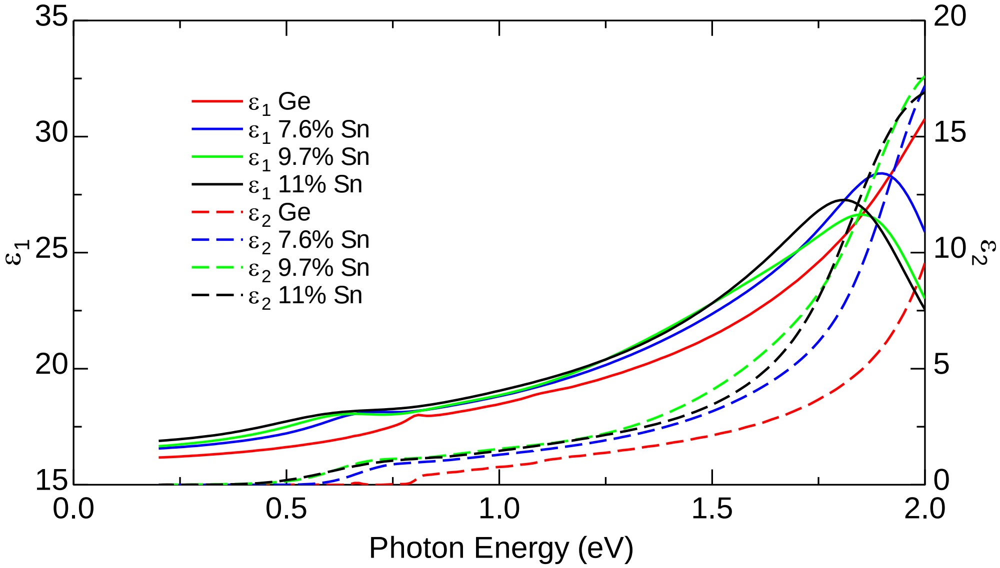
- FTIR ellipsometry →0.1 – 0.7 eV.
- Poor signal to noise ratio.

Parametric oscillator model fit (simultaneously with IR-UV data)

- E_0: 3D critical points

$$\boxed{\varepsilon \sim C - A(\omega - E + i\Gamma)^{1/2}\, e^{i\varphi}}$$

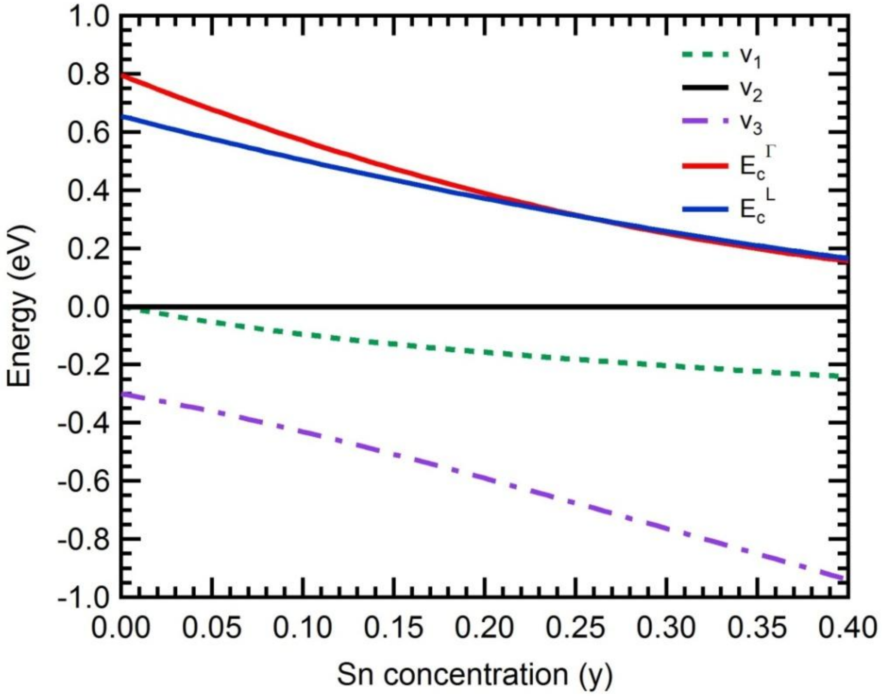
Viña *et al*., Phys. Rev. B **30**, 1979 (1984)

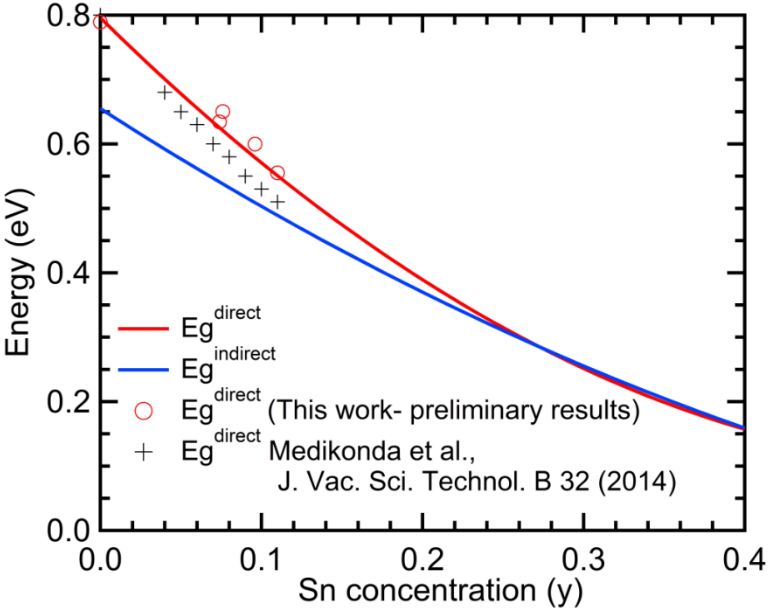


Decreasing direct band gap (E_0) with increasing Sn content.

Ge band Splitting and Shifting with Sn

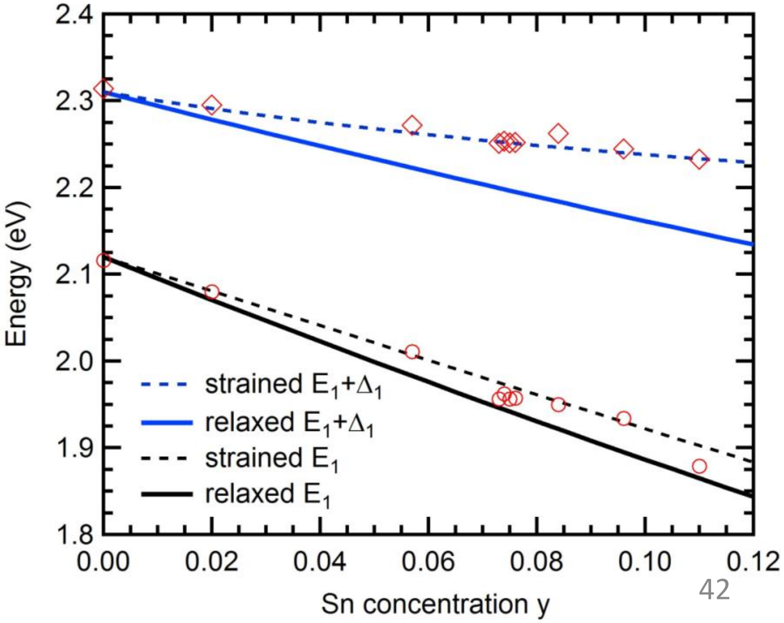
Pseudomorphic $Ge_{1-y}Sn_y$ on Ge





$E_c(L)$ always lower than the $E_c(\Gamma)$.
→ $E_{direct} > E_{indirect}$

Pseudomorphic GeSn alloys never become direct



Summary II

- **Direct** and **indirect** band gaps can be modeled using deformational potential theory for **pseudomorphic $Ge_{1-x-y}Si_xSn_y$** alloys grown on Ge.

- **Pseudomorphic $Ge_{1-x-y}Si_xSn_y$** alloys on Ge becomes a direct band gap material for Sn > ~15-20%.

- **Increasing the growth temperature of the Ge buffer** layer reduces the compressive strain → **reduces the x (Si) and y (Sn) for the indirect to direct crossover.**

- Deformation potential theory predicts **no indirect to direct band gap crossover** for pseudomorphic **(fully strained) $Ge_{1-y}Sn_y$** alloys on Ge.

- Theoretical predictions are validated using **ellipsometry** for pseudomorphic GeSn alloys (Si=0) on Ge.

❑ Introduction

- Role of germanium (Ge) in optoelectronic industry
- Band gap engineering of Ge for photonic applications
- $Ge_{1-x-y}Si_xSn_y$ alloys
- Strain, Composition, and temperature dependence

❑ Sample preparation and characterization

- MBE and CVD growth at UD and ASU
- Spectroscopic ellipsometry and high resolution X-ray diffraction
- X-ray reflectivity and atomic force microscopy

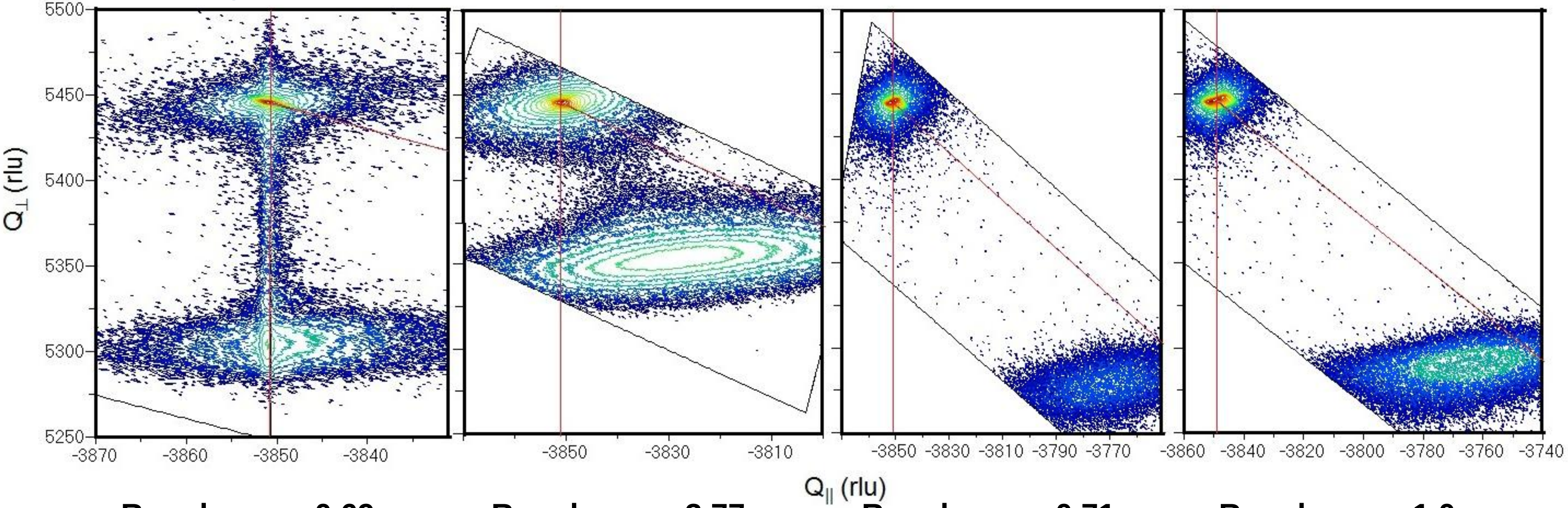
❑ Temperature dependent optical properties of Ge

❑ Optical properties of $Ge_{1-x-y}Si_xSn_y$ on Ge

❑ Effects of relaxation of $Ge_{1-y}Sn_y$ on Ge

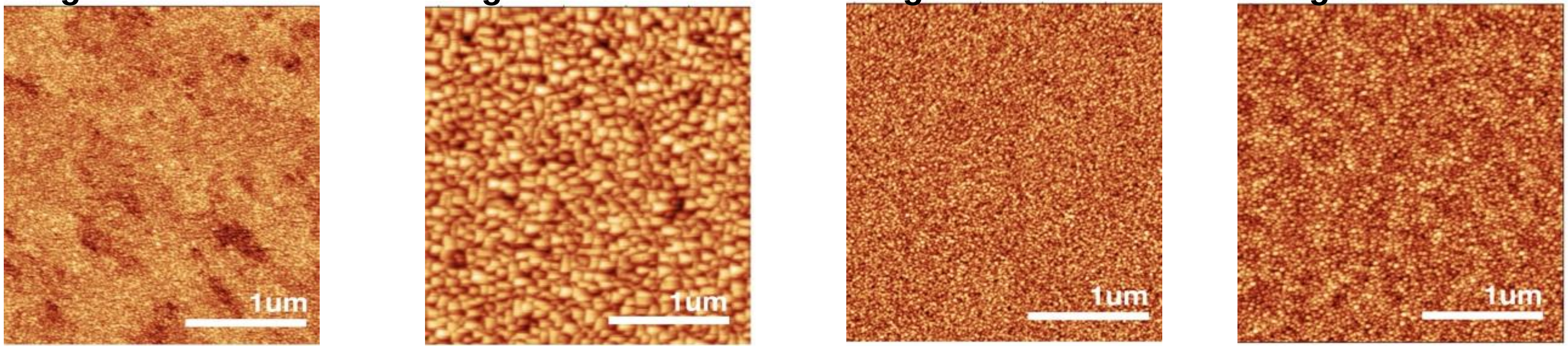
❑ Conclusion

Partially relaxed $Ge_{1-y}Sn_y$ on Ge



10% Sn, 0% relaxed | **8.4% Sn, 41% relaxed** | **18.5% Sn, 78% relaxed** | **18.3% Sn, 87% relaxed**

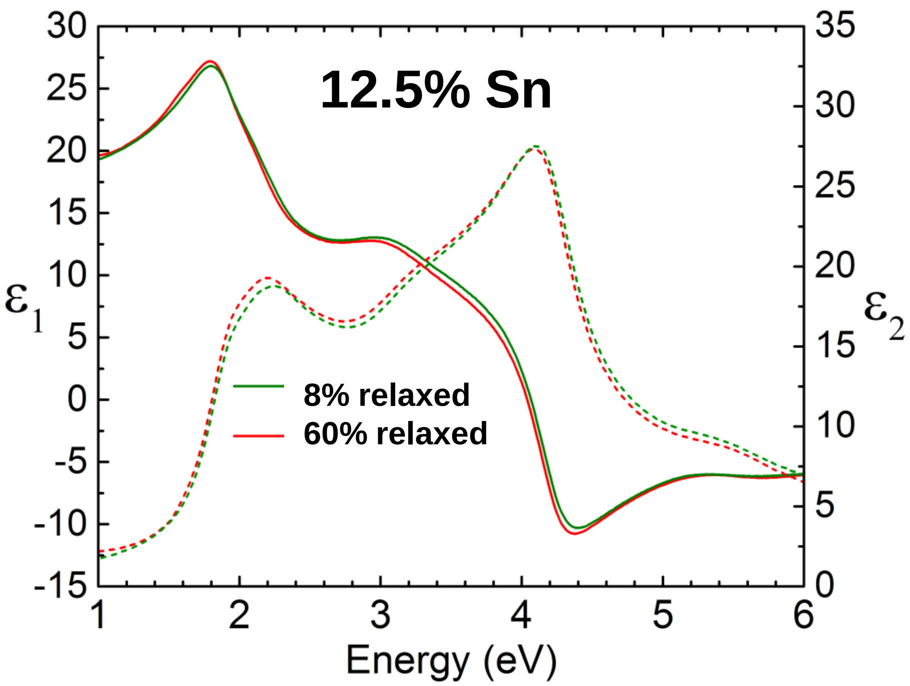
Roughness =0.69 nm | **Roughness =3.77 nm** | **Roughness =0.71 nm** | **Roughness =1.0 nm**

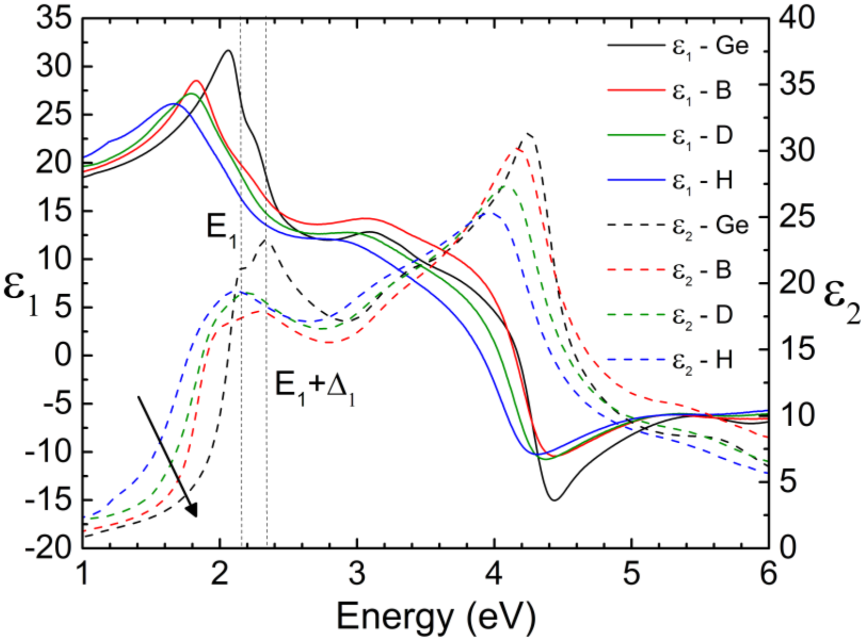


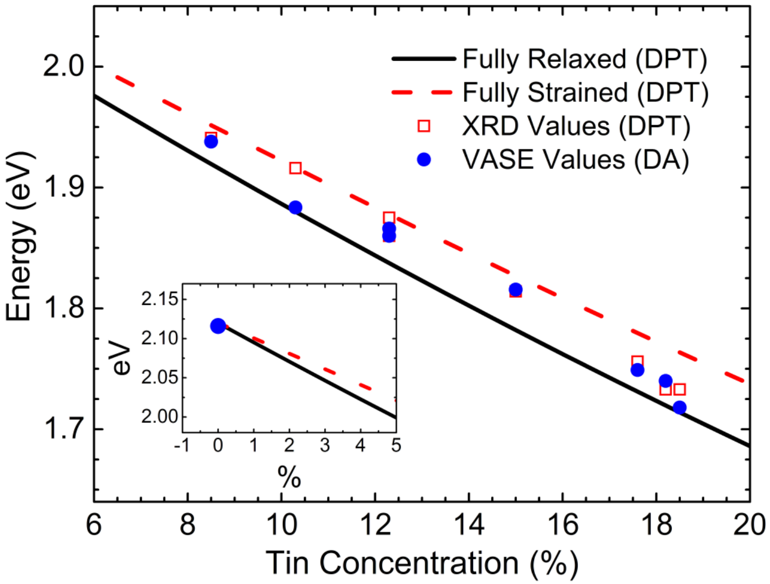
Thickness =100 nm | **Thickness =300 nm** | **Thickness =50 nm** | **Thickness =100 nm**

Surface roughness of the $Ge_{1-y}Sn_y$ films increases with layer thickness as well as with the relaxation.

Effects of Relaxation on E_1 Band Gap







E_1 band gap red shifted with incorporation of Sn and relaxation.

R. Hickey and N. Fernando, J. Vac. Sci. Technol. B **35**, 021205 (2017).

Summary III

- **Relaxation of $Ge_{1-y}Sn_y$** alloys on Ge is critical for the indirect-direct transition.
- **Dielectric function of $Ge_{1-y}Sn_y$ red shifted with incorporation of Sn as well as relaxation.**
- E_1 band gap red shifted with incorporation of Sn and relaxation **of the $Ge_{1-y}Sn_y$** alloys on Ge.

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❑ Conclusion

Conclusion

- **The indirect nature of the fundamental band gap has limited the large scale integration of Ge-based photonic devices on existing Si technology.**
- **Ge band structure is a strong function of strain and alloy composition.**
- **Controlling strain by thermal expansion mismatch:**
  - Strain is generated due to the **thermal expansivity mismatch** between Ge epilayer and Si substrates.
  - This strain **shifts the E_1 and $E_1+\Delta_1$ CP to lower energies.**
  - We determined the temperature-dependent energies of the **E_1 and $E_1+\Delta_1$ critical points** of Ge on Si.
  - Experimental energy shifts are in good agreement with theoretical prediction.

Conclusion

- **Controlling strain by lattice mismatch and alloying**
  - **$Ge_{1-x-y}Si_xSn_y$ allows to decouple lattice parameter and band structure.**
  - **Direct** and **indirect** band gaps can be modeled using deformational potential theory for **pseudomorphic $Ge_{1-x-y}Si_xSn_y$** alloys grown on Ge.
  - **Pseudomorphic $Ge_{1-x-y}Si_xSn_y$** alloys on Ge becomes a direct band gap material for Sn > ~15-20%.
  - Deformation potential theory predicts **no indirect to direct band gap crossover** for pseudomorphic **(fully strained) $Ge_{1-y}Sn_y$** alloys on Ge.
  - Theoretical predictions are validated using **ellipsometry** for pseudomorphic GeSn alloys (Si=0) on Ge.

Conclusion

- **Strain relaxation of $Ge_{1-y}Sn_y$ on Ge is critical for the indirect-direct transition.**
  - **Effects of relaxation on the dielectric function was investigated.**
  - **Deformation potential theory was used to predict the band gaps.**
  - **E_1 and $E_1+\Delta_1$ band gaps are in good agreement with the predictions.**

Acknowledgement

Current and former members of Dr. Zollner's ellipsometry group

Dr. Kolodzey group at University of Delaware

Dr. Menendez & Dr. Kouvetakis group at Arizona State University

Financial support from Department of Physics at NMSU,
Air Force Office of Scientific Research (FA9550-13-1-0022),
and National Science Foundation (DMR-1505172)- during 2016.

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