Optical Properties of Infrared Detector Materials

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Annual meeting of the
AVS Spectroscopic Ellipsometry Technical Group,
68th International AVS Symposium and Exhibition
Pittsburgh, PA, November 8th, 2022.

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Outline

1. Optical and X-ray Characterization of thick **GeSn alloys** (1-2% Sn) **on GaAs**
   Ken Hass Outstanding Student Paper Award March 2022, Forum on Industrial & Applied Physics, APS

2. Coherent Longitudinal Acoustic **Phonon Oscillations** in Ge
   using **Femtosecond** Pump-Probe Spectroscopic Ellipsometry (at ELI Beamlines, Prague, CR)
   phys. stat. solidi RRL ***16****, 220058 (2022)*

3. Temperature Dependence of the **Infrared Dielectric Function of InSb** near the Band Gap
   Two invited talks, 2023 DPG Spring and MRS Fall Meetings, submitted to JVST B

Maybe Next Year

4. *Structural Properties and Optical Constants of* ***$\mathrm{CaF_2}$*** *from 30 meV to 9 eV (UG/MS project)*
5. ***Photoluminescence*** *of Ge-Si-Sn Alloys under ambient and* ***high pressures*** *at low temperature*
6. *Spectroscopic Ellipsometry (30 meV to 6.5 eV)* ***at 10 K using Recirculating Helium Co****oler*

Optical and X-Ray Characterization of $Ge_{1-y}Sn_y$ alloys on GaAs

Haley B. Woolf,[1] **Matt Kim**,[2] Carola Emminger,[1] Carlos A. Armenta,[1] Stefan Zollner[1]

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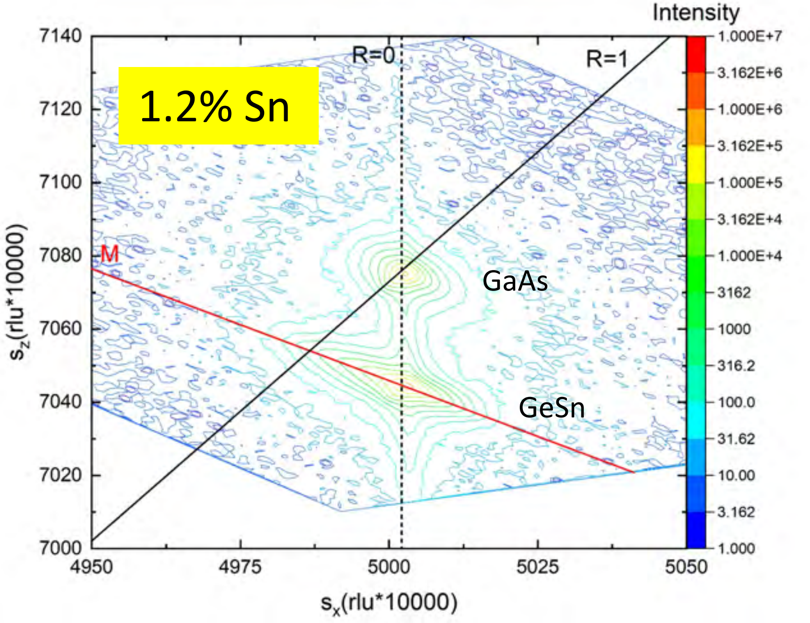
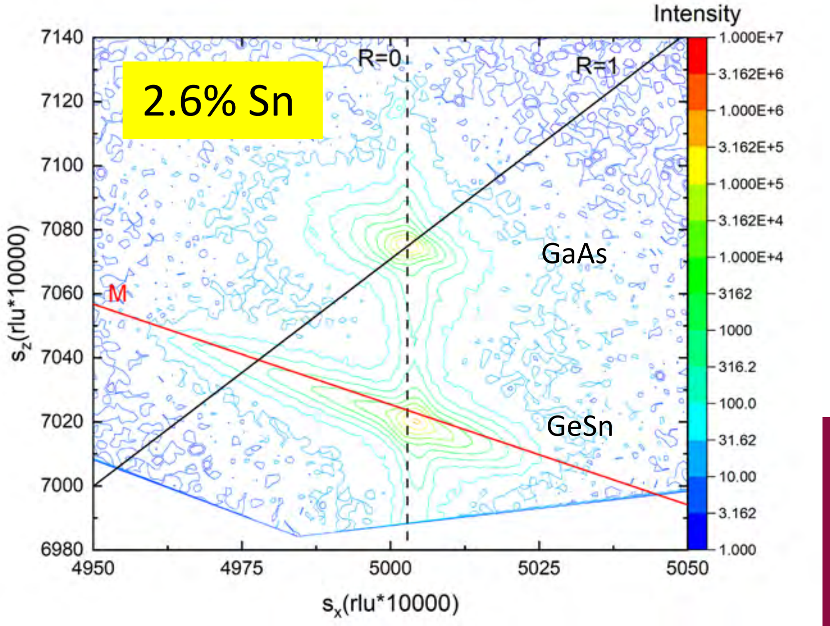
Ge$_{1-y}$Sn$_y$ on GaAs by CVD

- Provided by Matt Kim (commercial reactor)
- Sn content: 1.2% and 2.6% (XRD)
- Very thick: 160 and 115 nm (SE-interference)
- Fully pseudomorphic, no relaxation (XRD), broad asymmetric mosaic streak
- XRD, Ellipsometry, luminescence

(224) g. i. RSM





W-Wavelength Streak

M-Mosaic Spread (Relaxation Line)

Black line drawn from origin (Relaxed)

Dashed line drawn through substrate peak (Pseudomorphic)

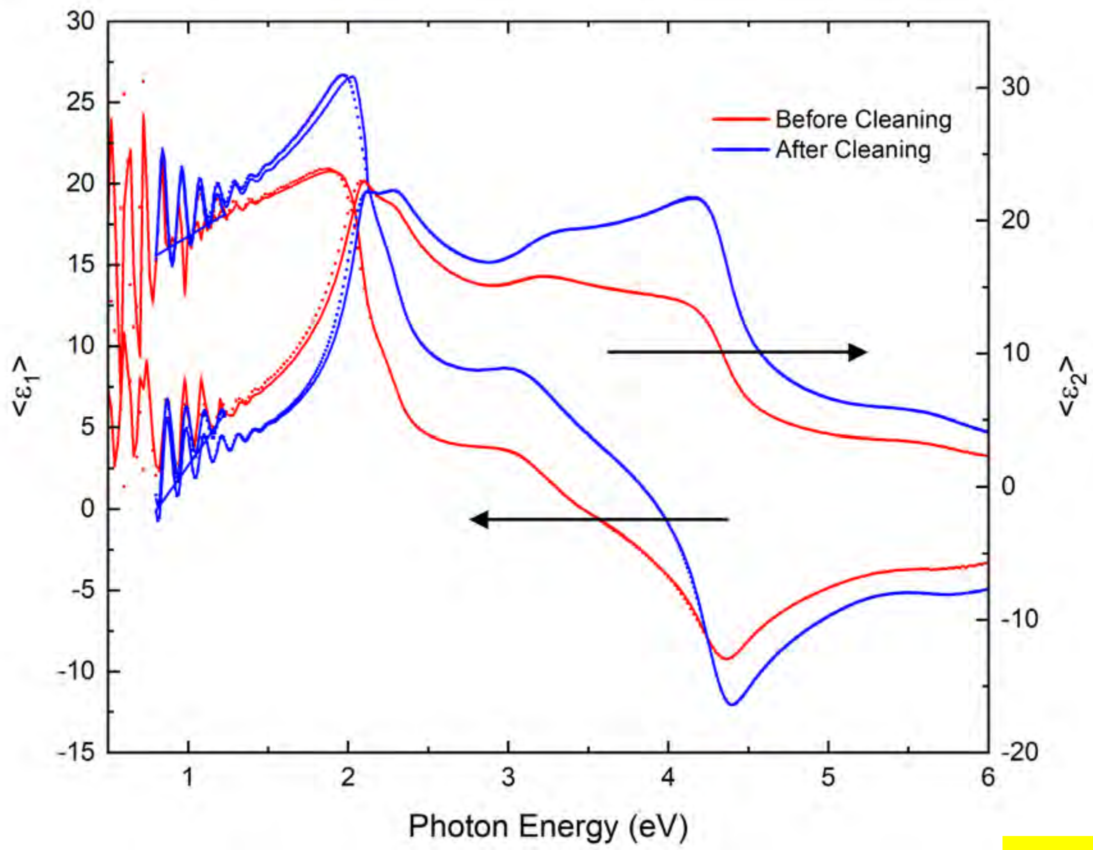
$$s_x = \frac{q_x}{2\pi} = \frac{1}{\lambda}[\cos(\omega) - \cos(2\theta - \omega)]$$

$$s_z = \frac{q_z}{2\pi} = \frac{1}{\lambda}[\sin(\omega) + \sin(2\theta - \omega)]$$

$$\lambda = 1.5406\ \text{Å}$$

Compare: N.S. Fernando, JVST B **36**, 021202 (2018)

Pseudodielectric Function Before / After Cleaning 2.6 %



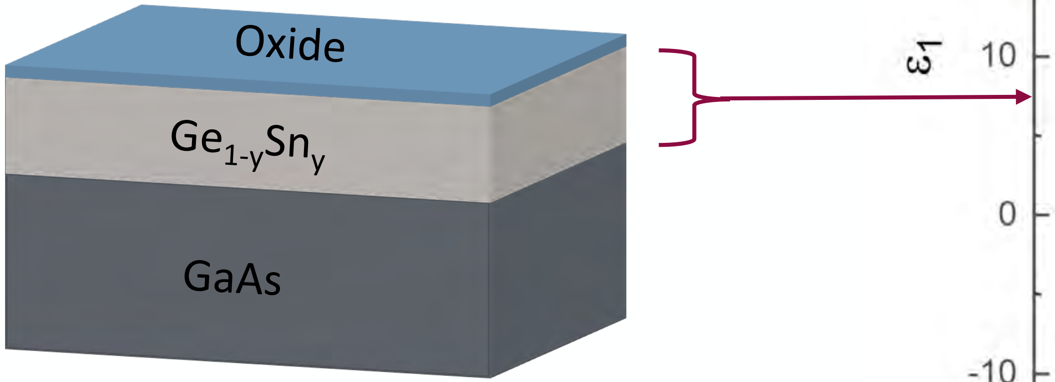
	Oxide Thickness
Before Cleaning (Oct 10th):	68.27 Å
After Cleaning (Oct 11th):	42.3 Å
After 2nd Cleaning (Oct 14th):	27.5 Å

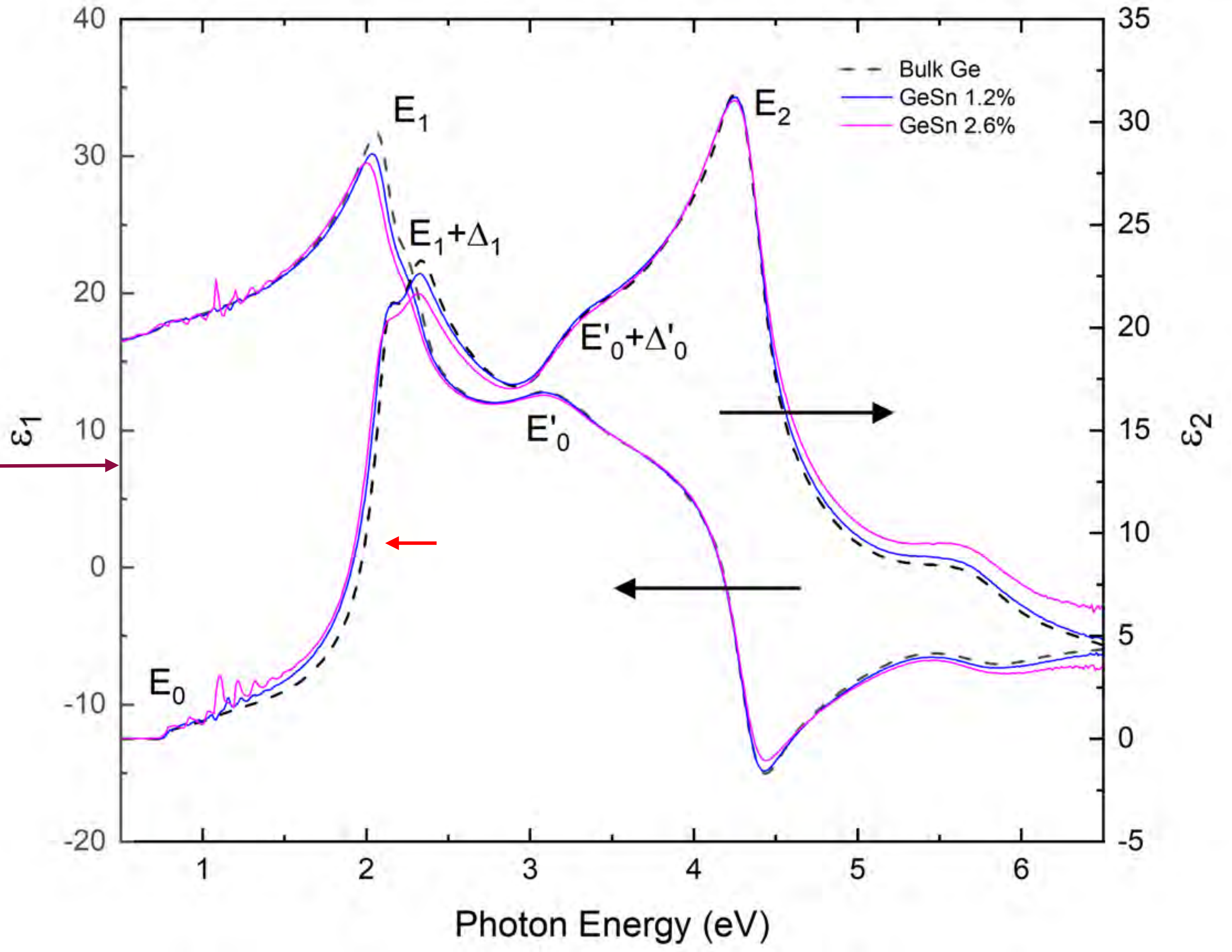
The $Ge_{1-y}Sn_y$ on GaAs sample was cleaned ultrasonically with **water** and then **isopropanol** for 10 mins each to remove organic layers and most of the native oxide.

The native oxide on Ge-Sn alloys is water soluble.

T.N. Nunley, JVST B **34**, 061205 (2016).

GeSn Optical Constants (after oxide correction)

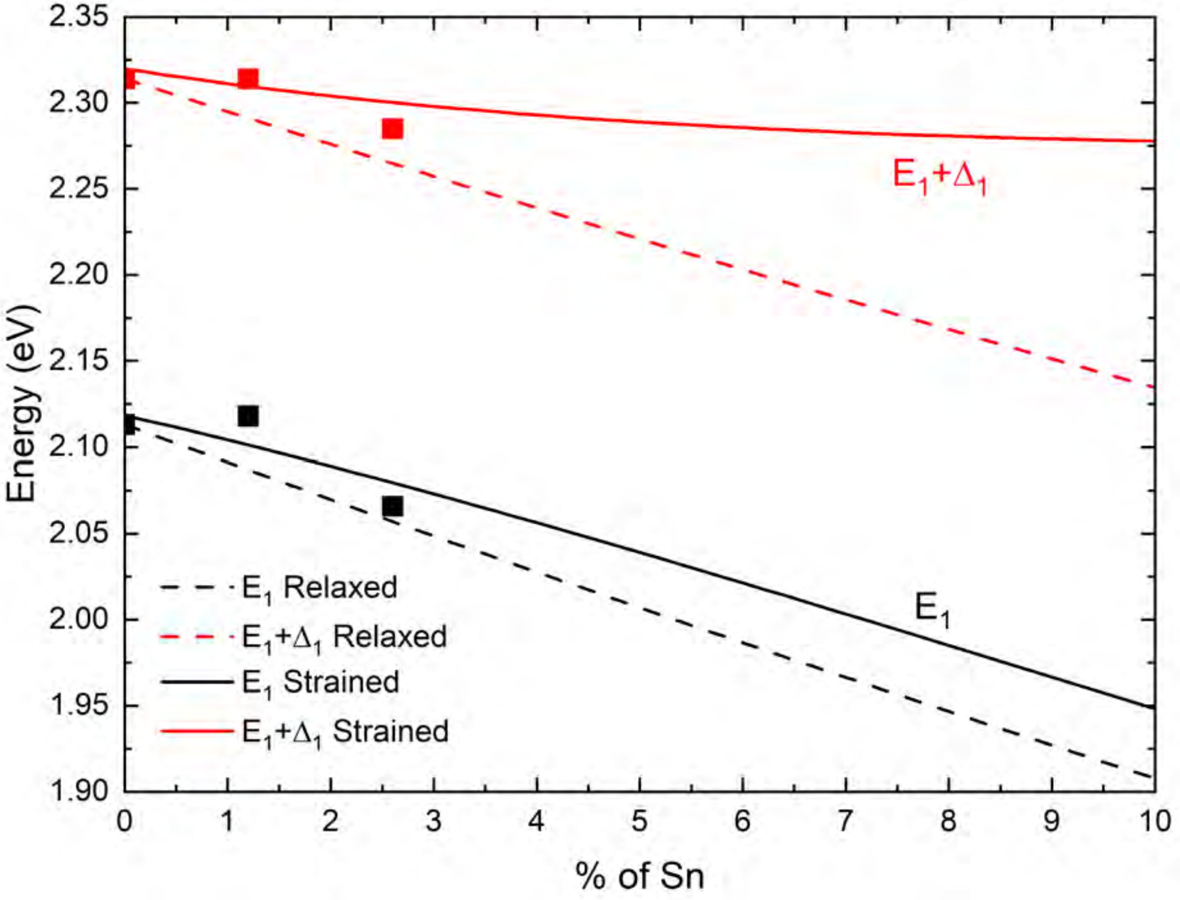




- GeSn optical constants similar to Ge (low Sn content)
- Small redshift below E_1

Compare: T.N. Nunley, JVST B **34**, 061205 (2016).

Dependence of E_1 and $E_1+\Delta_1$ on Tin Content



Relaxed:

$$E_1^{GeSn} = yE_1^{Sn} + (1-y)E_1^{Ge} - b_{GeSn}y(1-y)$$

$$(E_1+\Delta_1)^{GeSn} = y(E_1+\Delta_1)^{Sn} + (1-y)(E_1+\Delta_1)^{Ge} - b_{GeSn}y(1-y)$$

$$b_{GeSn} = 1.350\text{ eV}$$

Continuum elasticity theory

Strained:

$$E_1^{GeSn} = E_1^{Relaxed} + \Delta E_H - \frac{\Delta E_s^2}{\Delta_1}$$

$$(E_1+\Delta_1)^{GeSn} = (E_1+\Delta_1)^{Relaxed} + \Delta E_H + \frac{\Delta E_s^2}{\Delta_1}$$

small shear approximation $\Delta E_s \ll \Delta_1$

$$\Delta E_H = \sqrt{3}\left[yD_1^{1\,Sn} + (1-y)D_1^{1\,Ge}\right]\varepsilon_H$$

$$D_1^{1\,Sn} = -5.4\text{ eV},\quad D_1^{1\,Ge} = -8.7\text{eV},\quad \varepsilon_H = \frac{\varepsilon_\perp + 2\varepsilon_{||}}{3}$$

$$\Delta E_S = \sqrt{6}\left[yD_3^{3\,Sn} + (1-y)D_3^{3\,Ge}\right]\varepsilon_S$$

$$D_3^{3\,Sn} = -3.8\text{ eV},\quad D_3^{3\,Ge} = -5.6\text{ eV},\quad \varepsilon_S = \frac{\varepsilon_\perp - \varepsilon_{||}}{3}$$

More scatter than usual, but consistent with pseudomorphic strain.

Compare: N.S. Fernando, JVST B **36**, 021202 (2018)

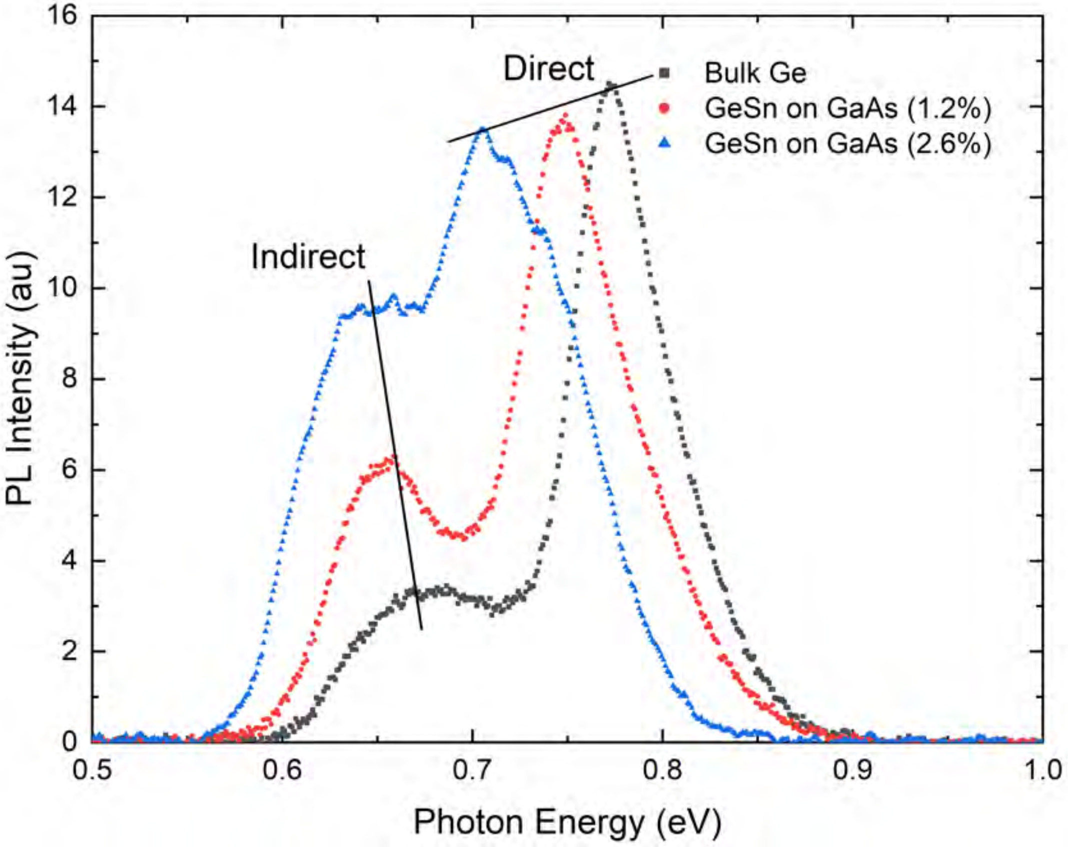
Photoluminescence Data at 300 K (900 mW, 808 nm)

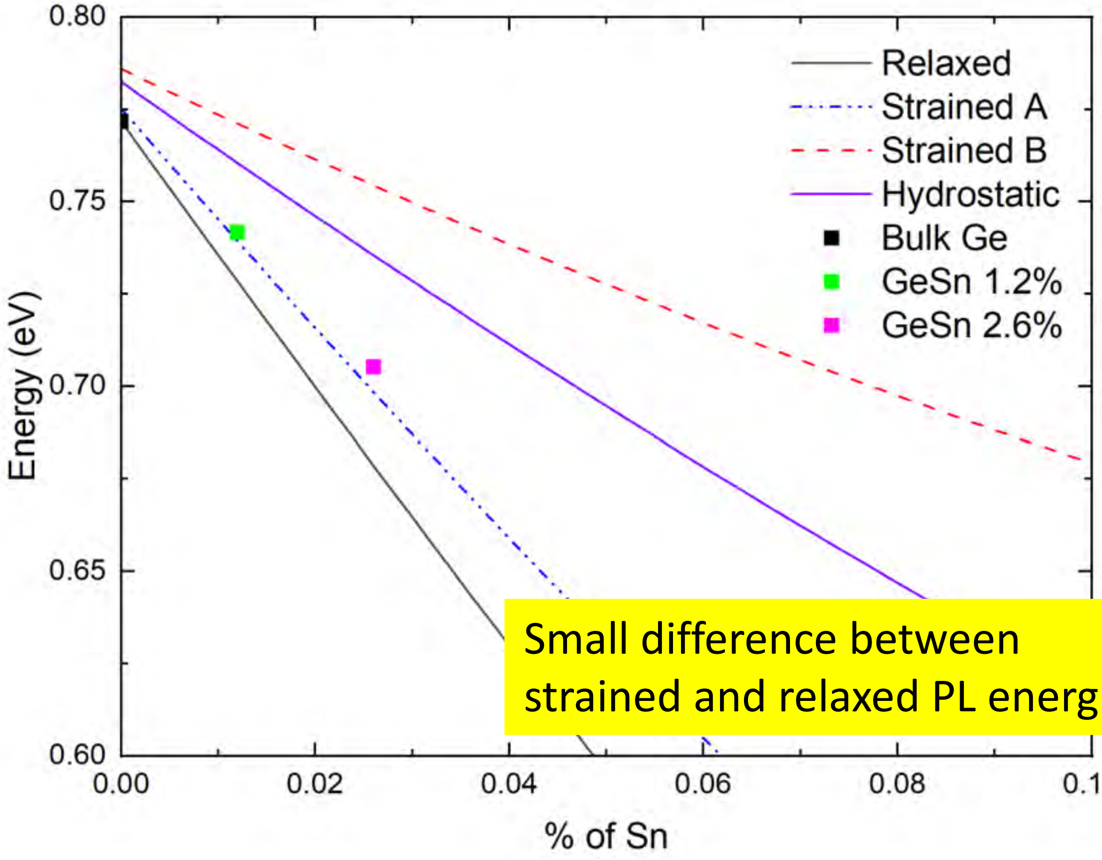
Relaxed: $E_0^{GeSn} = yE_0^{Sn} + (1-y)E_0^{Ge} - b_{GeSn}y(1-y)$

$b_{GeSn} = 2.46\text{ eV}$

Small Shear Strain:

$$E_0^{GeSn} = E_0^{Relaxed} + 3a\varepsilon_H \pm \frac{3}{2}b\varepsilon_S$$

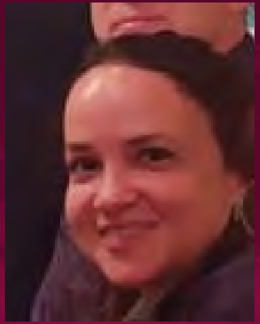




Small difference between strained and relaxed PL energies.

Haley can analyze Raman data under pressure with the same formalism.

Coherent Acoustic Phonon Oscillations in Ge Using Pump-Probe Time-Resolved Spectroscopic Ellipsometry



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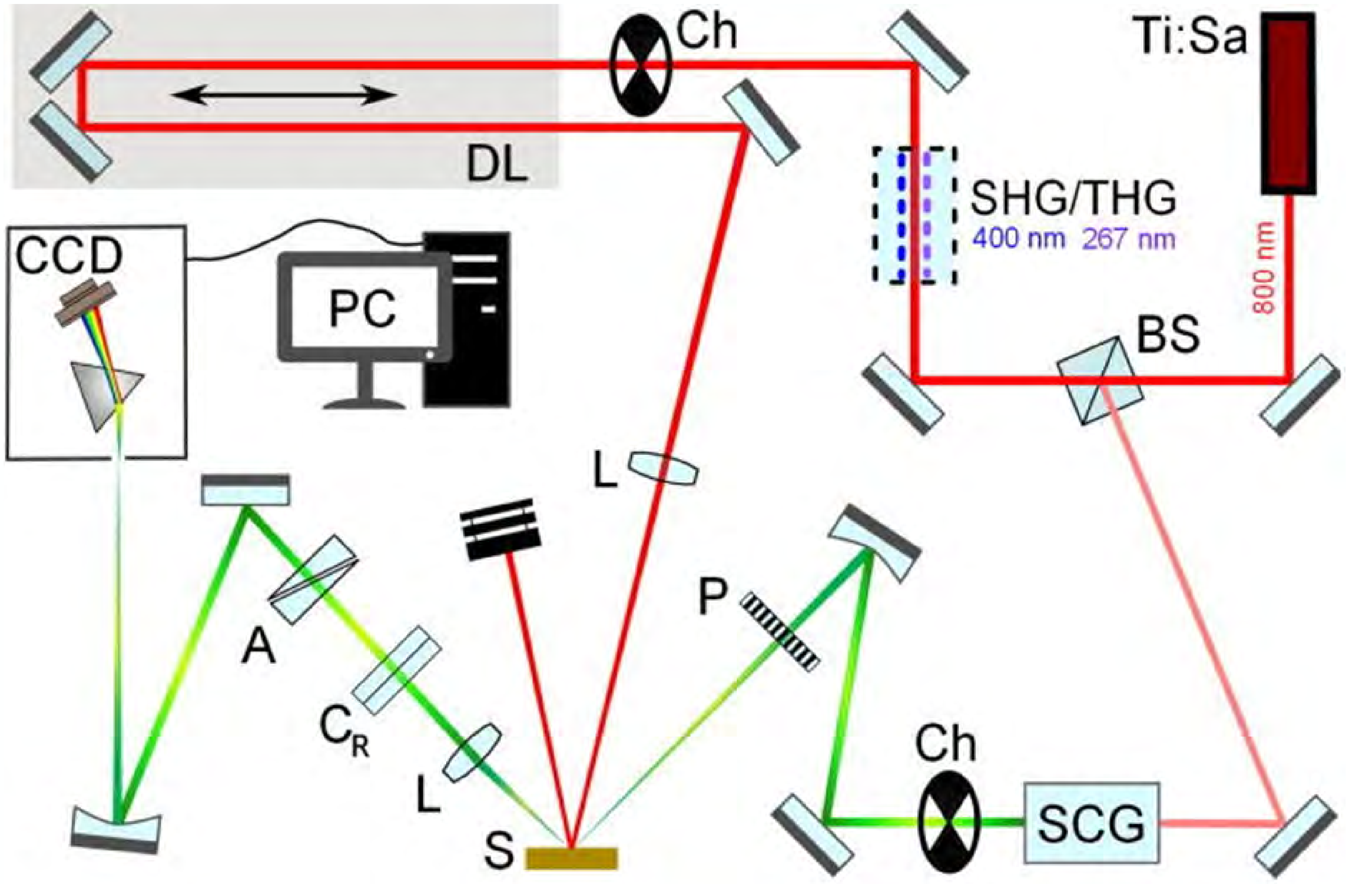
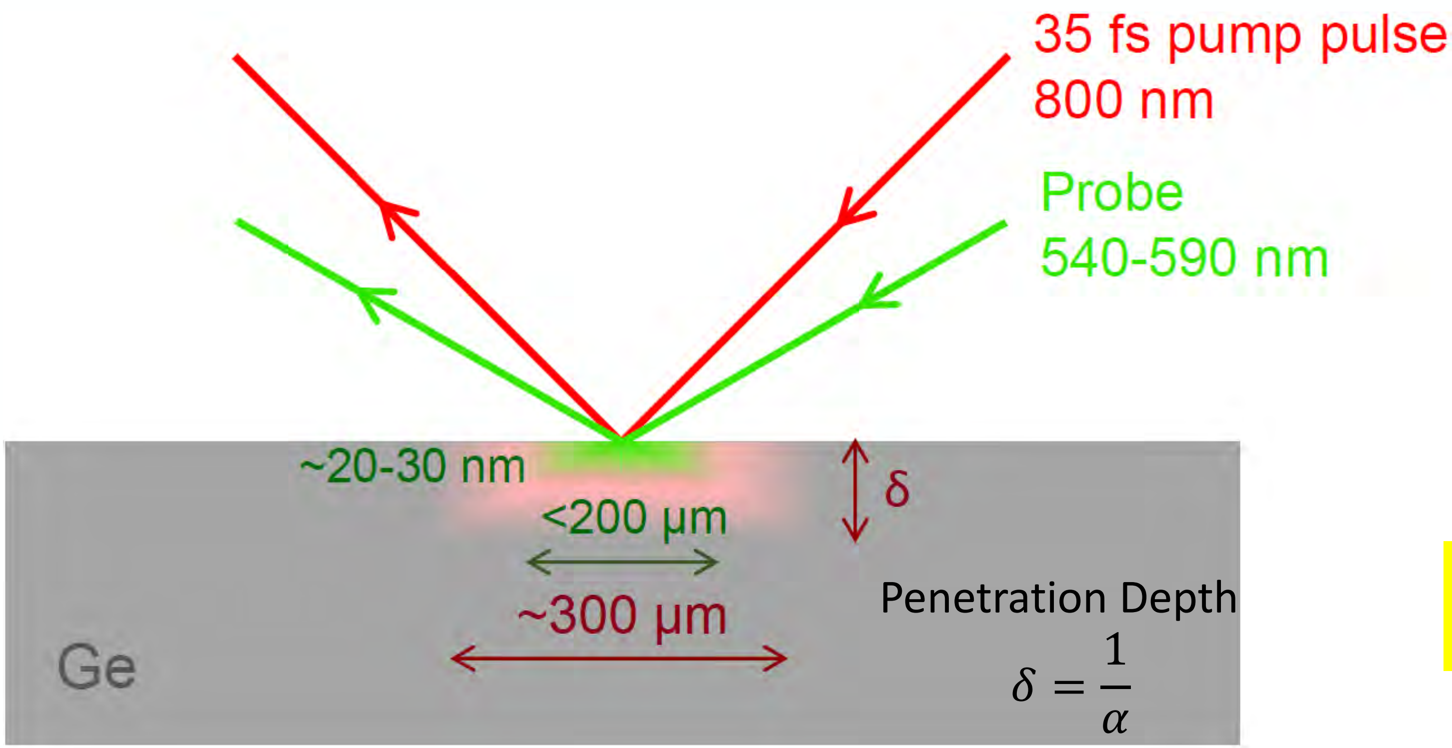
Experimental Setup: Femtosecond Pump-probe Ellipsometry



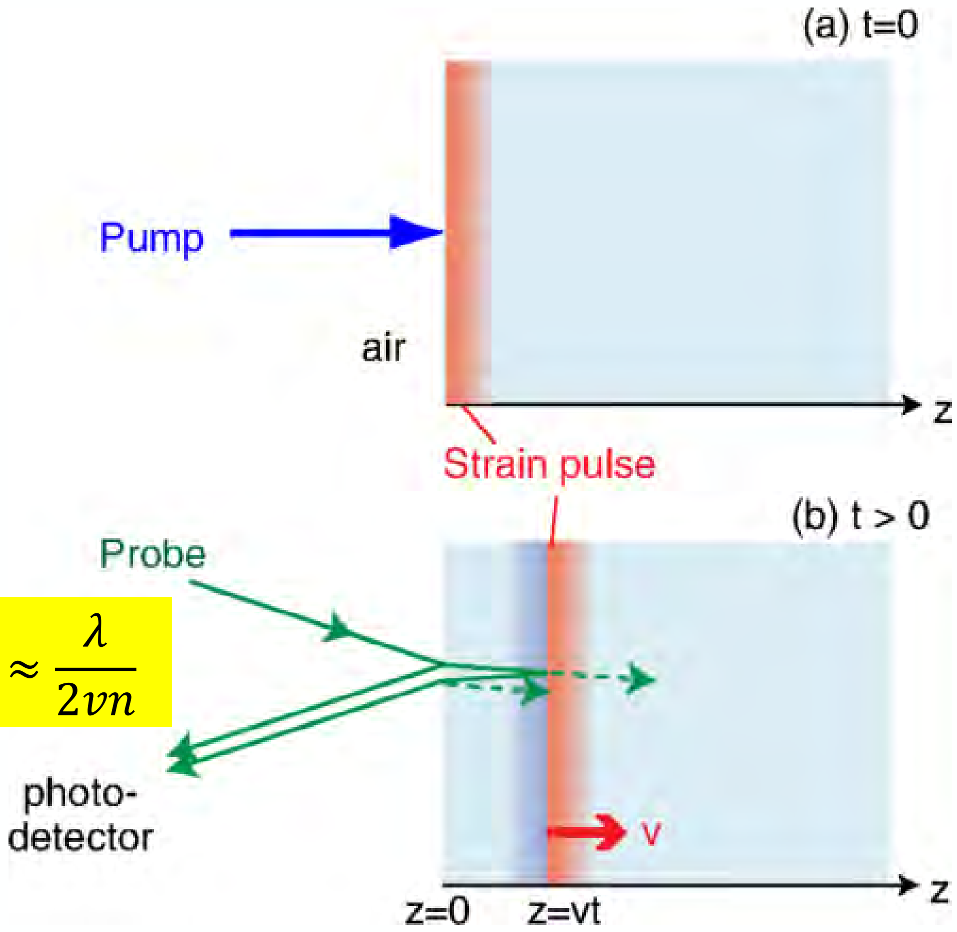
- Ch: Chopper (500 Hz, 250 Hz)
- A: Analyzer
- P: Polarizer
- C_R: Rotating Compensator
- L: Lens
- S: Sample
- DL: Delay Line (~6.67 ns pump-probe delay and 3 fs resolution)
- BS: Beam Spliter
- SHG/THG: Second/Third Harmonic Generation
- SCG: Super-continuum Generation
- CCD: Charge-coupled device detector

ELI Beamlines, Prague, Czech Republic

Femtosecond pump-probe ellipsometry



$$\delta = \frac{1}{\alpha}$$

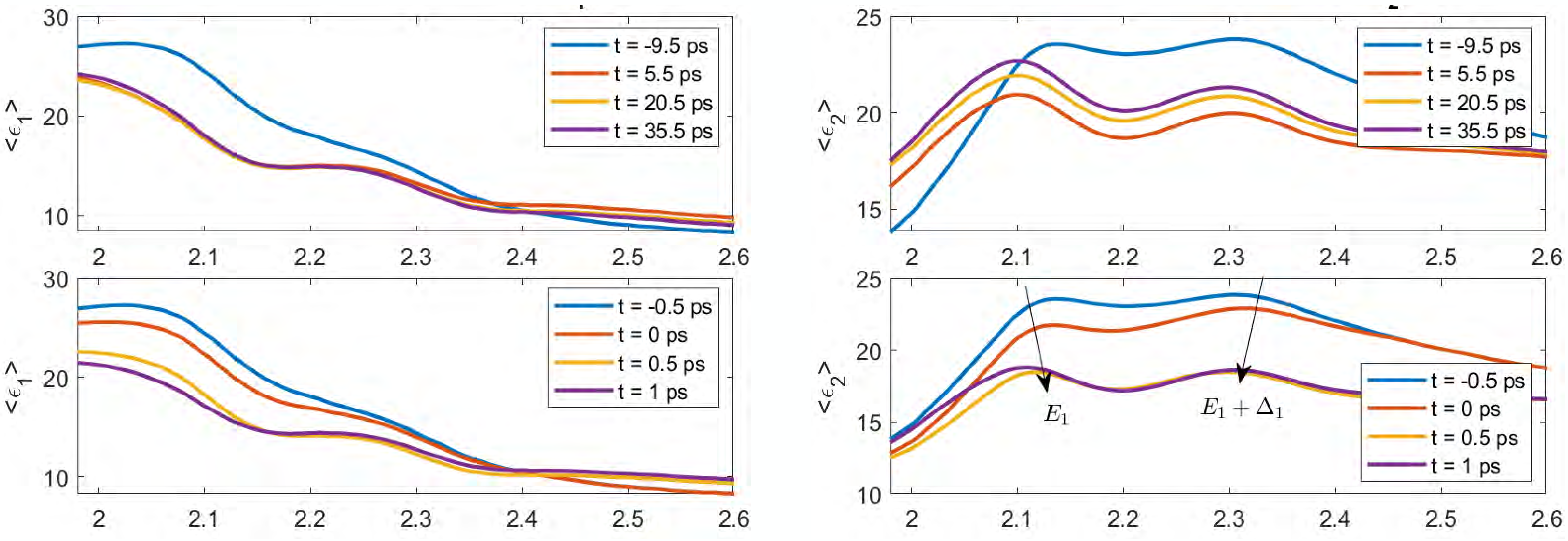


$$T \approx \frac{\lambda}{2vn}$$

Carrier concentration: 1-3×10^{21} cm^{-3}
Band filling and exciton screening

Coherent longitudinal acoustic phonon oscillations

Pseudo-dielectric constant as function of delay time



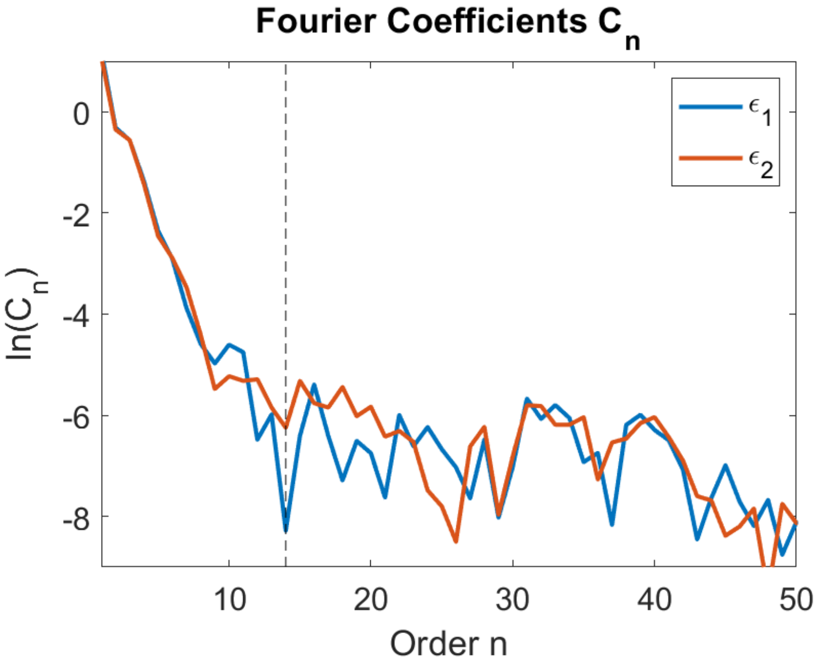
E_1 energy and broadening change as a function of time.
Absorption is reduced and recovers.
Band filling, exciton screening, band gap renormalization.
Modeling is in progress: C. Xu, JAP **125**, 085704 (2019)

High Intensity Ge (100)
3×10^{21} cm^{-3}

Digital Filtering with Fourier transforms, Gauss filters

Reduce noise

Calculate second derivative of ellipsometry spectra



Direct Space Convolution

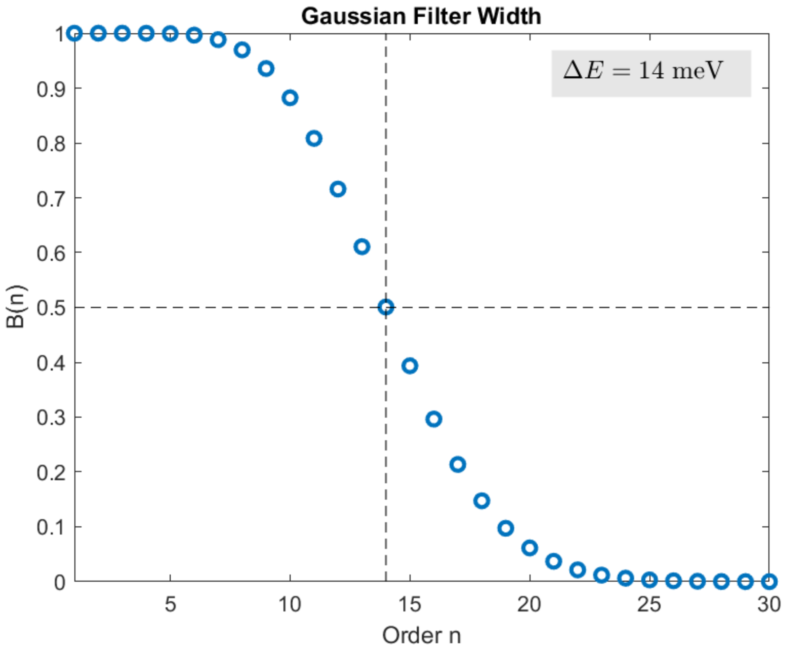
$$\bar{f}(E) = \int_{-\infty}^{\infty} dE' f(E') b_M(E - E')$$

Extended Gauss (EG) Filter:

$$b_M(x) = \sum_{M=0}^{\infty} (-1)^M \frac{a^M}{M!} \frac{d^M}{da^M} \frac{1}{2\sqrt{\pi a}} e^{-\frac{x^2}{4a}}$$

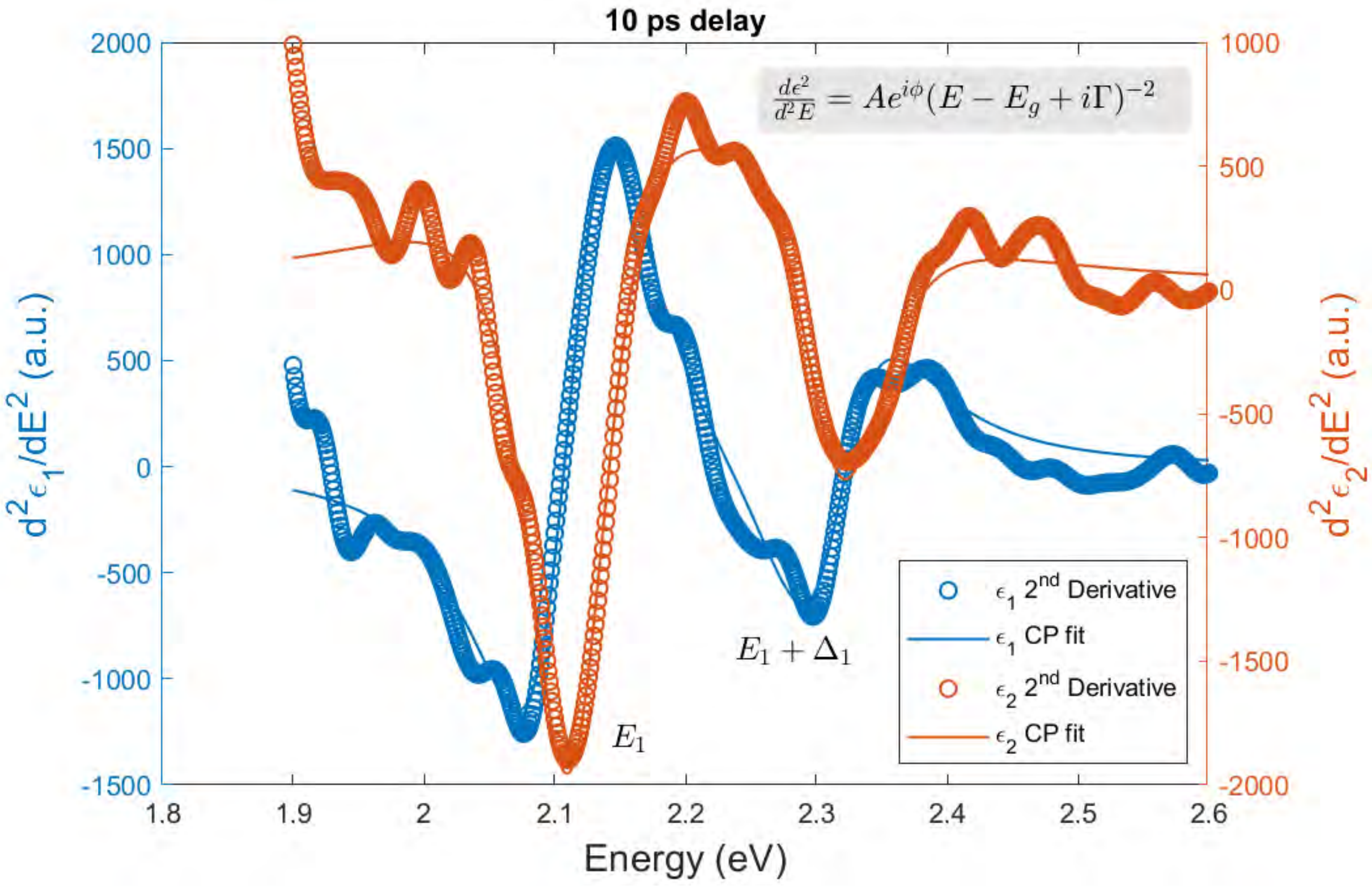
$$a = \frac{1}{\Delta k^2} = \Delta E^2$$

Filter width ΔE is chosen according to white noise onset.



Carola Emminger, phys. stat. solidi RRL 16, 220058 (2022)

Critical Point Parameters as a Function of Delay Time



E_1 and $E_1+\Delta_1$ critical points:

Second derivative calculated using linear filters method (LKKA).

Model dielectric function

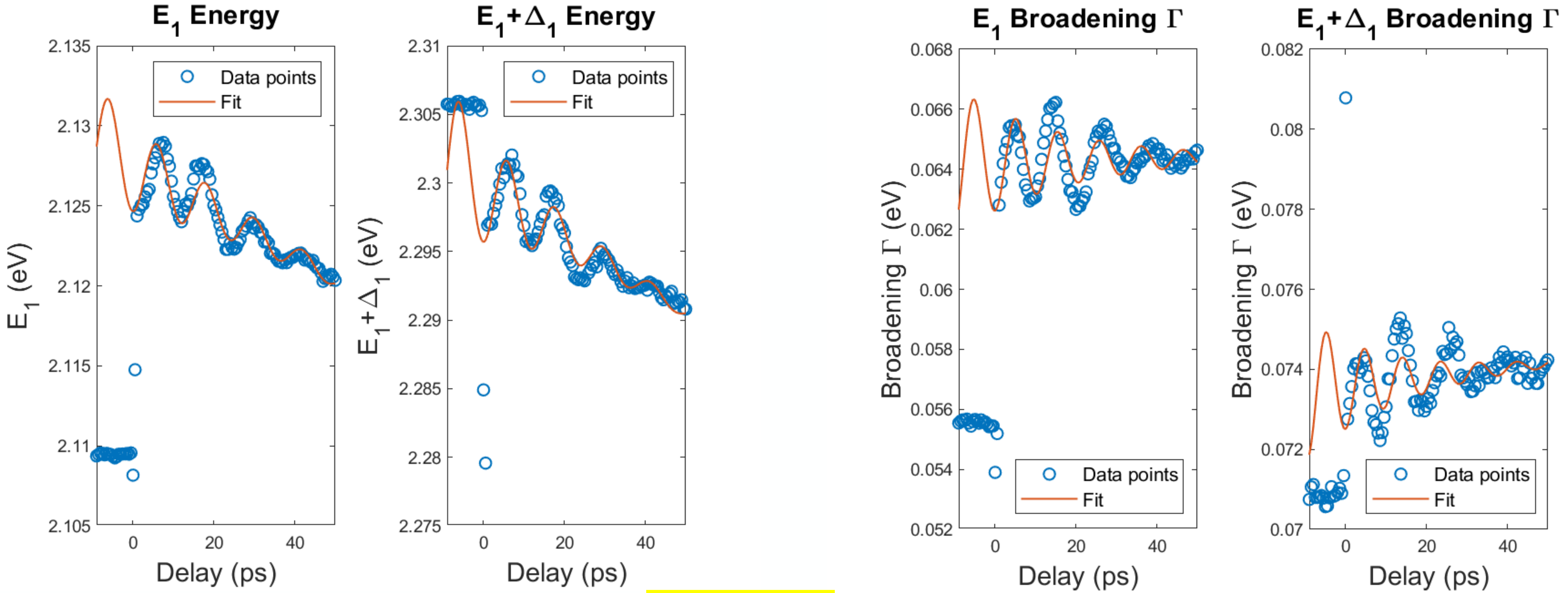
$\epsilon_{2D}(E) = B - Ae^{i\phi}\ln(E - E_g + i\Gamma)$,

where:

- **Amplitude A**
- **Phase angle ϕ**
- **Energy E_g**
- **Broadening Γ**

Compare:
Carola Emminger, phys. stat. solidi RRL 16, 220058 (2022)

E_1 and $E_1+\Delta_1$ CP parameters: Acoustic phonon oscillations



Oscillations fitting function:

$$f(t) = A\cos(\omega t)e^{-ct} - bt + c$$

$$T \approx \frac{\lambda}{2vn}$$

Dependence on surface orientation is under investigation.

High Intensity Ge (100)
11/26/2021*

Compare:
Carola Emminger, phys. stat. solidi RRL 16, 220058 (2022)

Period of oscillation of parameters

$$T \approx \frac{\lambda}{2vn}$$

Oscillation Period						
	(111) HI	(111) MI	(110) HI	(110) MI	(100) HI*	(100) MI
Theory Period E_1 (ps)	9.39		9.65		10.62	
Theory Period $E_1+\Delta_1$ (ps)	9.65		9.92		10.91	
Energy E_1 (ps)	12.2 (0.6)	11.5 (1.2)	9.2 (0.9)	8.6 (1.3)	12.0 (0.4)	10.7 (0.8)
Energy $E_1+\Delta_1$ (ps)	14.6 (3.3)	11.0 (1.1)	9.5 (1.5)	8.4 (0.7)	11.9 (0.4)	11.0 (0.5)

Good agreement with theory for (100) surface orientation.

Dependence on surface orientation is under investigation.
Error bars too large to see dependence of period on surface orientation.
More measurements in February 2023.

Temperature Dependence of the Infrared Dielectric Function of InSb near the Direct Band Gap

FA9550-20-1-0135
W911NF-2210130

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CESY M. ZAMARRIPA, JADEN R. LOVE, AND STEFAN ZOLLNER

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Submitted to J. Vac. Sci. Technol. B (under review)

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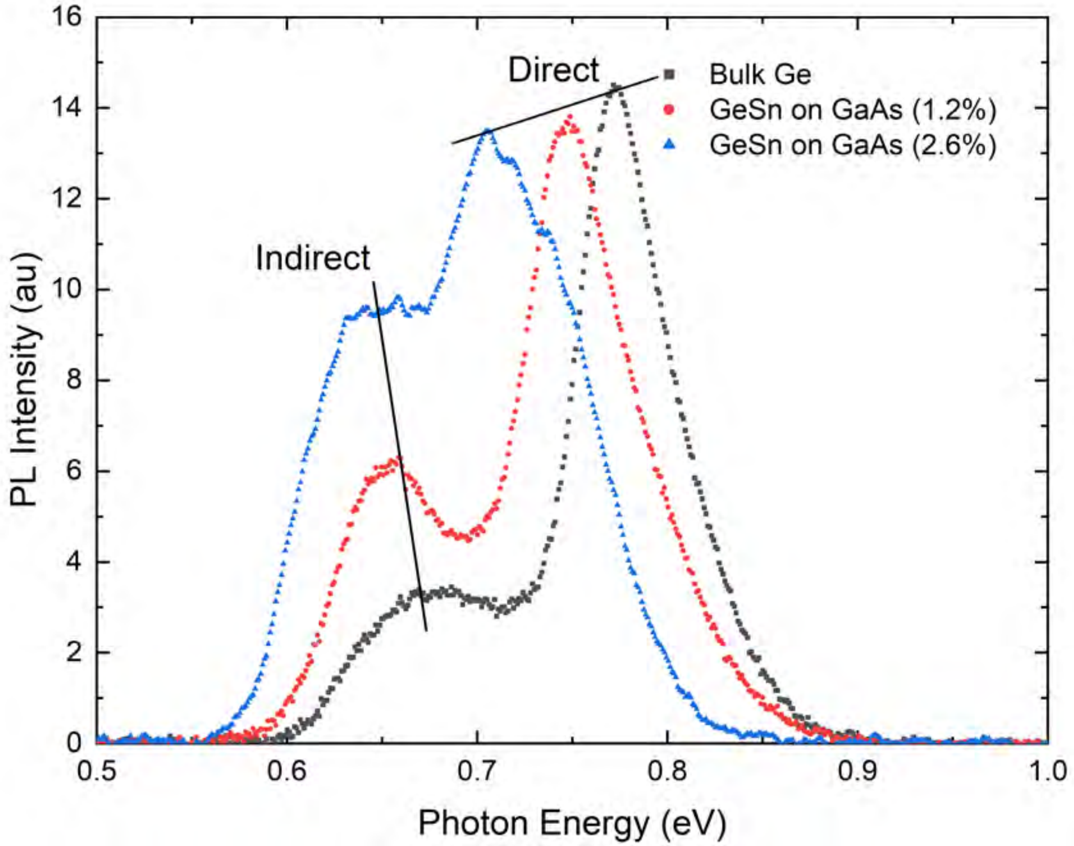
Motivation: Modeling of Detector Spectral Response

Photoluminescence of Ge-Sn Alloys:
300 K, 900 mW, 808 nm

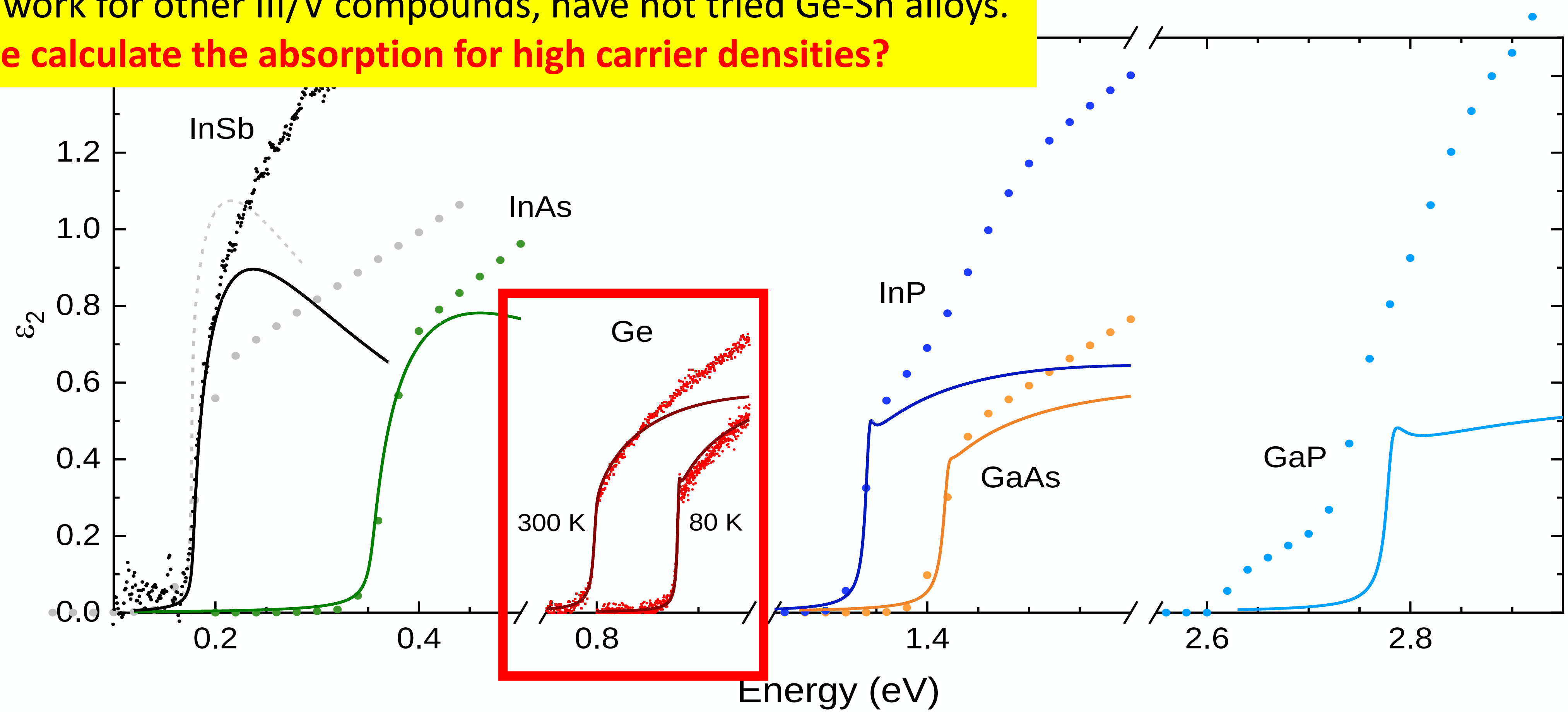


Questions:

- If we see a photoluminescence spectrum, can you calculate the detector response?
- Can we calculate the absorption spectrum?
- Would that be useful?

Calculation of Absorption Spectrum from k.p Theory

Can we calculate the absorption spectrum?
Yes, we can for Ge in the low carrier density limit.
It does not work for other III/V compounds, have not tried Ge-Sn alloys.
How can we calculate the absorption for high carrier densities?

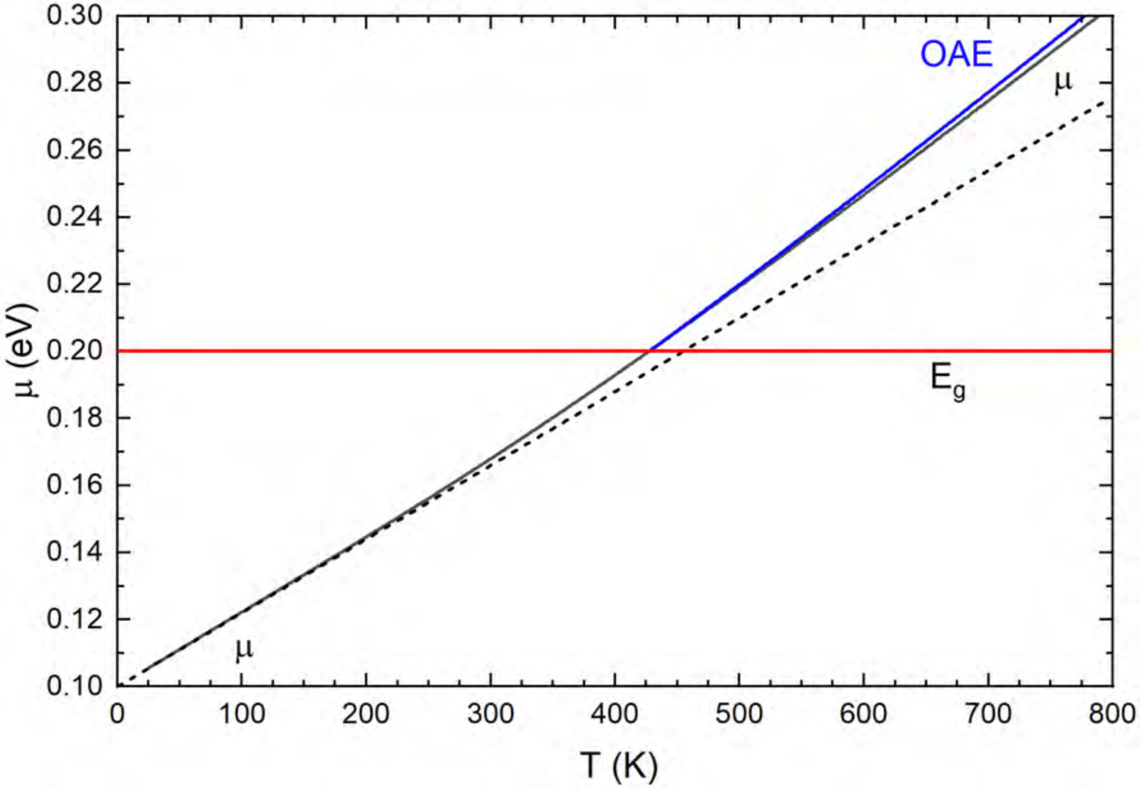


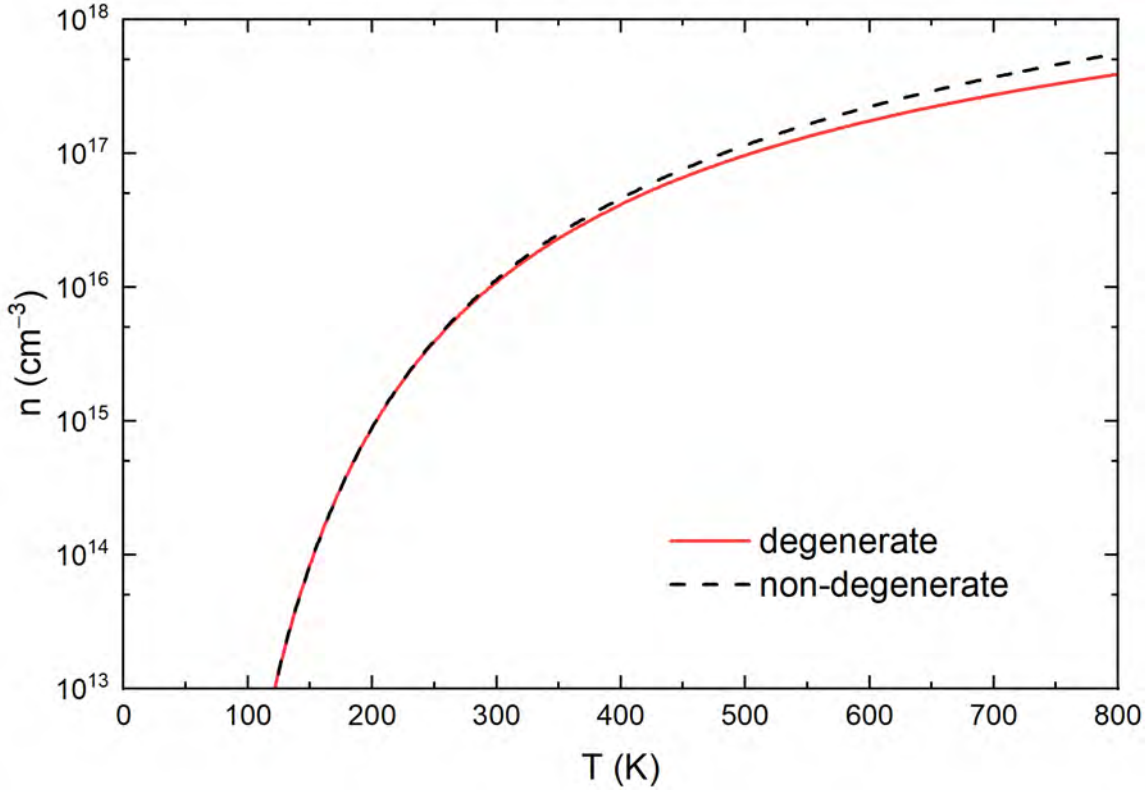
Carola Emminger, JAP **131**, 165701 (2022).

Temperature Changes Intrinsic Carrier Concentration in InSb

Above 400 K, the Fermi level is above the conduction band minimum.

Carrier concentration reaches 10^{18} cm^{-3} near the melting point of InSb (800 K)

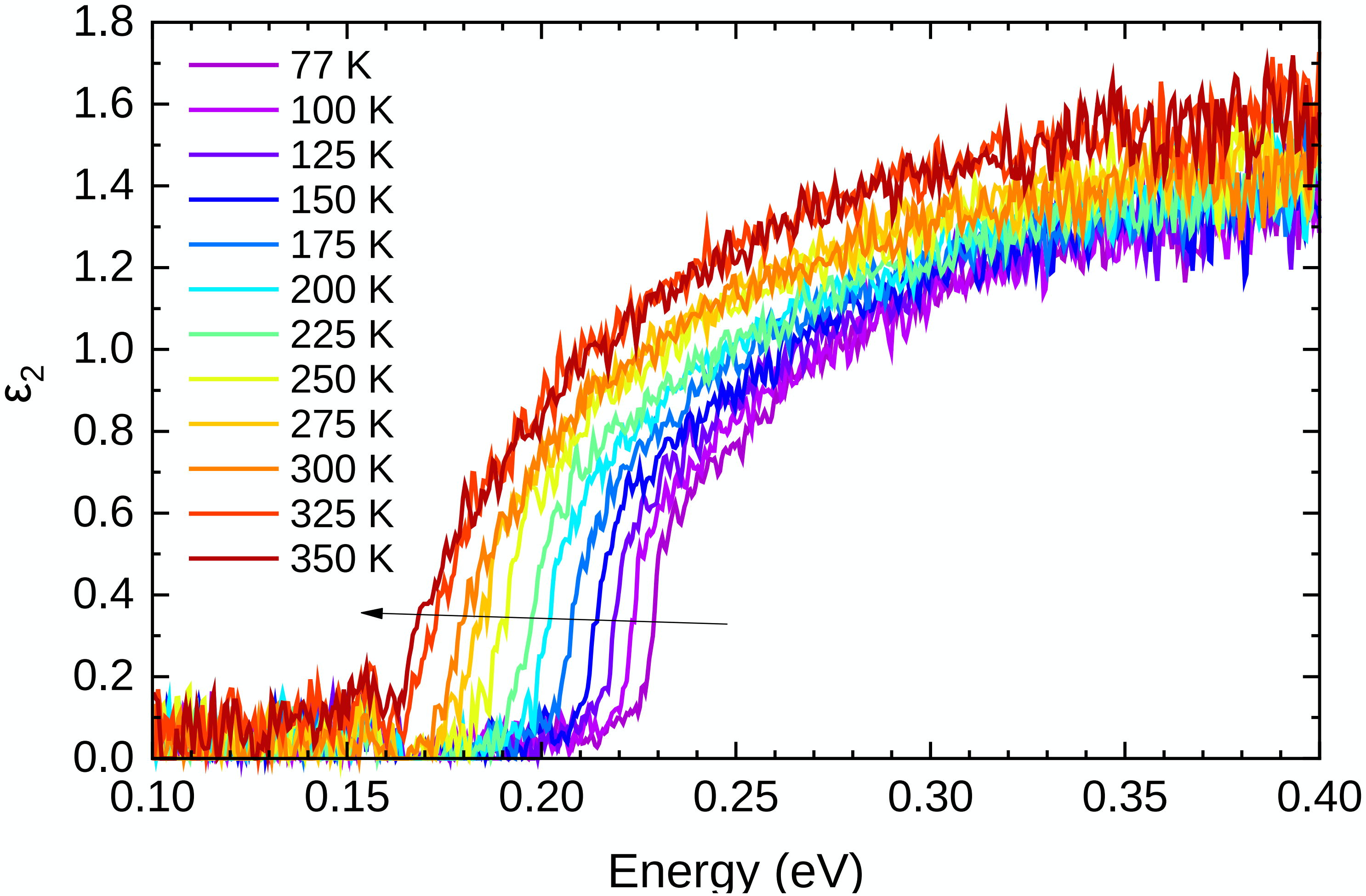




InSb: How do many-body effects influence the absorption by MWIR detectors?

Sonam Yadav (unpublished)
Marc D. Ulrich, J. Comp. Electron. **1**, 431 (2002)

InSb (100): Initial attempt promising, but that is not the whole story



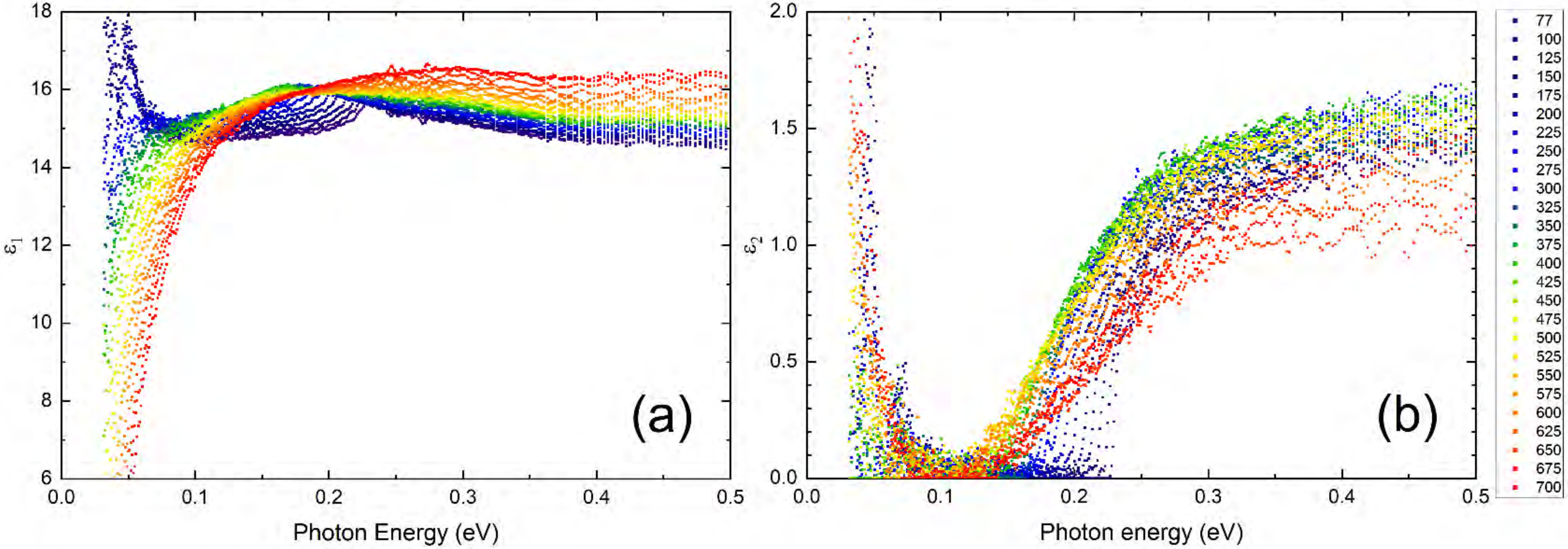
Multiple experimental issues:

- InSb sample cracks, melts, reacts with the Cu sample holder.
- Adhesive (carbon nanoparticles, silver paint) expands, evaporates, redeposits on the windows.
- Beam larger than sample: Depolarization from sample holder reflections.
- Black-body radiation, heat shield.
- Cryostat leaks, thermocouple breaks.

Initial result: **Clear redshift with increasing temperature (up to 450 K).** Strange things happen above 450 K.

Cesy M. Zamarripa, Nuwanjula Samarasingha (unpublished)

Dielectric Functions of InSb from 80 to 800 K

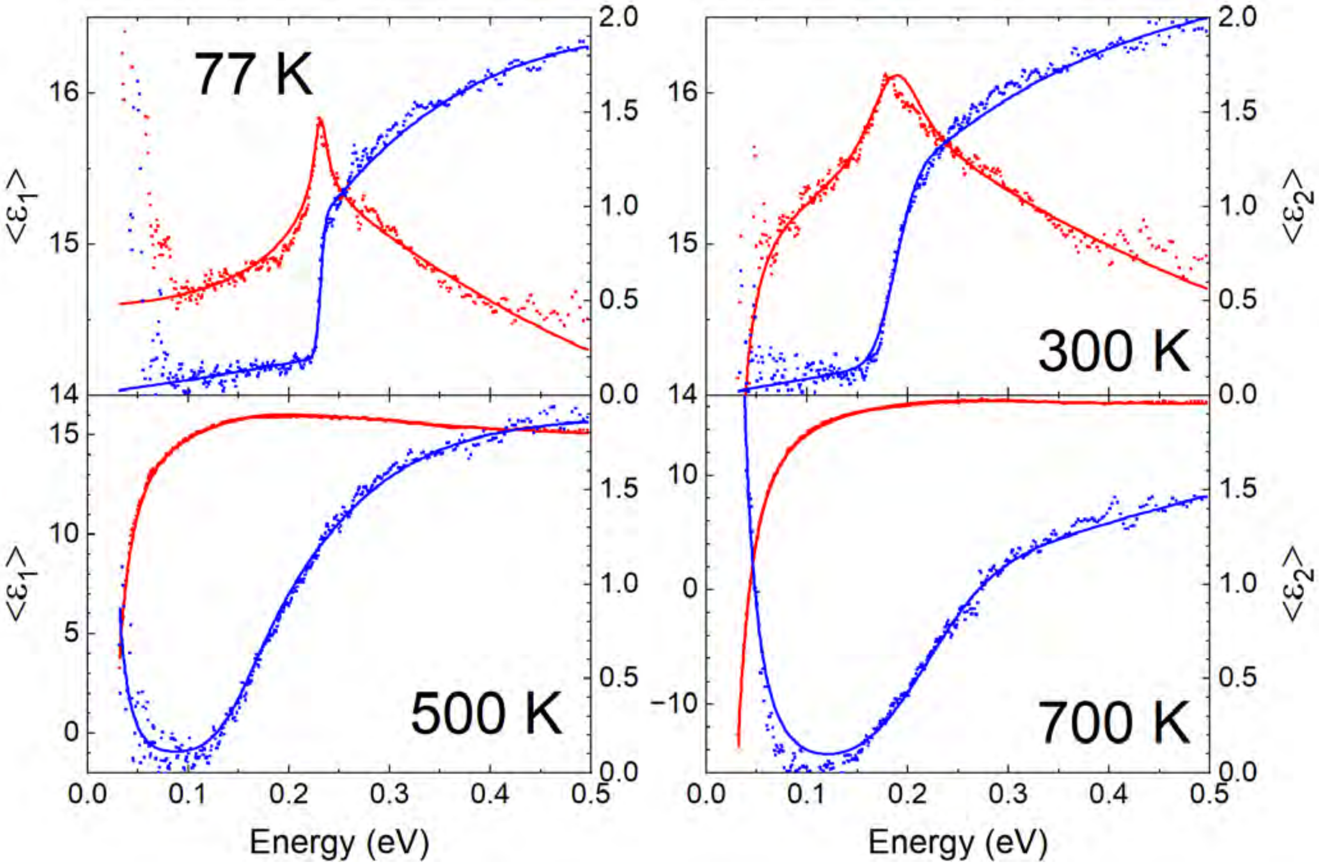


- Band gap changes with temperature (but only below 500 K).
- Reduction of absorption coefficient at high temperatures.
- Drude response at high temperatures (thermally excited carriers).
- *Depolarization artifacts at long wavelengths (below 300 K).*

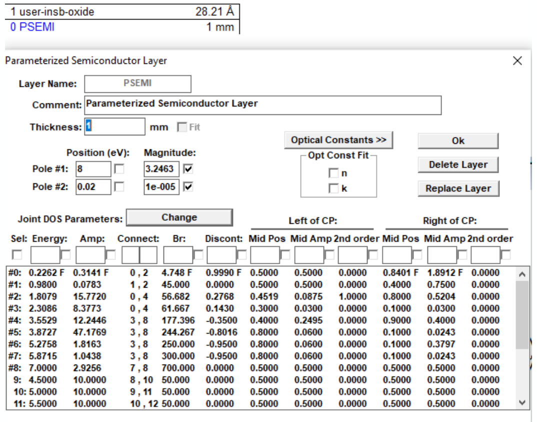
M. Rivero Arias *et al.*, JVST B (submitted).

Band gap analysis: Parametric semiconductor model

- How does the band gap of InSb change with temperature?



Parametric-Semiconductor Model:



1 user-insb-oxide	28.21 Å
0 PSEMI	1 mm

Parameterized Semiconductor Layer

Layer Name: PSEMI

Comment: Parameterized Semiconductor Layer

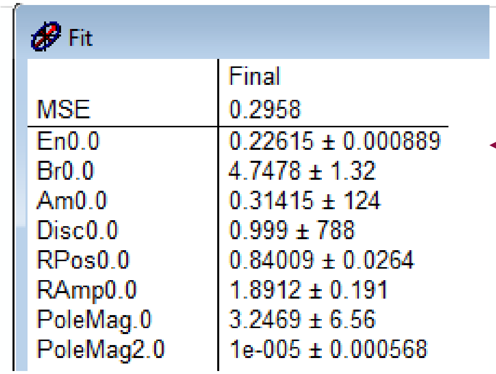
Thickness: 1 mm ☐ Fit

	Position (eV):		Magnitude:	
Pole #1:	8	☐	3.2463	☑
Pole #2:	0.02	☐	1e-005	☑

Opt Const Fit: ☐ n ☐ k

Joint DOS Parameters:

						Left of CP:			Right of CP:		
Sel:	Energy:	Amp:	Connect:	Br:	Discont:	Mid Pos	Mid Amp	2nd order	Mid Pos	Mid Amp	2nd order
#0:	0.2262 F	0.3141 F	0 , 2	4.748 F	0.9990 F	0.5000	0.5000	0.0000	0.8401 F	1.8912 F	0.0000
#1:	0.9800	0.0783	1 , 2	45.000	0.0000	0.5000	0.5000	0.0000	0.4000	0.7500	0.0000
#2:	1.8079	15.7720	0 , 4	56.682	0.2768	0.4519	0.0875	1.0000	0.8000	0.5204	0.0000
#3:	2.3086	8.3773	0 , 4	61.667	0.1430	0.3000	0.0300	0.0000	0.1000	0.0300	0.0000
#4:	3.5529	12.2446	3 , 8	177.396	-0.3500	0.4000	0.2495	0.0000	0.9000	0.4000	0.0000
#5:	3.8727	47.1769	3 , 8	244.267	-0.8016	0.8000	0.0600	0.0000	0.1000	0.0243	0.0000
#6:	5.2758	1.8163	3 , 8	250.000	-0.9500	0.8000	0.0600	0.0000	0.1000	0.3797	0.0000
#7:	5.8715	1.0438	3 , 8	300.000	-0.9500	0.8000	0.0600	0.0000	0.1000	0.0243	0.0000
#8:	7.0000	2.9256	7 , 8	700.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000
9:	4.5000	10.0000	8 , 10	50.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000
10:	5.0000	10.0000	9 , 11	50.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000
11:	5.5000	10.0000	10 , 12	50.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000



Fit

	Final
MSE	0.2958
En0.0	0.22615 ± 0.000889
Br0.0	4.7478 ± 1.32
Am0.0	0.31415 ± 124
Disc0.0	0.999 ± 788
RPos0.0	0.84009 ± 0.0264
RAmp0.0	1.8912 ± 0.191
PoleMag.0	3.2469 ± 6.56
PoleMag2.0	1e-005 ± 0.000568

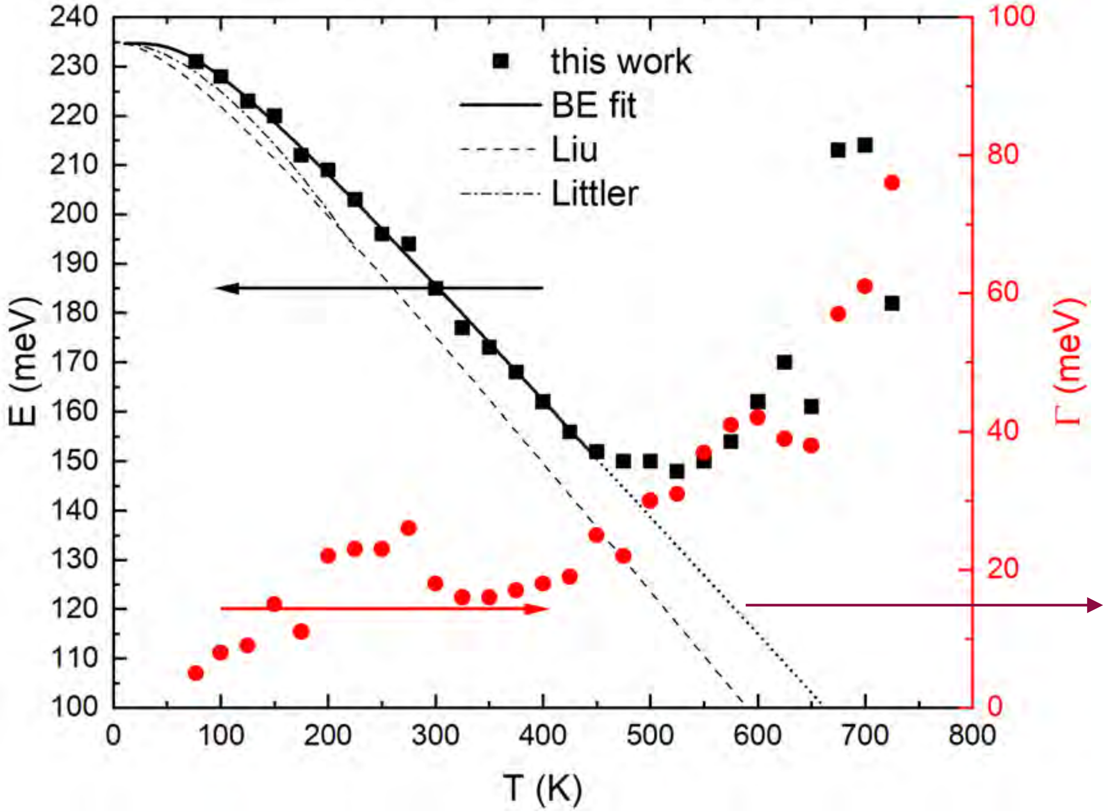
Also vary "shape parameters".

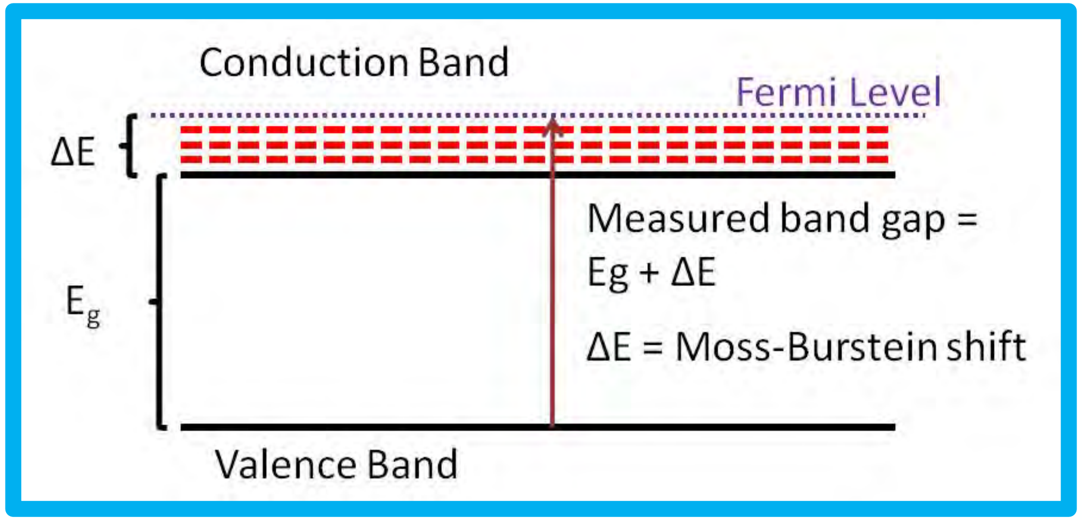
Asymmetric peak shape poorly described.

Try Tanguy oscillator for excitonic line shape.

C. M. Herzinger, B. Johs, et al., J. Appl. Phys. **83**, 3323 (1998).

Direct Band Gap of InSb versus Temperature





Conduction Band

Fermi Level

ΔE

E_g

Measured band gap = Eg + ΔE

ΔE = Moss-Burstein shift

Valence Band

Bose-Einstein

$$E_g(T) = a - b\left[1 - \frac{2}{e^{\frac{\theta}{T}}-1}\right]$$

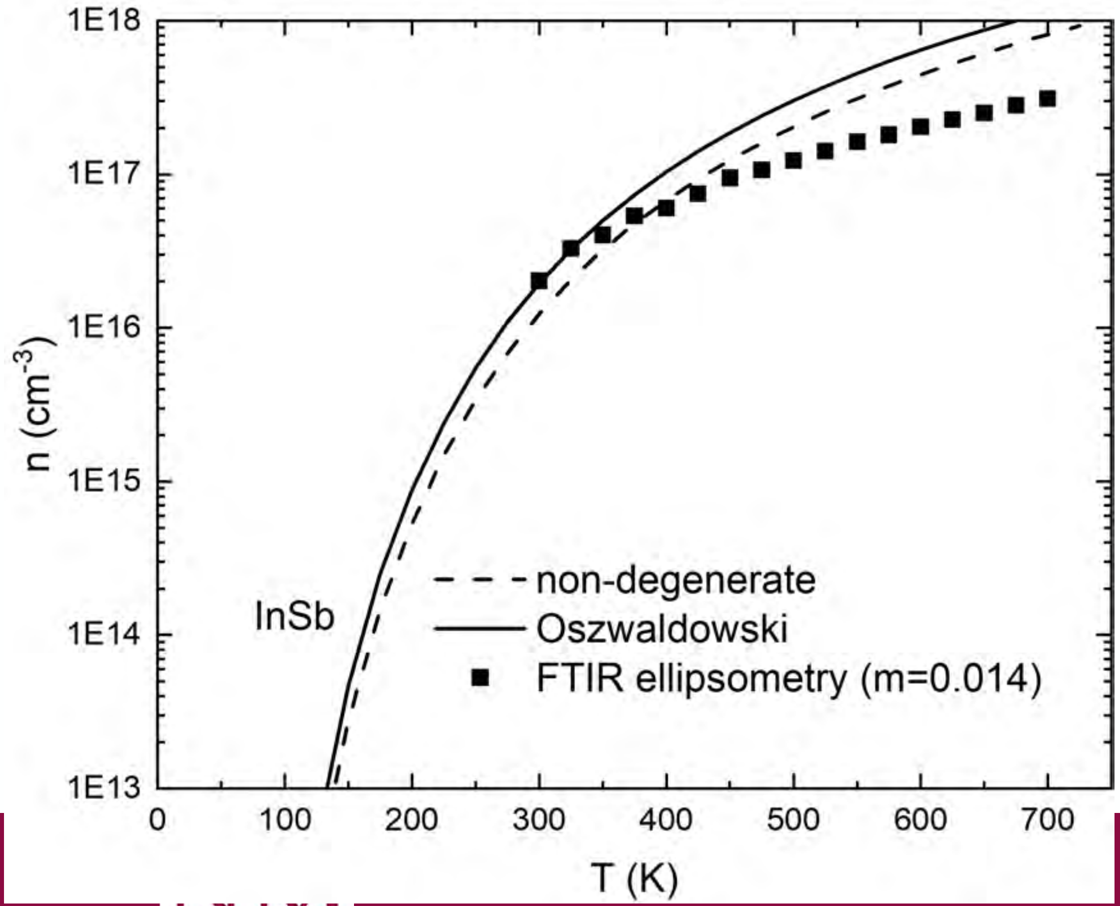
- Band gap changes with temperature (but only below 500 K)
- Described by Bose-Einstein model below 500 K: Logothetidis, PRB **31**, 947 (1985).
- Increase above 500 K: thermal Burstein-Moss shift.

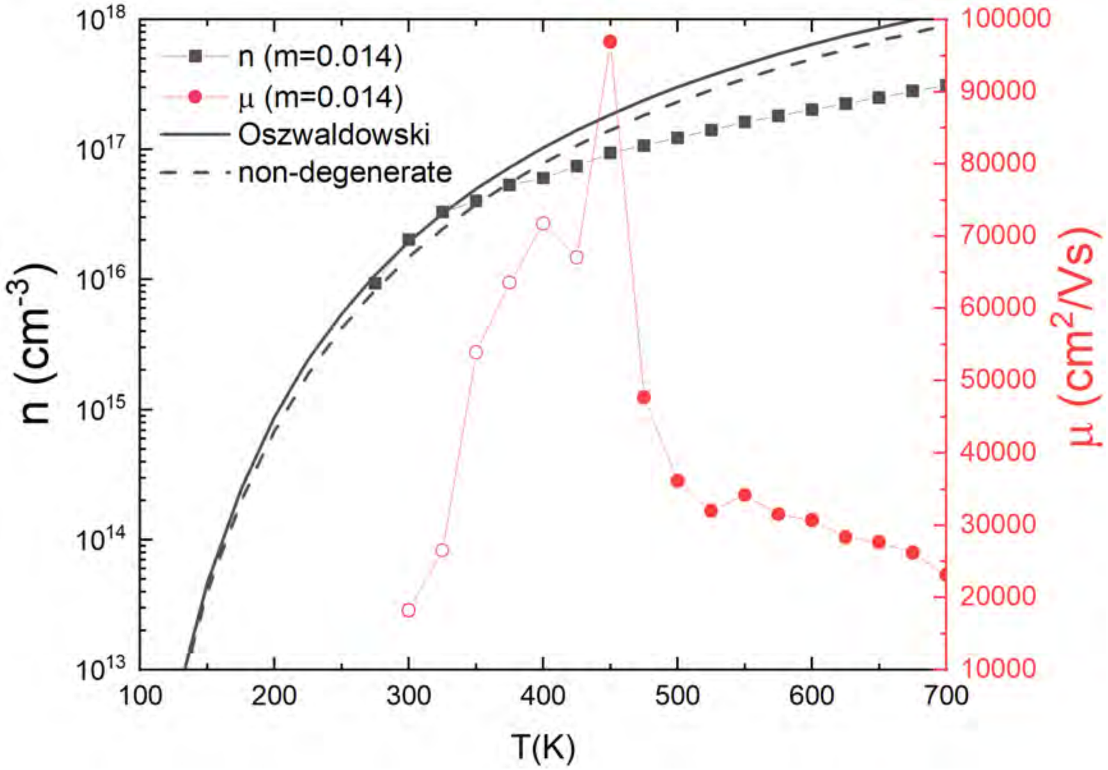
T.S. Moss, Proc. Phys. Soc. **67**, 775 (1954).
E. Burstein, Phys. Rev. **93**, 632 (1954).

Free-carrier absorption

To model the Drude response, we make some really bad assumptions:

- Parabolic bands (ignore non-parabolicity)
- Effective mass constant m_e=0.014 (independent of temperature)





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Required model improvements

$$\varepsilon_2(E) = \frac{2\pi A\sqrt{R}}{E^2}\left\{\sum_{n=1}^{\sqrt{g}} \frac{2R}{n}\left(\frac{1}{n^2}-\frac{n^2}{g^2}\right)\delta\left[E-E_0+\frac{R}{n^2}\left(1-\frac{n^2}{g}\right)^2\right] + \frac{\sinh(\pi g k)\mathrm{H}(E-E_0)}{\cosh(\pi g k)-\cosh\left(\pi g\sqrt{k^2-\frac{4}{g}}\right)}\right\}[f_h(E)-f_e(E)]$$

- **Absorption by screened excitons** (Hulthen potential)
- Kramers-Kronig transform following Tanguy (includes broadening Γ)
- **Degenerate Fermi-Dirac statistics to calculate f_h and f_e.**
- Two terms for light and heavy excitons
- Non-parabolicity and temperature-dependent mass included from k.p theory
- **Screening parameter $g=12/\pi^2 a_R k_{TF}$ (large: no screening)**
- Only two free parameters: Band gap E_0 and broadening Γ
- Amplitude A and exciton binding energy R from k.p theory and effective masses

Christian Tanguy, Phys. Rev. B **60**, 10660 (1999).
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Conclusion

1. Optical and X-ray Characterization of thick **GeSn alloys** (1-2% Sn) **on GaAs**
   Ken Hass Outstanding Student Paper Award March 2022, Forum on Industrial & Applied Physics, APS

2. Coherent Longitudinal Acoustic **Phonon Oscillations** in Ge
   using **Femtosecond** Pump-Probe Spectroscopic Ellipsometry (at ELI Beamlines, Prague, CR)
   *phys. stat. solidi RRL **16**, 220058 (2022)*

3. Temperature Dependence of the **Infrared Dielectric Function of InSb** near the Band Gap
   Two invited talks, 2023 DPG Spring and MRS Fall Meetings, submitted to JVST B

Maybe Next Year

4. *Structural Properties and Optical Constants of **CaF$_2$** from 30 meV to 9 eV (UG/MS project)*
5. ***Photoluminescence** of Ge-Si-Sn Alloys under ambient and **high pressures** at low temperature*
6. *Spectroscopic Ellipsometry (30 meV to 6.5 eV) **at 10 K using Recirculating Helium Cooler***