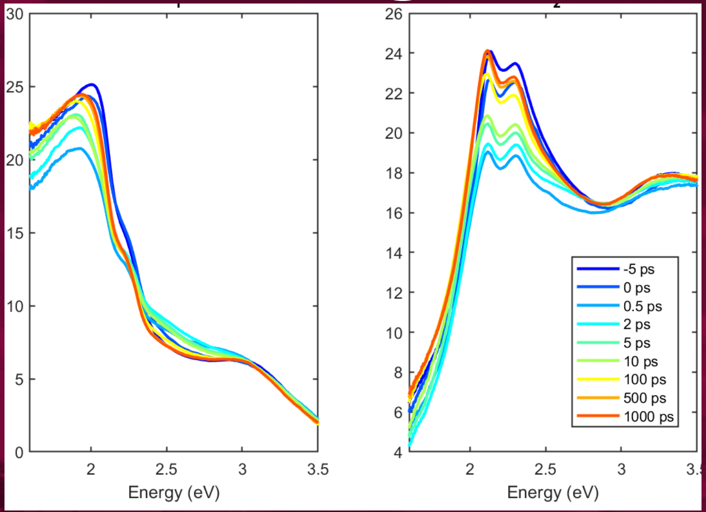
Quantum Materials from Theory to Practice
Austin, TX, 26 October 2024, 16:50-17:10

FA9550-20-1-0135 AFOSR
FA9550-24-1-0061 AFOSR
DMR-2235447 NSF
DMR-2423992 NSF

Femtosecond pump-probe ellipsometry and screening of two-dimensional excitons in Ge



Stefan Zollner

in collaboration with:

Carlos A. Armenta, Carola Emminger, Sonam Yadav, Melissa Rivero Arias, Jaden R. Love (NMSU), Jose Mendendez (Arizona State)

Department of Physics, New Mexico State University, Las Cruces, NM, USA
Email: zollner@nmsu.edu. WWW: http://femto.nmsu.edu.

Precision measurements of optical constants

1) Bulk materials: Semiconductors, metals, insulators
SiC, $SrTiO_3$, AlSb, Ge, GaAs, GaP, GaSb, InSb, SiC (4H and 6H), Ni, Pt, Au,
$MgAl_2O_4$, NiO (excitons), LiF, LSAT, $ZnGa_2O_4$, $LaAlO_3$

2) Epitaxial layers (many grown by Alex Demkov and his group):
NbO_2, Co_3O_4, $SrTiO_3$ (doped, quantum wells), $BaSnO_3$, ZnO, SnO_2, HfO_2, $Gd_xGa_{2-x}O_3$, silicides, SiGe:C, GeSn, $GaAs_{1-x}P_x$, alpha-tin on InSb and CdTe, native oxides on semiconductors (GeO_2)

3) Comparison with *ab initio* theory by Alex Demkov and with k.p theory (Jose Menendez)

4) Ellipsometry measurements over a broad spectral range (30 meV to 9.5 eV)
and broad temperature range (4 K to 800 K)

5) Applications: Microelectronics industry (CMOS, bipolar, III/V), mid-wave infrared detectors

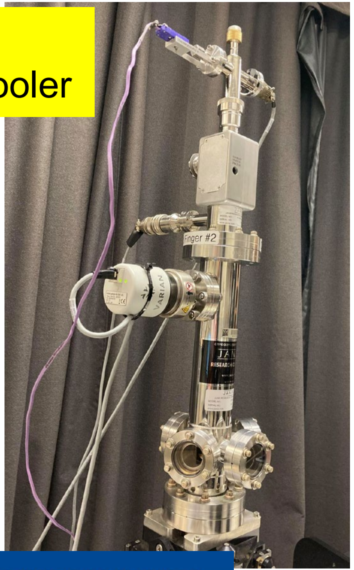
Ellipsometry at NMSU

diamond windows
closed-cycle He cooler

Ellipsometry on anything (inorganic, 3D)

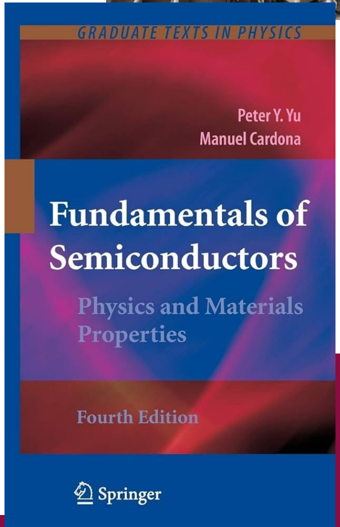
- Metals, insulators, semiconductors
- Mid-IR to vacuum UV (150 nm to 40 μm)
- **10 to 800 K, ultrafast ellipsometry**

Ellipsometry tells us a lot about materials quality (not necessarily what we want to know).



Optical critical points of thin-film $Ge_{1-y}Sn_y$ alloys: A comparative $Ge_{1-y}Sn_y$ / $Ge_{1-x}Si_x$ study VR D'costa, CS Cook, AG Birdwell, CL Littler, M Canonico, S Zollner, ... Physical Review B—Condensed Matter and Materials Physics 73 (12), 125207	445	2006
Growth and strain compensation effects in the ternary $Si_{1-x-y}Ge_xC_y$ alloy system K Eberl, SS Iyer, S Zollner, JC Tsang, FK LeGoues Applied physics letters 60 (24), 3033-3035	397	1992
Ge–Sn semiconductors for band-gap and lattice engineering M Bauer, J Taraci, J Tolle, AVG Chizmeshya, S Zollner, DJ Smith, ... Applied physics letters 81 (16), 2992-2994	341	2002

http://femto.nmsu.edu



Problem statement: optical constants

(1) Achieve a **quantitative** understanding of **photon absorption** and **emission** processes.

- Our **qualitative** understanding of excitonic absorption is 50-100 years old (Einstein coefficients),
- But **insufficient** for modeling of detectors and emitters.

(2) How are optical processes affected by high carrier concentrations **(screening)**?

- High carrier densities can be achieved with
  - In situ doping (Menendez, Kouvetakis)
  - **high temperatures (narrow-gap or gapless semiconductors)**
  - **ultrafast (femtosecond) lasers**
- **Application:** CMOS-integrated mid-infrared camera (thermal imaging with a phone).

Problem statement: screening of 2D excitons

- Excitonic direct gap absorption: **3D hydrogen problem with Coulomb potential** treated in every quantum mechanics course
  Sommerfeld enhancement of the absorption.
- Screened exciton absorption: 3D hydrogen problem with **Yukawa potential**
  Not solvable analytically, use Hulthen potential (Banyai & Koch, Haug & Koch)
- Excitonic direct gap absorption in 2D materials or E_1 excitons
  2D hydrogen problem with Coulomb potential (Flügge: Rechenmethoden der QM)
- **Excitonic direct gap absorption with screening (femtosecond ellipsometry)**
  No known solution for screened Sommerfeld enhancement in 2D.
  Can you help with an approximate analytical solution?

Fermi's Golden Rule: Tauc plot

Direct band gap absorption

constant **k·p** matrix element

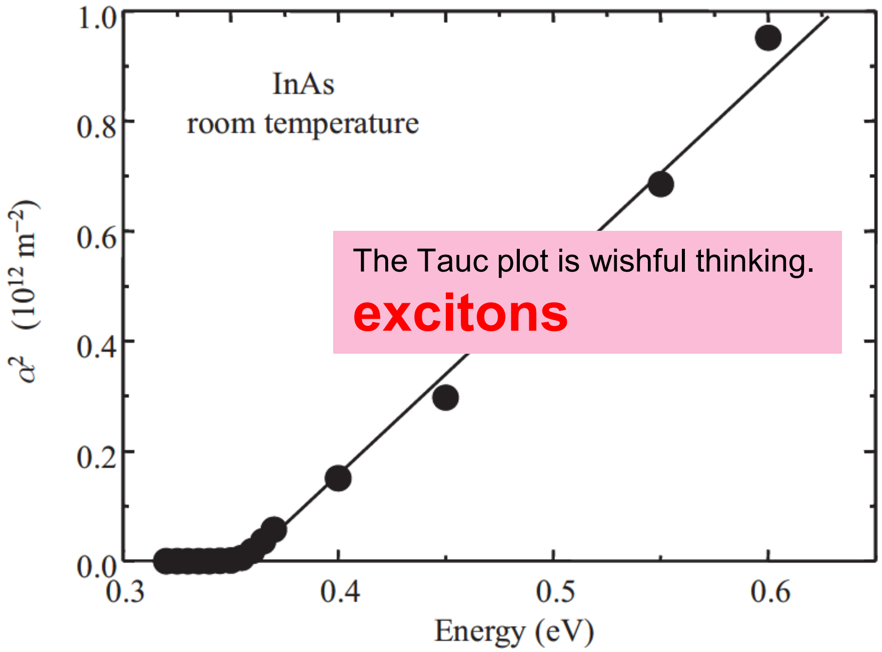
$$\frac{1}{\tau}=\frac{2\pi}{\hbar}\int_{i,f}|\langle f|H_{eR}|i\rangle|^2\delta\left(E_f-E_i-\hbar\omega\right)=\frac{2\pi}{\hbar}|\langle f|H_{eR}|i\rangle|^2 g_{fi}(\hbar\omega)$$

Joint DOS
parabolic bands

$$\langle f|H_{eR}|i\rangle=\frac{e}{m_0}\langle \boldsymbol{f}|\vec{\boldsymbol{p}}|\boldsymbol{i}\rangle\cdot\vec{A}_0$$

Use **k·p** matrix element *P*: $E_P=2P^2/m_0$

$$\varepsilon_2(\hbar\omega)=\frac{e^2\sqrt{m_0}\mu^{\frac{3}{2}}}{3\pi\sqrt{2}\varepsilon_0\hbar}\frac{E_P\sqrt{E_0}}{(\hbar\omega)^2}\sqrt{\frac{\hbar\omega}{E_0}-1}$$



BE BOLD. Shape the Future.

Fox, Chapter 3

Sommerfeld enhancement (3D)

Excitonic Rydberg energy

$$R = \frac{\mu}{m_0 \varepsilon_r^2} R_H$$

Discrete states

$$E_n = E_g - \frac{1}{n^2} R_X$$

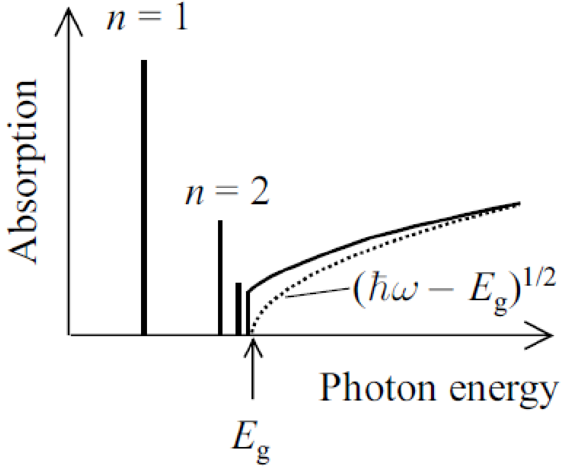
Discrete absorption

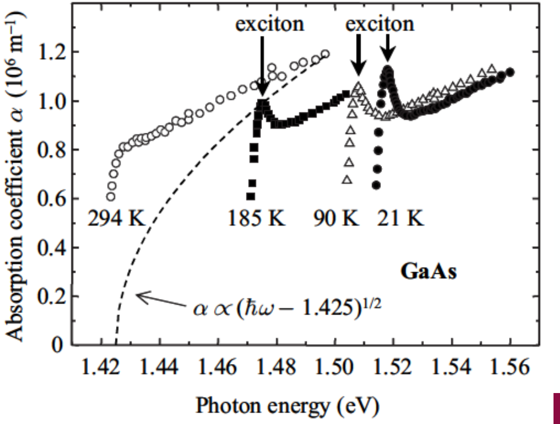
$$\varepsilon_2(E) = \frac{8\pi |P|^2 \mu^3}{3\omega^2 (4\pi\varepsilon_0)^3 \varepsilon_r^3} \sum_{n=1}^{\infty} \frac{1}{n^3} \delta(E - E_n)$$

Continuum absorption

$$\varepsilon_2(E) = \frac{2|P|^2 (2\mu)^{3/2} \sqrt{E - E_0}}{3\omega^2} \frac{\xi e^{\xi}}{\sinh \xi}$$

$$\xi = \pi \sqrt{R / E - E_0}$$





Use Bohr wave functions to calculate ε_2.
Toyozawa discusses broadening.

R. J. Elliott, Phys. Rev. **108**, 1384 (1957)
Yu & Cardona; Fox, Chapter 4; Tanguy 1995

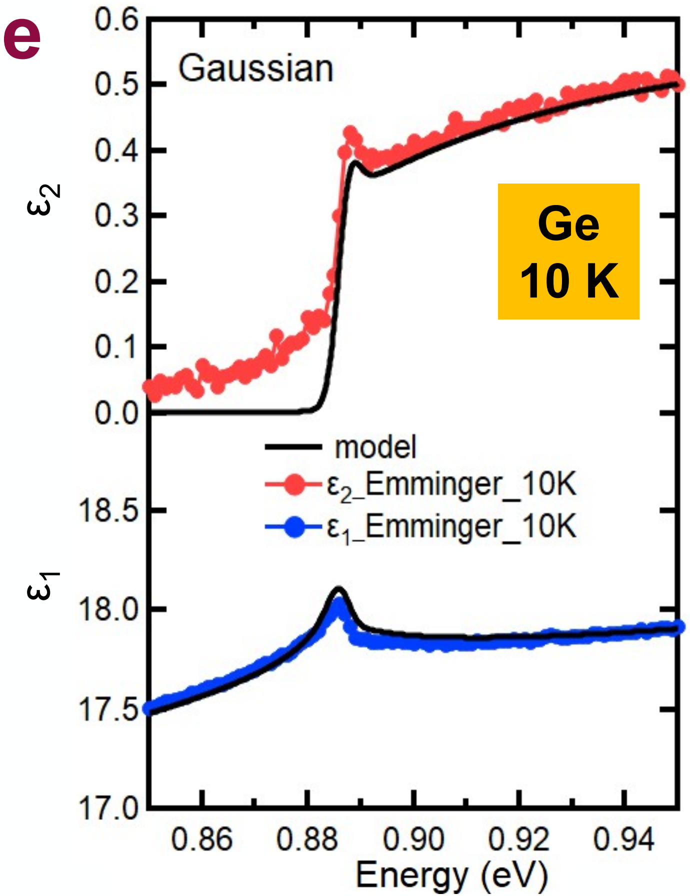
Elliott-Tanguy theory applied to Ge

- **Fixed parameters:**
- Electron and hole masses (temperature dependent)
- Excitonic binding energy R
- Amplitude A (derived from matrix element P)

- **Adjustable parameters:**
- Broadening Γ: 2.3 meV
- Band gap E_0
- Linear background A_1 and B_1 (contribution from E_1 to real part of ε)

Quantitative agreement

- **Problems:**
- Broadening below the gap (band tail, oxide correction)



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

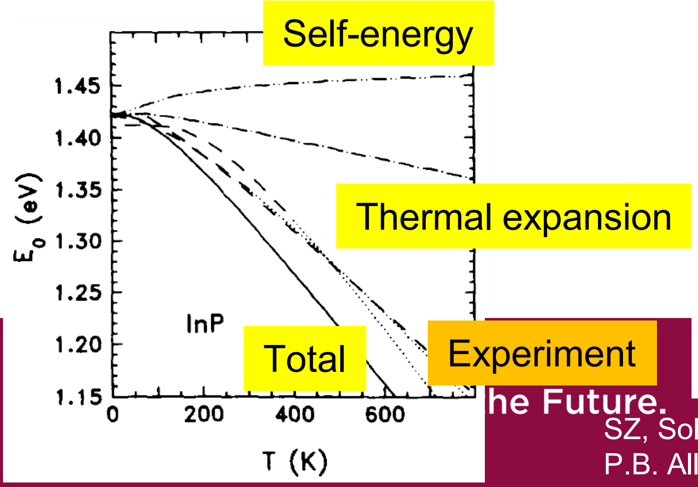
Temperature dependence of the effective mass

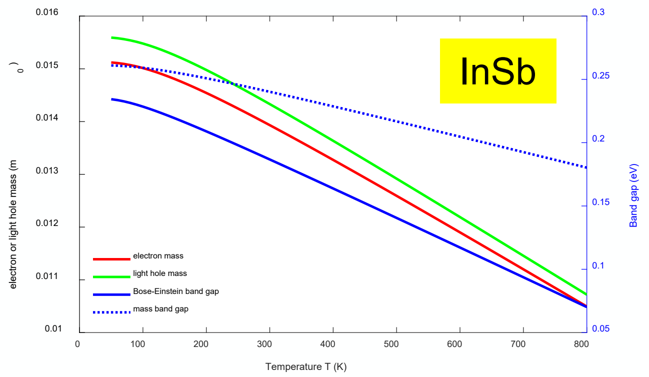
- Effective electron mass given by k·p theory

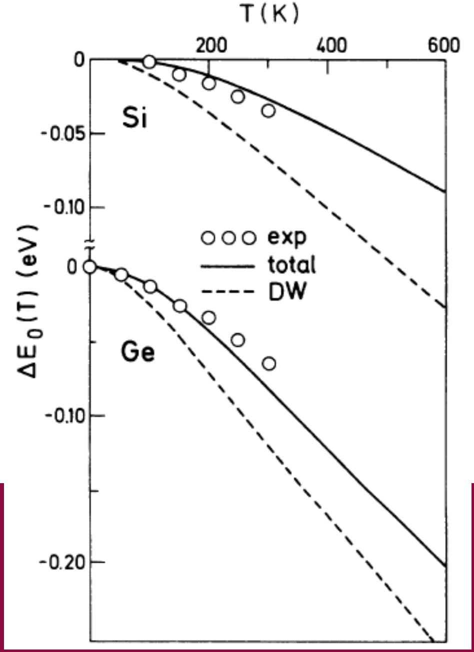
$$\frac{1}{m_e(T)} = 1 + \frac{E_P}{3}\left(\frac{2}{E_0(T)} + \frac{1}{E_0(T)+\Delta_0}\right)$$

E_0: direct band gap
k·p matrix element P: $E_P=2P^2/m_0$

- Temperature dependence of the direct band gap has two contributions:
  - Thermal expansion of the lattice
  - Electron-phonon interaction (Debye-Waller term and self-energy)
- "Mass band gap" should **only include the thermal expansion**.







he Future.

SZ, Solid State Commun. **77**, 485 (1991).
P.B. Allen and M. Cardona, Phys. Rev. B **27** 4760 (1983).

Two-dimensional Bohr problem

$$H = -\frac{\hbar^2}{2\mu_\perp}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right) - \frac{\hbar^2}{2\mu_\parallel}\frac{\partial^2}{\partial z^2} - \frac{e^2}{\varepsilon_r r}$$

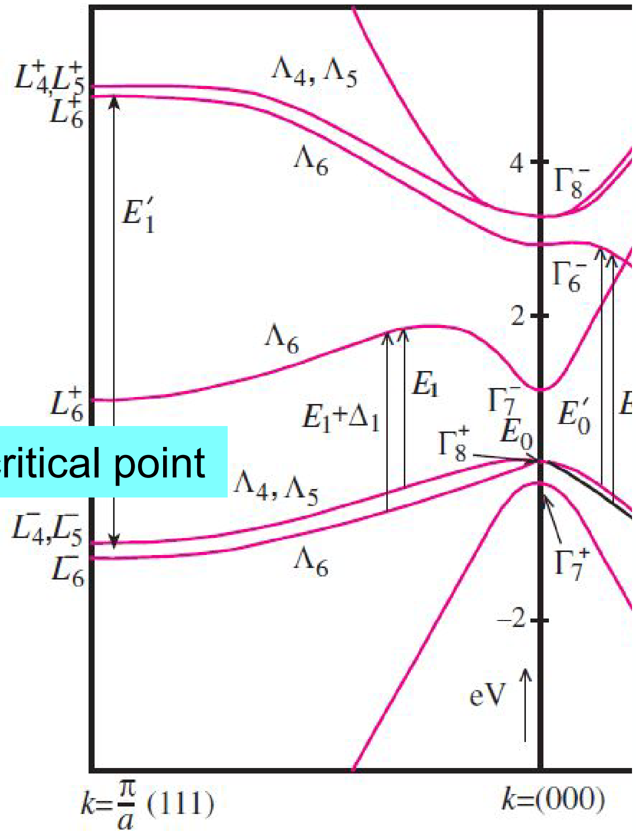
Assume that $\mu_{||}$ is infinite (separate term).
Use cylindrical coordinates.
Separate radial and polar variables.
Similar Laguerre solution as 3D Bohr problem.

$$a_X = \frac{4\pi\varepsilon_0\varepsilon_r\hbar^2 m_0}{\mu_\perp \mu e^2}$$

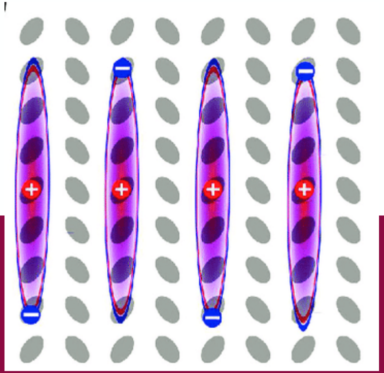
$$R = \frac{\mu_\perp e^4}{2\hbar^2 m_0 (4\pi\varepsilon_0\varepsilon_r)^2}$$

$$E_n = -\frac{R}{\left(n-\frac{1}{2}\right)^2}, \qquad n = 1,2,\ldots$$

Half-integral quantum numbers



2D critical point



M. Shinada and S. Sugano, J. Phys. Soc. Jpn. **21**, 1936 (1966).
Flügge (Rechenmethoden QM).

Two-dimensional excitons at E_1 critical points of Ge

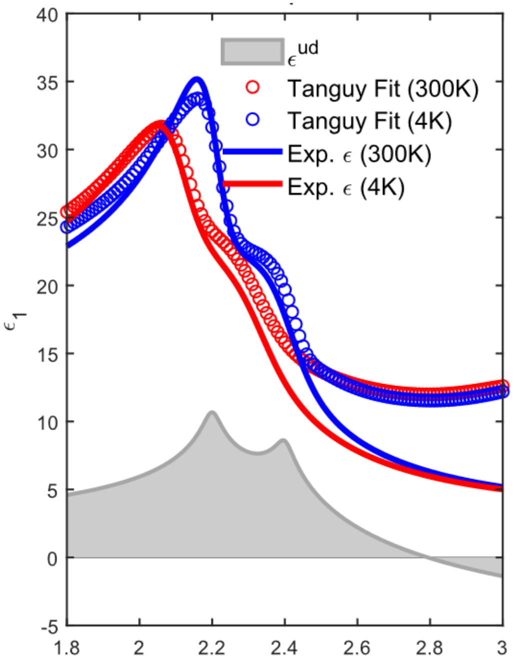
$$\varepsilon(E) = \frac{k_{max} e^2 \bar{P}^2 \mu_\perp^{(E_1)}}{3\varepsilon_0 m^2 \pi (E+i\Gamma)^2}\left\{ g_a\left[\sqrt{\frac{R}{E_g-(E+i\Gamma)}}\right] + g_a\left[\sqrt{\frac{R}{E_g-(-E-i\Gamma)}}\right] - 2g_a\left[\sqrt{\frac{R}{E_g-(0)}}\right]\right\}$$

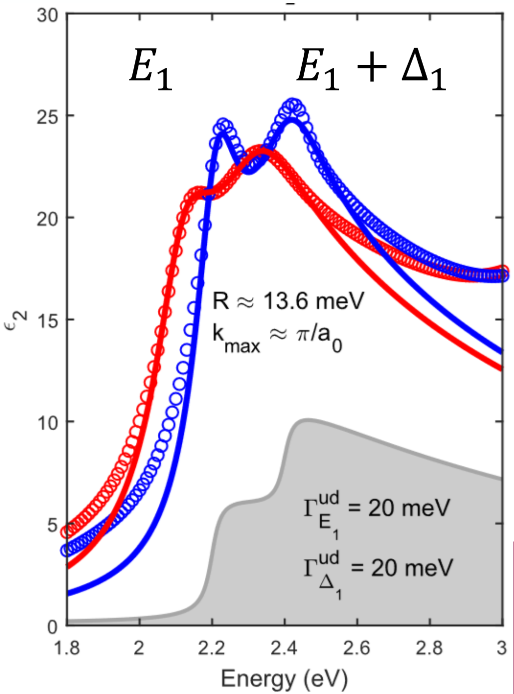
with

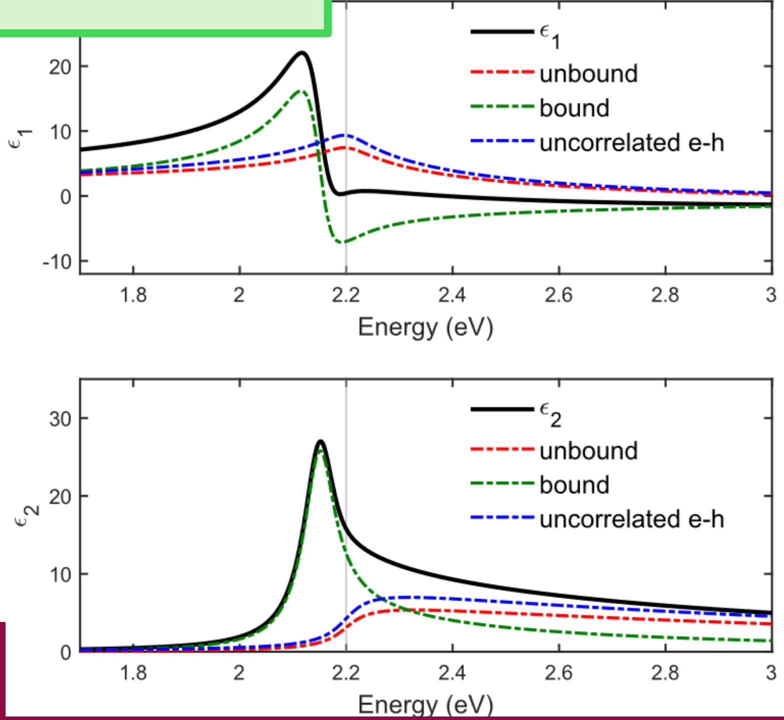
$$g_a(\xi) = 2\ln\xi - 2\psi(\xi)$$

Peak at $p = 0$ for

$$E_g - \frac{R}{(p-1/2)^2}$$







C. Tanguy, SSC **98**, 65 (1996).

Problem statement: optical constants

*(1) Achieve a **quantitative** understanding of **photon absorption** and **emission** processes.*

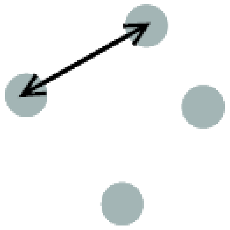
- *Our **qualitative** understanding of excitonic absorption is 50-100 years old (Einstein coefficients),*
- *But **insufficient** for modeling of detectors and emitters.*

(2) How are optical processes affected by **high carrier concentrations** (screening)?

- High carrier densities can be achieved with
  - In situ doping (Menendez, Kouvetakis)
  - **high temperatures (narrow-gap or gapless semiconductors)**
  - **ultrafast (femtosecond) lasers**
- **Application:** CMOS-integrated mid-infrared camera (thermal imaging with a phone).

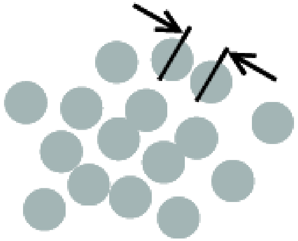
Condensation of excitons at high density

Exciton gas



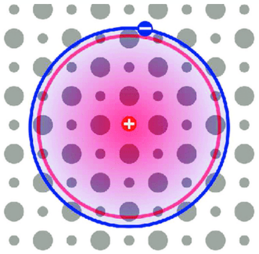
(a) Low density
Separation $\gg$ diameter

Electron-hole liquid



(b) High density
Separation $\approx$ diameter

Mott transition (insulator-metal) when electron separation equals exciton radius.



Electron separation d for density N

$$d = \sqrt[3]{\frac{3}{4\pi n}}$$

$$r_s = \frac{d}{a_X}$$

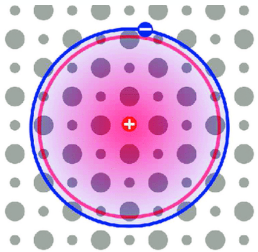
dimensionless

Mott transition occurs at r_s near 1.
GaAs: $n=10^{17}$ cm^{-3}.

Biexciton, triexciton molecule formation.
Electron-hole droplets. Bose-Einstein condensation.

Excitons in doped or excited semiconductors

Need to include exciton screening due to doping.
Yukawa potential: Schrödinger equation not solvable.
Use Hulthen potential as an approximation



Debye screening length

Coulomb $$V(r) = -k\frac{1}{r}$$

$$k = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r}$$

Yukawa $$V(r) = -k\frac{\exp(-r/\lambda_D)}{r}$$

$$\lambda_D = \sqrt{\frac{\varepsilon_r\varepsilon_0 k_B T}{ne^2}} = \frac{1}{k_D}$$

Hulthen $$V(r) = -k\frac{2/ga_X}{\exp\left(\frac{2r}{ga_X}\right) - 1}$$

$$g = \frac{\lambda_D}{a_X}$$

Unscreened: g=∞
Fully screened: g=0
Mott criterion: g=1

Hulthen exciton

e Future.

C. Tanguy, Phys. Rev. **60**, 10660 (1999).
Banyai & Koch, Z. Phys. B **63**, 283 (1986). Haug & Koch (2009).

Tanguy: Dielectric function of screened excitons

Bound exciton states (finite number):

$$A = \frac{\hbar^2 e^2}{6\pi\varepsilon_0 m_0^2}\left(\frac{2\mu}{\hbar^2}\right)^{3/2} |P|^2$$

$$\varepsilon_2(\omega) = \frac{2\pi A\sqrt{R}}{E^2} \sum_{n=1}^{n^2<g} 2R \frac{1}{n}\left(\frac{1}{n^2} - \frac{n^2}{g^2}\right) \delta\left[E - E_0 + \frac{R}{n^2}\left(1 - \frac{n^2}{g}\right)^2\right]$$

Reduced Rydberg energy

exciton continuum:

$$\varepsilon_2(\omega) = \frac{2\pi A\sqrt{R}}{E^2} \frac{\sinh \pi g k}{\cosh(\pi g k) - \cosh\left(\pi g\sqrt{k^2 - \frac{4}{g}}\right)} \theta(E - E_0)$$

$$k = \pi\sqrt{(E - E_0)/R}$$

Need to introduce Lorentzian broadening and perform numerical KK transform.

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

k·p theory (band structure method)

Schrödinger equation

$$H\Phi_{n\vec{k}} = \left(\frac{\vec{p}^2}{2m_0} + V\right)\Phi_{n\vec{k}} = E_{n\vec{k}}\Phi_{n\vec{k}}$$

Use Bloch's theorem:

$$\Phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r})$$

Product rule

$$(fg)'' = f''g + 2f'g' + fg''$$

Solve equation for **k**=0.

$$\left(\frac{\vec{p}^2}{2m_0} + \frac{\hbar^2\vec{\boldsymbol{k}}^2}{2\boldsymbol{m_0}} + \frac{\hbar\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{p}}}{\boldsymbol{m_0}} + V\right)u_{n\vec{k}} = E_{n\vec{k}}u_{n\vec{k}}$$

Eliminate green free-electron term with substitution of variables (Kane 1957).

Then treat red term in perturbation theory.

Works very well for semiconductors with local V(**r**) potentials.

Yu & Cardona, Fundamentals of Semiconductors
Kane, J. Phys. Chem. Solids **1**, 249 (1957). Kane 1966.

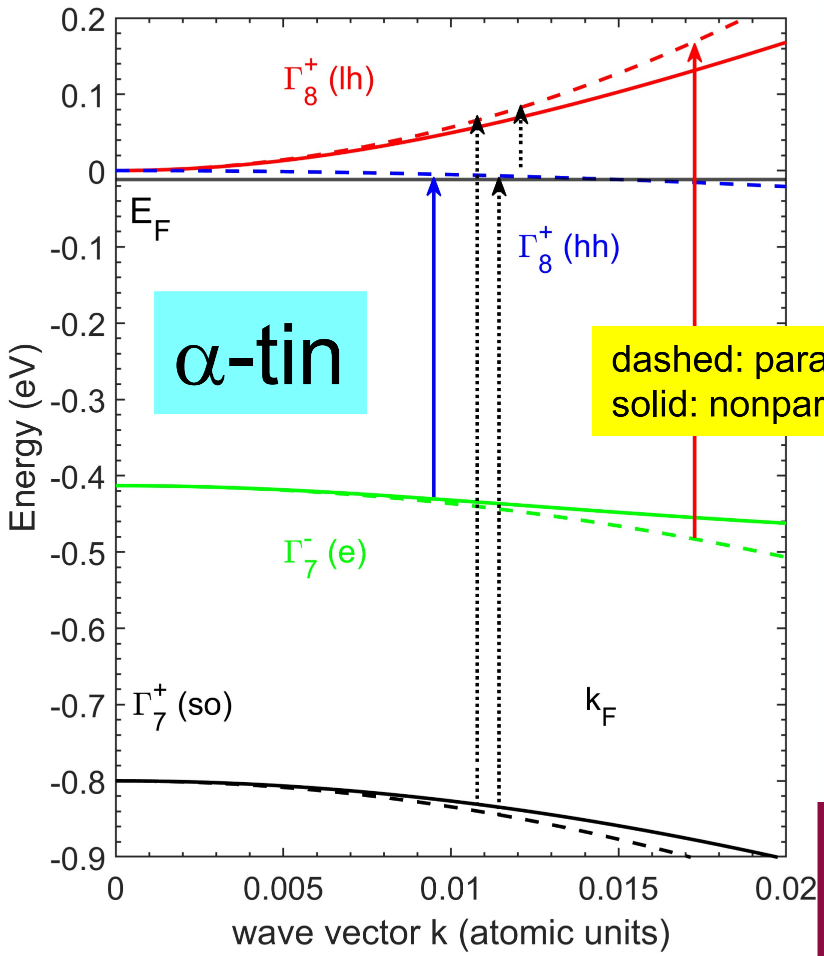
Simple 8x8 k·p band structure of α-tin (Kane)

Kane 8x8 k·p Hamiltonian:

$$\widetilde{H}_{\vec{k}} = \begin{pmatrix} E_0 & 0 & -\frac{\hbar\vec{k}}{m_0} iP & 0 \\ 0 & -\frac{2\Delta_0}{3} & \frac{\sqrt{2}\Delta_0}{3} & 0 \\ \frac{\hbar\vec{k}}{m_0} iP & \frac{\sqrt{2}\Delta_0}{3} & -\frac{\Delta_0}{3} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Cubic characteristic equation:

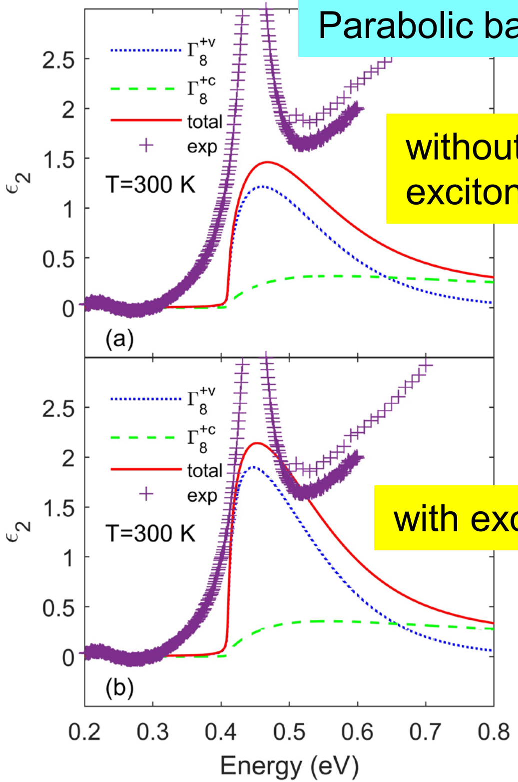
$$\tilde{E}\left(\tilde{E} - E_0\right)\left(\tilde{E} + \Delta_0\right) - \frac{\hbar^2 k^2 E_P}{2m_0}\left(\tilde{E} + \frac{2\Delta_0}{3}\right) = 0$$



S. Zollner, JVST B **42**, 022203 (2024).

Excitonic intravalence band absorption in α-tin

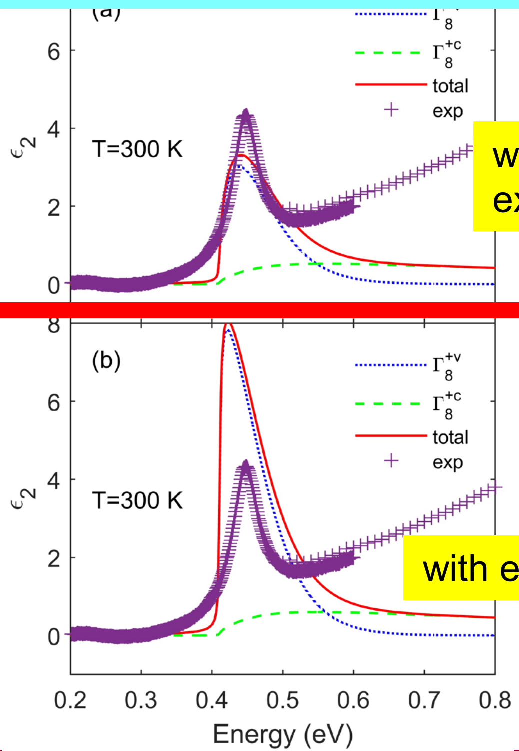
Parabolic bands



without excitons

with excitons

nonparabolicity affects exciton radius (screening)



without excitons

with excitons

Screening:

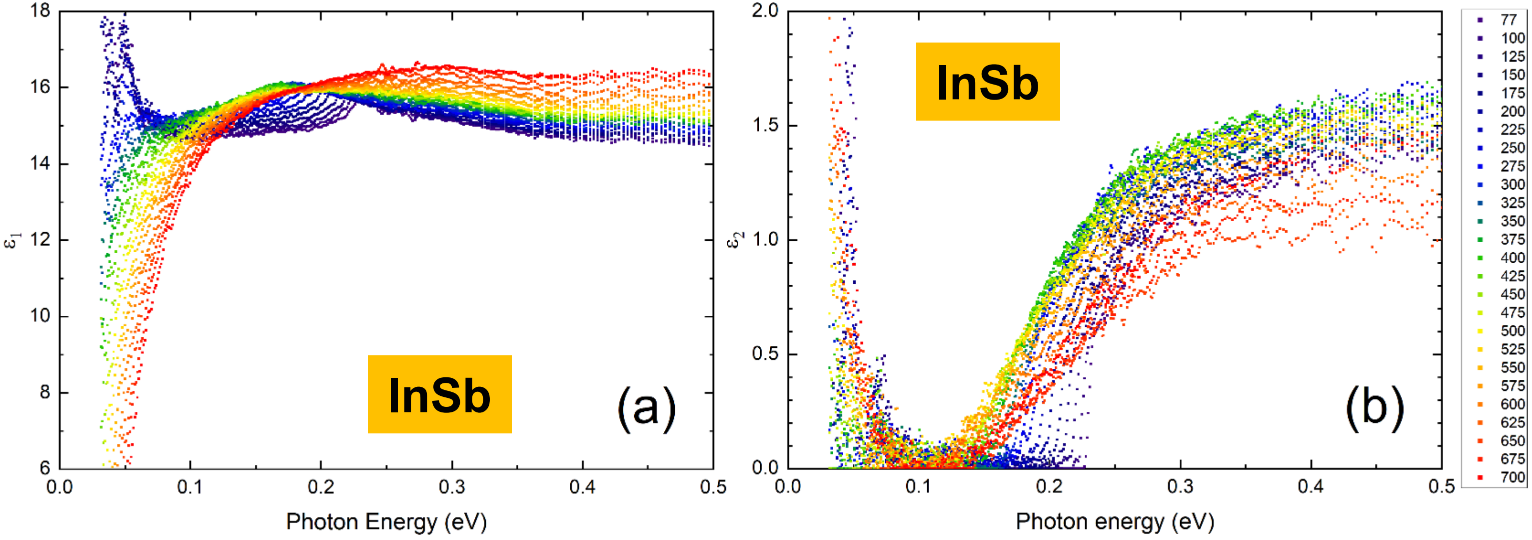
$$r_s = \frac{1}{a_x}\sqrt[3]{\frac{3}{4\pi n}}$$

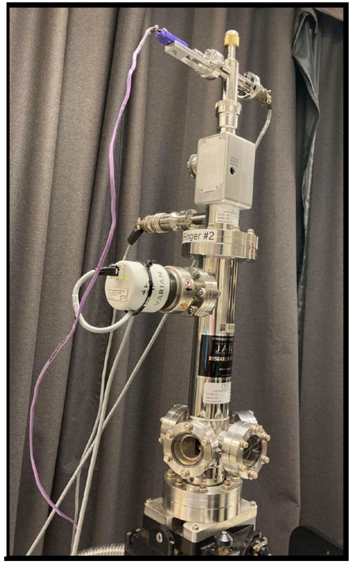
$$V(r) = -k\frac{\exp(-r/\lambda_D)}{r}$$

$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{pe^2}} = \frac{1}{k_D}$$

S. Zollner, JVST B **42**, 022203 (2024).

Dielectric function of InSb from 80 to 800 K



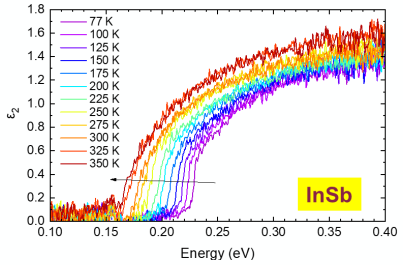


Woollam FTIR-VASE cryostat with CVD diamond windows

- **Band gap** changes with temperature (but only below 500 K).
- **Amplitude reduction at high temperatures (Pauli blocking, bleaching)**
- **Drude response** at high temperatures (thermally excited carriers).
- Depolarization artifacts at long wavelengths (below 300 K).

Optical constants model: screened excitons

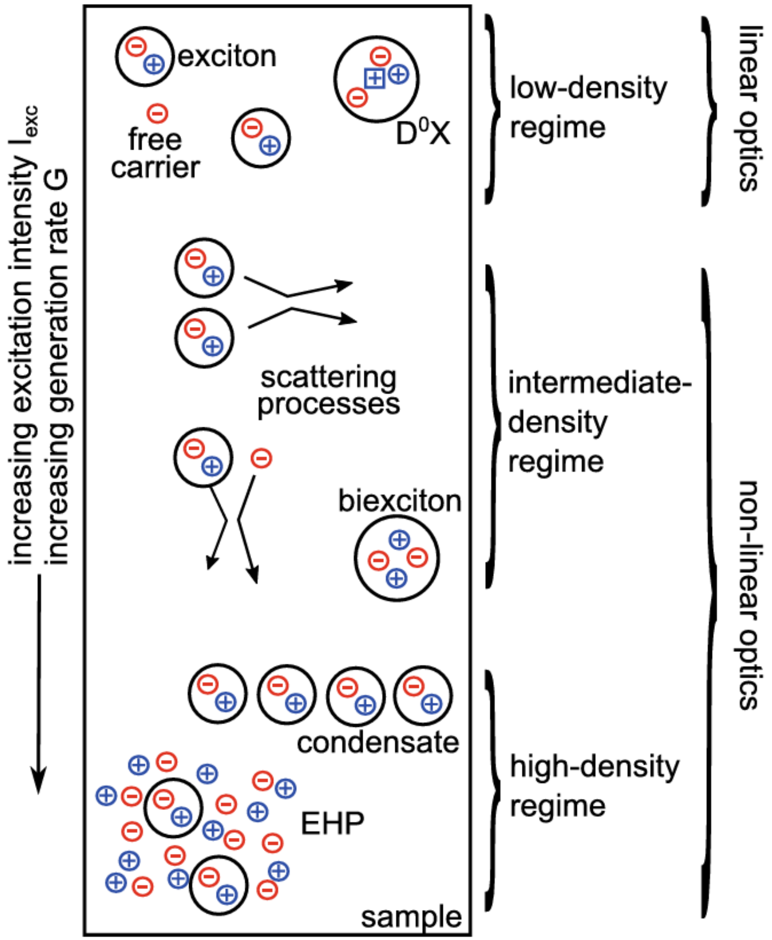
$$\varepsilon_2(E)=\frac{2\pi A\sqrt{R}}{E^2}\left\{\sum_{n=1}^{\sqrt{g}}\frac{2R}{n}\left(\frac{1}{n^2}-\frac{n^2}{g^2}\right)\delta\left[E-E_0+\frac{R}{n^2}\left(1-\frac{n^2}{g}\right)^2\right]+\frac{\sinh(\pi g k)\mathrm{H}(E-E_0)}{\cosh(\pi g k)-\cosh\left(\pi g\sqrt{k^2-\frac{4}{g}}\right)}\right\}[f_h(E)-f_e(E)]$$

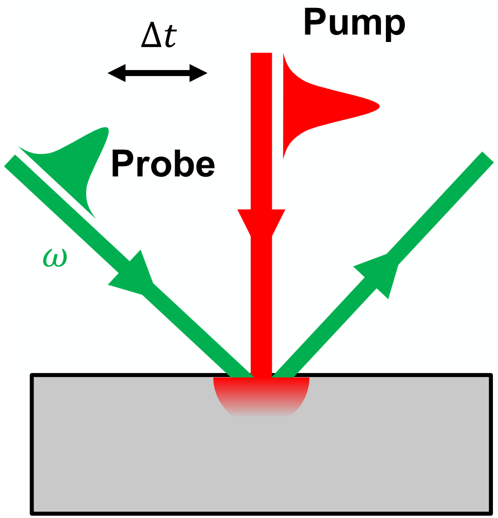


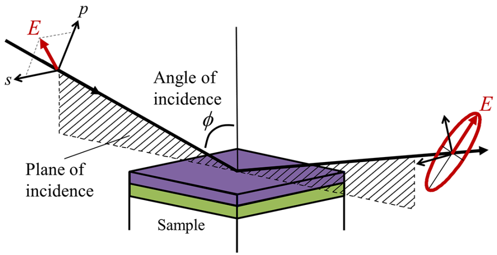
- **Absorption by screened excitons** (Hulthen potential)
- **Degenerate Fermi-Dirac statistics** to calculate f_h and f_e.
- Numerical Kramers-Kronig transform (need occupation factors)
- Two terms for light and heavy excitons
- **Non-parabolicity and temperature-dependent mass** included from k.p theory
- **k-dependent matrix element *P***.
- Screening parameter $g=12/\pi^2 a_R k_{TF}$ (large: no screening)
  Sommerfeld enhancement persists well above the Mott density.
- **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).
Jose Menendez, Phys. Rev. B **101**, 195204 (2020).
Carola Emminger, J. Appl. Phys. **131**, 165701 (2022).

Femtosecond Pump-Probe Ellipsometry





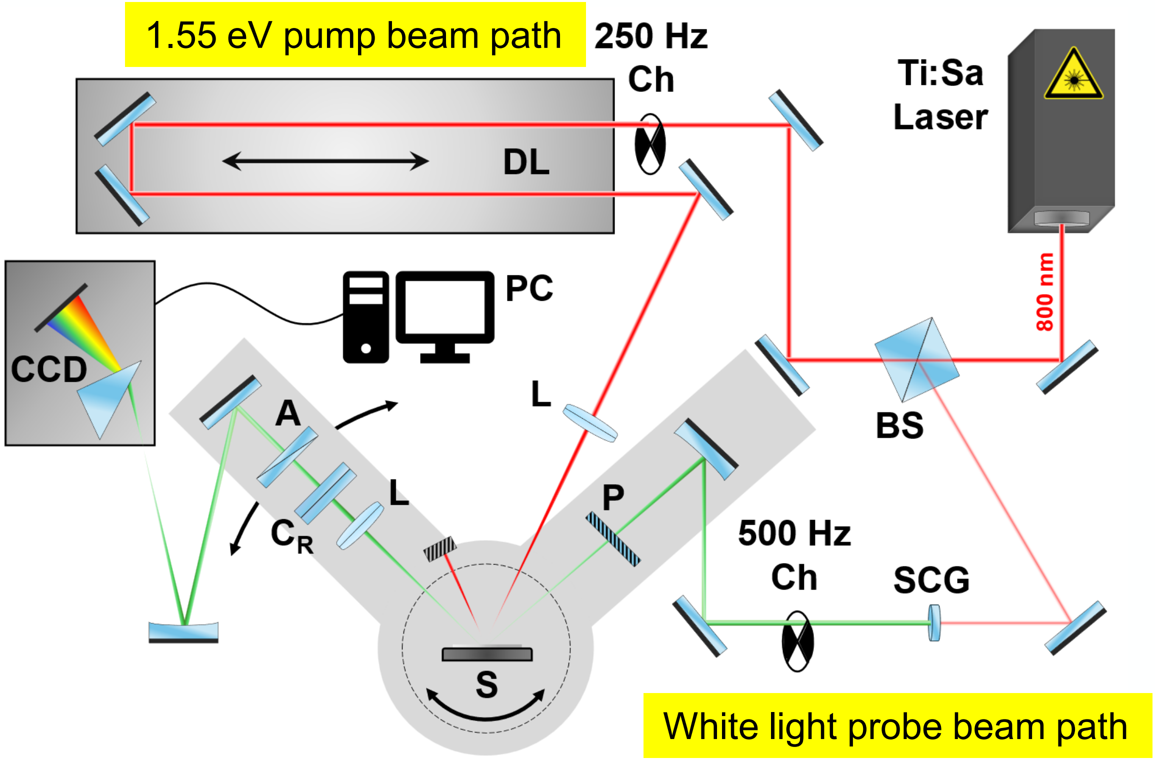


Non-linear effects in germanium induced by photoexcited carriers:

- Screening (many-body)
- Carrier-carrier scattering.
- Carrier-phonon scattering.
- Intervalley scattering.
- Momentum and energy relaxation of hot carriers.

H. Kalt, Semiconductor Optics 2 (2024).
Tompkins & Hilfiker, Spectroscopic Ellipsometry (2016)

Experimental setup: 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, 3 fs resolution)

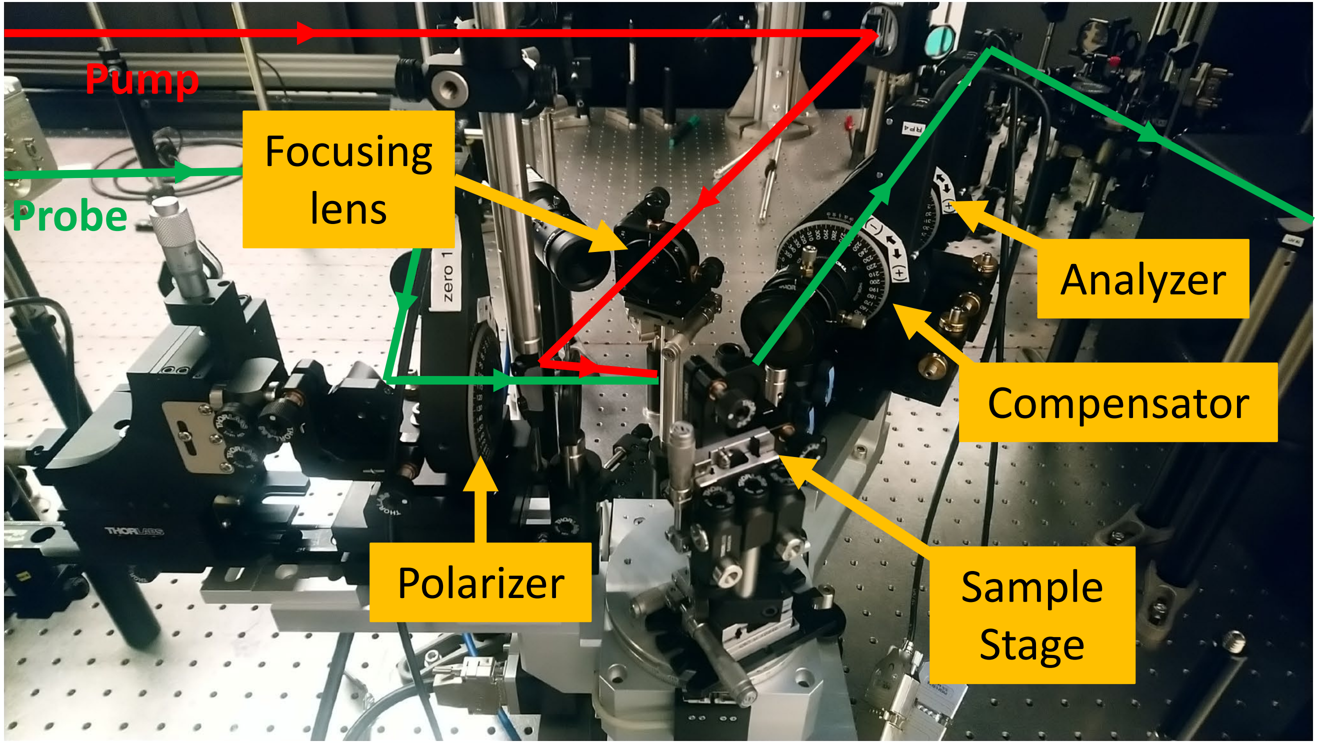
BS: Beam Splitter

SCG: Super-continuum Generation

CCD: Charge-coupled device detector

S. Richter, Rev. Sci. Instrum. **92**, 033104 (2021).
S. Espinoza, Appl. Phys. Lett. **115**, 052105 (2019).

Set-up: Femtosecond pump-probe ellipsometry



Rotating compensator ellipsometer:

Compensator was rotated in steps of 10° for a total of 55-65 angles.

Probe beam of 350-750 nm at 60° incidence angle.

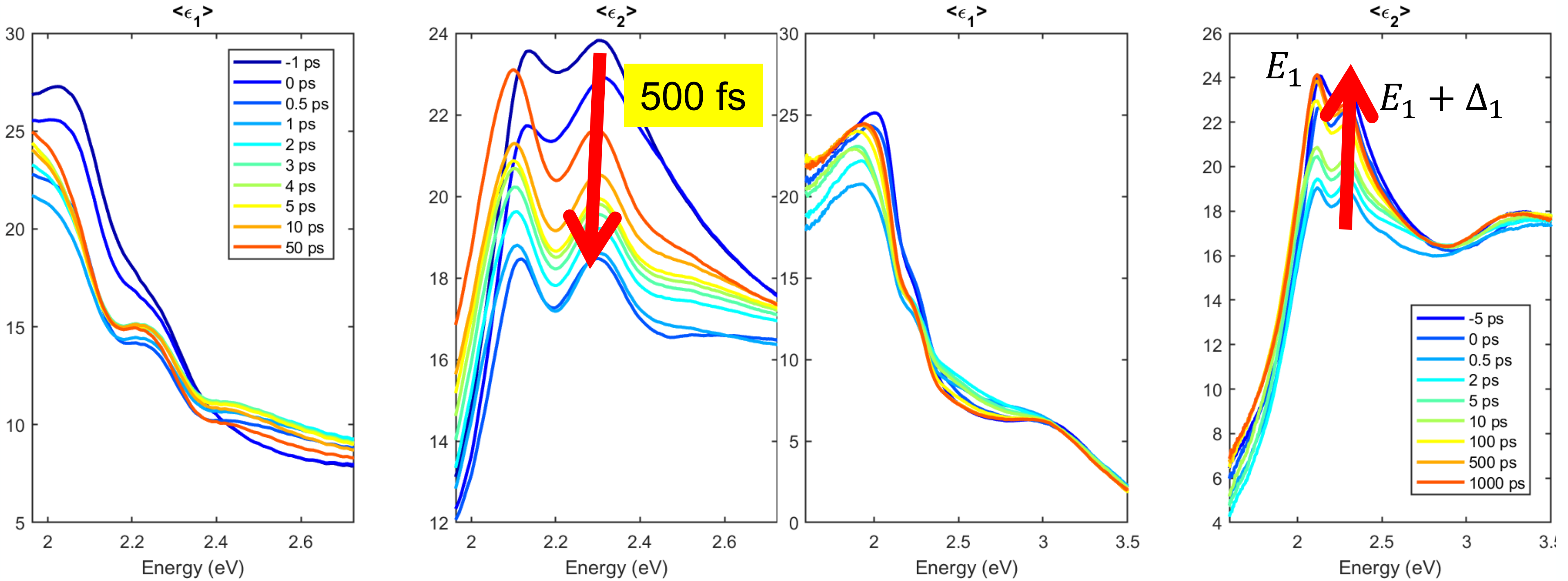
P-polarized pump beam: 35 fs pulses of 800 nm wavelength at 1 kHz repetition rate.

Delay time from -10 to 50 ps.

Time resolution of about 500 fs.

Espinoza et al., APL **115**, 052105 (2019).

Pseudo-dielectric constant as function of delay time

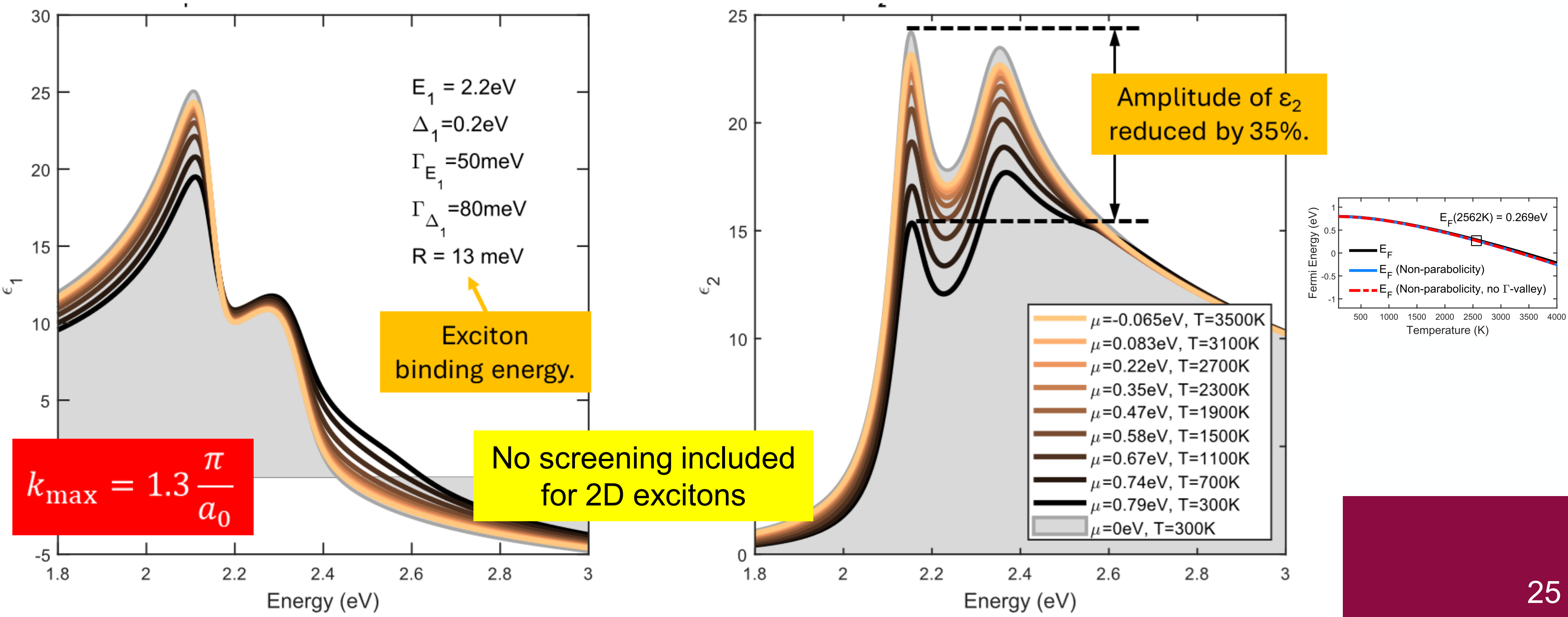


Rapid decrease of ε within first 500 fs.

Recovery takes 1 ns or longer.

2D excitons with band filling - no screening

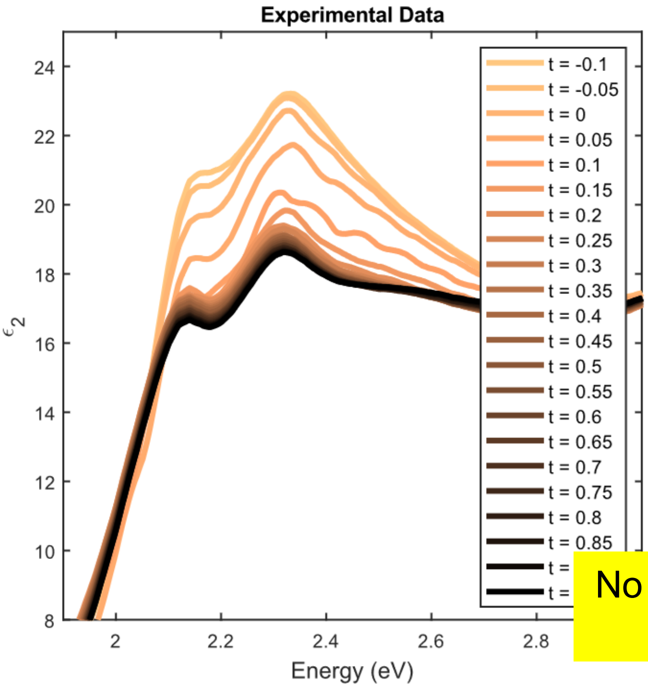
$$\varepsilon_2(E) = \frac{e^2 \mu_\perp^{(E_1)} \bar{P}^2}{6\varepsilon_0 m^2 \pi} \mathrm{Im}\left\{\frac{\{g_a[\xi(E+i\Gamma)] + g_a[\xi(-E-i\Gamma)] - 2g_a[\xi(0)]\}}{(E+i\Gamma)^2}\right\} \int_{-k_{\max}}^{k_{\max}} \{1 - f[E_c(E, k_z^2)]\} dk_z$$

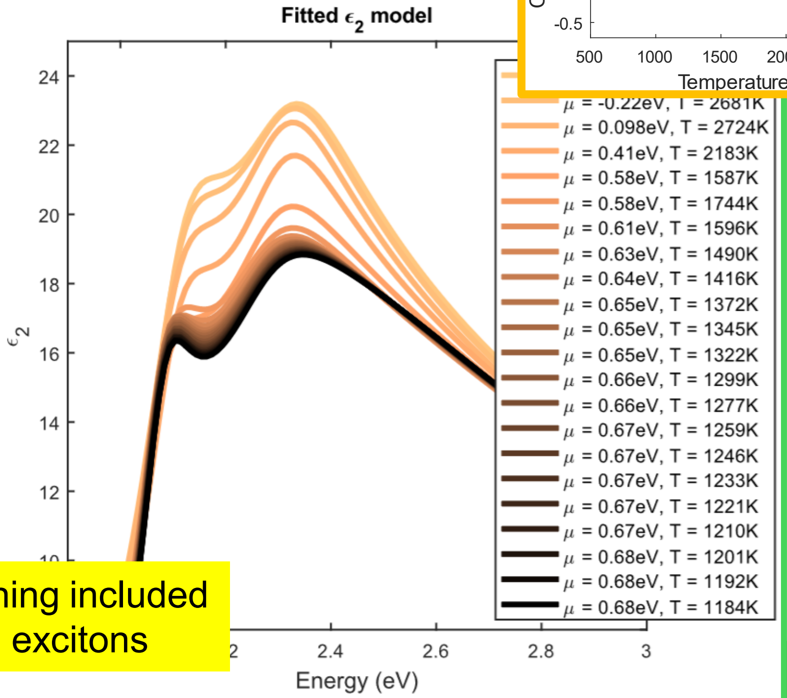


Band-filling effects

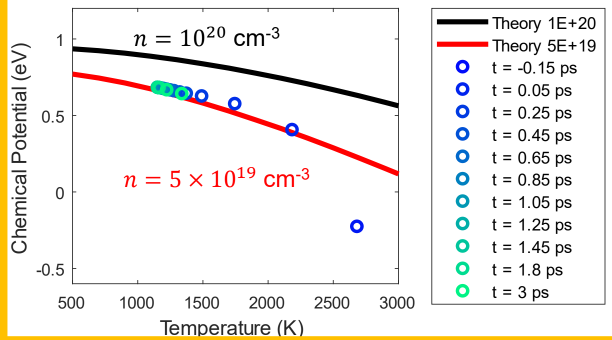
We combine Tanguy's line shape for 2D excitons with Xu's band-filling model:

$$\varepsilon_2(E) = \frac{e^2 \mu_\perp^{(E_g)} \bar{P}^2}{6\varepsilon_0 m^2 \pi} \mathrm{Im}\left\{ \frac{\{g_a[\xi(E+i\Gamma)] + g_a[\xi(-E-i\Gamma)] - 2g_a[\xi(0)]\}}{(E+i\Gamma)^2} \right\} \int_{-k_{\max}}^{k_{\max}} \{1 - f[E_c(E,k_z^2)]\} dk_z$$





No screening included for 2D excitons



Simulation of the chemical potential as a function of temperature for different carrier densities.

C. Xu, J. Appl. Phys. **125**, 085704 (2019).
C. Xu, Phys. Rev. Lett. **118**, 267402 (2017).

Problem statement: screening of 2D excitons

- Excitonic direct gap absorption: **3D hydrogen problem with Coulomb potential** treated in every quantum mechanics course
  Sommerfeld enhancement of the absorption.
- Screened exciton absorption: 3D hydrogen problem with **Yukawa potential**
  Not solvable analytically, use Hulthen potential (Banyai & Koch, Haug & Koch)
- Excitonic direct gap absorption in 2D materials or E_1 excitons
  2D hydrogen problem with Coulomb potential (Flügge: Rechenmethoden der QM)
- **Excitonic direct gap absorption with screening (femtosecond ellipsometry)**
  No known solution for screened Sommerfeld enhancement in 2D.
  Can you help with an approximate analytical solution?

Conclusions

- Quantitative modeling of low-density optical processes is possible with basic physics and matrix elements from k.p theory:
  - Photoluminescence in Ge (Menendez)
  - Indirect gap absorption in Ge (Menendez)
  - **Direct gap absorption in Ge at low T (excitons in 3D); E_1 critical points in Ge (excitons in 2D)**
  - More work is needed at high temperatures and for materials other than Ge.
- High carrier excitations:
  - High electron doping density in Ge
  - **Thermal excitation of electron-hole pairs in InSb and α-tin (3D screening and band filling).**
  - **Femtosecond laser generation of electron-hole pairs in Ge (2D screening)**
  - Experimental data and qualitative explanations exist
- We need more experiments and more detailed theory and simulations.

Thank you!

Questions?

Many students contributed to this project.

http://femto.nmsu.edu