Optical characterization of compound semiconductor materials using spectroscopic ellipsometry

Ph.D. Dissertation Defense

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New Mexico State University
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US Army (W911NF-16-1-0492)

Curriculum Vitae

EDUCATION:

M.S. (Physics)- New Mexico State University, Spring 2018.

B.Sc. (Physics: Second Class Honors-Upper Division)- University of Peradeniya, Sri Lanka, January 2013.
Minors: Statistics and Applied Mathematics.

AWARDS:

- 2nd place in oral presentation, Research and Creativity Week presentation, New Mexico State University, November 2020.
- Winner, Research and Creativity Week presentation, New Mexico State University, November 2019.
- Outstanding Graduate Assistant Award from the New Mexico State University Graduate School 2018.
- Best student presentation in Ellipsometry focus topic session -AVS 63rd International Symposium and Exhibition, Nashville, TN, 2016.
- 3rd place in oral presentation - AVS New Mexico Symposium, Albuquerque, NM, May 16th, 2017.

JOURNAL PUBLICATIONS (8):

- **Nuwanjula Samarasingha** and Stefan Zollner, Temperature dependence of optical phonon reflection bands in GaP, J. Vac. Sci. Technol. B **39**, 052201 (2021).
- **Nuwanjula S. Samarasingha**, Stefan Zollner, Dipayan Pal, Rinki Singh, and Sudeshna Chattopadhyay, Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition, J. Vac. Sci. Technol. B **38**, 042201 (2020).
- Carola Emminger, **Nuwanjula S. Samarasingha**, Melissa Rivero Arias, Farzin Abadizaman, Jose Menendez, and Stefan Zollner, Excitonic effects of the temperature-dependent direct band gap of Ge (in progress).
- Carola Emminger, Farzin Abadizaman, **Nuwanjula S. Samarasingha**, Thomas E. Tiwald, and Stefan Zollner, Temperature dependent dielectric function and direct bandgap of Ge, J. Vac. Sci. Technol. B **38**, 012202 (2020).
- I. S. A. Abeysiriwardana-Arachchige, **N. Samarasingha** , R. Rosalez, S. Munasinghe-Arachchige, H. Dilanke-Pedige, C. E. Brewer and N. Nirmalakhandan, Maximizing phosphorus recovery as biofertilizer in an algal wastewater treatment system, Resources, Conservation and Recycling **170**, 105552 (2021).
- Stefan Zollner, Pablo P. Paradis, Farzin Abadizaman, and **Nuwanjula S. Samarasingha**, Drude and Kukharskii mobility of doped semiconductors extracted from Fourier transform infrared ellipsometry spectra, J. Vac. Sci. Technol. B **37**, 012904 (2019).
- T.N. Nunley, N.S. Fernando, **N. Samarasingha**, J.M. Moya, C.M. Nelson, A.A. Medina, and 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).
- T.N. Nunley, N. Fernando, J.M. Moya, **N.S. Arachchige**, C.M. Nelson, A.A. Medina, and S. Zollner, Precise Optical Constants of Ge and GeO_2 from 0.5 to 6.6 eV, IEEE Summer Topicals Conference on Emerging Technology for Integrated Photonics, 11-13 July 2016, Newport Beach, CA.

Curriculum Vitae

CONFERENCE PRESENTATIONS:

- Nuwanjula Samarasingha and Stefan Zollner, Temperature Dependence of Optical Phonon Bands in GaP, 63rd Electronic Materials Conference (Virtual), June 23-25, 2021.
- Nuwanjula Samarasingha and Stefan Zollner, Temperature dependence of optical phonon bands in GaP, APS March Meeting (Virtual), 16 March 2021.
- Nuwanjula Samarasingha and Stefan Zollner, Temperature dependence of optical phonon bands in GaP, APS Four Corners Section Meeting (Virtual), 23 October 2020.
- Nuwanjula Samarasingha, Stefan Zollner, Dipayan Pal, Aakash Mathur, Ajaib Singh, Rinki Singh, Sudeshna Chattopadhyay, Thickness-dependent Optical Properties of ZnO Films from the Mid-infrared to the Vacuum-ultraviolet, 8th International Conference on Spectroscopic Ellipsometry, Barcelona, Spain, May 26- May 31, 2019.
- Nuwanjula Samarasingha, Stefan Zollner, Dipayan Pal, Aakash Mathur, Ajaib Singh, Rinki Singh, and Sudeshna Chattopadhyay, Phonon confinement and excitonic absorption in the optical properties of ZnO films, AVS 65th International Symposium and Exhibition, Long Beach, CA, 21-26 October 2018.
- Nuwanjula Samarasingha, Stefan Zollner, Dipayan Pal, Aakash Mathur, Ajaib Singh, Rinki Singh, and Sudeshna Chattopadhyay, Phonon and exciton absorption in the optical properties of ZnO films, 2018 NMAVS Symposium and Exhibition, Albuquerque, NM, 22 May 2018.
- Nuwanjula Samarasingha, Zachary Yoder, Stefan Zollner, Dipayan Pal, Aakash Mathur, Ajaib Singh, Rinki Singh, Sudeshna Chattopadhyay, Excitonic absorption and optical properties of ZnO films, APS March Meeting, Los Angeles, California, March 5 – March 9, 2018.
- Nuwanjula Samarasingha, Zachary Yoder, Stefan Zollner, Dipayan Pal, Aakash Mathur, Ajaib Singh, Rinki Singh, Sudeshna Chattopadhyay, Excitonic effects on the optical properties of thin ZnO films on different substrates, AVS 64th International Symposium & Exhibition, Tampa, Florida, October 30 – November 3, 2017.
- Nuwanjula Samarasingha, Cesar Rodriguez, Jaime Moya, Nalin Fernando, Stefan Zollner, Patrick Ponath, Kristy J. Kormondy, Alex Demkov, Dipayan Pal, Aakash Mathur, Ajaib Singh, Surjendu Dutta, Jaya Singhal, Sudeshna Chattopadhyay, Excitonic effect at interfaces in thin oxide films, AVS New Mexico Symposium, Albuquerque, NM, May 16th, 2017.
- Nuwanjula Samarasingha, Cesar Rodriguez, Jaime Moya, Nalin Fernando, Stefan Zollner, Patrick Ponath, Kristy J. Kormondy, Alex Demkov, Dipayan Pal, Aakash Mathur, Ajaib Singh, Surjendu Dutta, Jaya Singhal, Sudeshna Chattopadhyay, Excitons at interfaces in ellipsometric spectra, AVS 63rd International Symposium & Exhibition, Nashville, TN, 6-11, November 2016.
- Nuwanjula Samarasingha, Cesar Rodriguez, Jaime Moya, Nalin Fernando, Stefan Zollner, Patrick Ponath, Kristy J. Kormondy, Alex Demkov, Dipayan Pal, Aakash Mathur, Ajaib Singh, Surjendu Dutta, Jaya Singhal, Sudeshna Chattopadhyay, Excitons at interfaces in thin oxide films, APS Four Corners Section Meeting, Las Cruces, NM, 21-22 October 2016.
- N. Samarasingha, C. Rodriguez, J. Moya, S. Zollner, N. Fernando, S. Chattopadhyay, P. Ponath, and A.A. Demkov, Structural and optical properties of $SrTiO_3$ thin films on different substrates, Lawrence Symposium on Epitaxy, Scottsdale, AZ, 21-24 February 2016.
- N. Samarasingha, C. Rodriguez, J. Moya, S. Zollner, N. Fernando, S.Chattopadhyay, P. Ponath, and A.A. Demkov, Structural and optical properties of $SrTiO_3$ thin films on semiconductors, The 43rd Conference on the Physics and Chemistry of Surfaces and Interfaces, Palm Springs, CA, 17-21 January 2016.
- N. Samarasingha, J. Moya, S. Zollner, S. Chattopadhyay, P. Ponath, and A. Demkov, Structural properties of $SrTiO_3$ thin films on semiconductors, APS Four Corners Section Meeting, Tempe, AZ, 16 October 2015.

Outline

- ❑ Introduction-part I
  - Zinc Oxide (ZnO:II-VI compound semiconductor) for optoelectronic industry
  - Role of ZnO **film thickness** for optoelectronic and photonic devices

- ❑ Sample characterization
  - Optical Characterization: Spectroscopic Ellipsometer (IR-VASE, UV-VASE)
  - Structural Characterization: X-ray diffraction (XRD), X-ray reflectivity (XRR), Atomic force microscope (AFM)

- ❑ Results: **Thickness dependence** of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition (ALD)

[**Nuwanjula S. Samarasingha**, Stefan Zollner, Dipayan Pal, Rinki Singh, and Sudeshna Chattopadhyay, Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition, J. Vac. Sci. Technol. B **38**, 042201 (2020)]

- ❑ Introduction-part II
  - Gallium Phosphide (GaP:III-V compound semiconductor) for optoelectronic industry
  - Why we study **temperature** dependence of lattice vibration in GaP

- ❑ Results: **Temperature dependence** of the optical phonon reflection band in GaP

[**Nuwanjula Samarasingha** and Stefan Zollner, Temperature dependence of optical phonon reflection bands in GaP, J. Vac. Sci. Technol. B **39**, 052201 (2021)].

- ❑ Conclusions

☐ Introduction-part I
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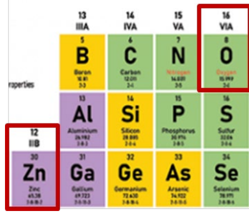
[[Nuwanjula Samarasingha and Stefan Zollner, Temperature dependence of optical phonon reflection bands in GaP, J. Vac. Sci. Technol. B (under review) arXiv:2105.06662, (2021)]

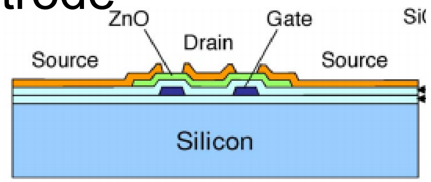
☐ Conclusions

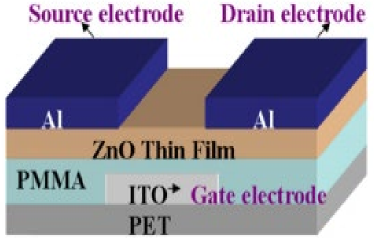
Zinc Oxide (ZnO:II-VI compound semiconductor)



Attractive material for optoelectronics and photonics application

- ❑ Thermal and chemical stabilities of ZnO ➤ thin film transistors, solar cells, and gas sensors
- ❑ High power, high temperature electronics
- ❑ Less toxic and relatively easy to synthesize with a variety of techniques ➤ hybrid solar cells
- ❑ Wide band gap and a very good optical transmittance ➤ transparent electrode in organic and hybrid solar cells
- ❑ Direct band gap semiconductor with large exciton binding energy





➤ **It is very important to have a universal description and better understanding of optical properties of this semiconductor.**

HOW OPTICAL PROPERTIES OF ZnO CHANGE WITH THE ,

- **Film thicknesses (is a key parameter in photovoltaic devices)**
- **Substrate material**

C. Y. Lee, M. Y. Li, W. H. Wu, J. Y. Wang, Y. Chou, W. F. Su, Y. F. Chen and C. F. Lin, *Semiconductor Science and Technology* **25.10**, 105008 (2010).
D. Pal, A. Mathur, A. Singh, J. Singhal, A. Sengupta, S. Dutta, S. Zollner, and S. Chattopadhyay, J. Vac. Sci. Technol. A **35**, 01B108 (2017).
D. Pal, J. Singhal, A. Mathur, A. Singh, S. Dutta, S. Zollner, and S. Chattopadhyay, Appl. Surf. Sci. 421, 341 (2016).

ZnO for optoelectronic and photonic devices

OPTICAL PROPERTIES

- ❑ **Spectroscopic Ellipsometry (SE): Widely used optical metrology technique in the semiconductor industry**

SE is a powerful and more accurate method to measure **optical constants**, especially the **dielectric function DF** ($\tilde{\varepsilon}(\omega)$) of materials.

$$\tilde{\varepsilon}(\omega)=\underbrace{\varepsilon_1(\omega)}+i\underbrace{\varepsilon_2(\omega)}$$

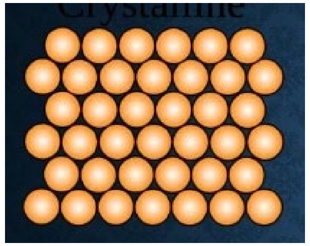
Real part: related to energy stored in the material

Imaginary part: related to lost of energy in the material (absorption)

- ❑ How the dielectric functions ($\tilde{\varepsilon}$) of semiconductors depend on
  - ▪ Film thickness • Substrate material • Excitonic effects • Strain • Variation in electron density**??**

STRUCTURAL PROPERTIES

Ex: **Crystallinity**



- ❑ Degree of structural order in a solid
- ❑ Crystallinity aids to avoid unwanted charge trapping
- ❑ Trapping reduces charge mobility (how quickly an electron can move through a metal or semiconductor)

➤ **Affect performance of devices**

The knowledge developed through this study is valuable for its application in optoelectronic and photonic devices to achieve their best performance.

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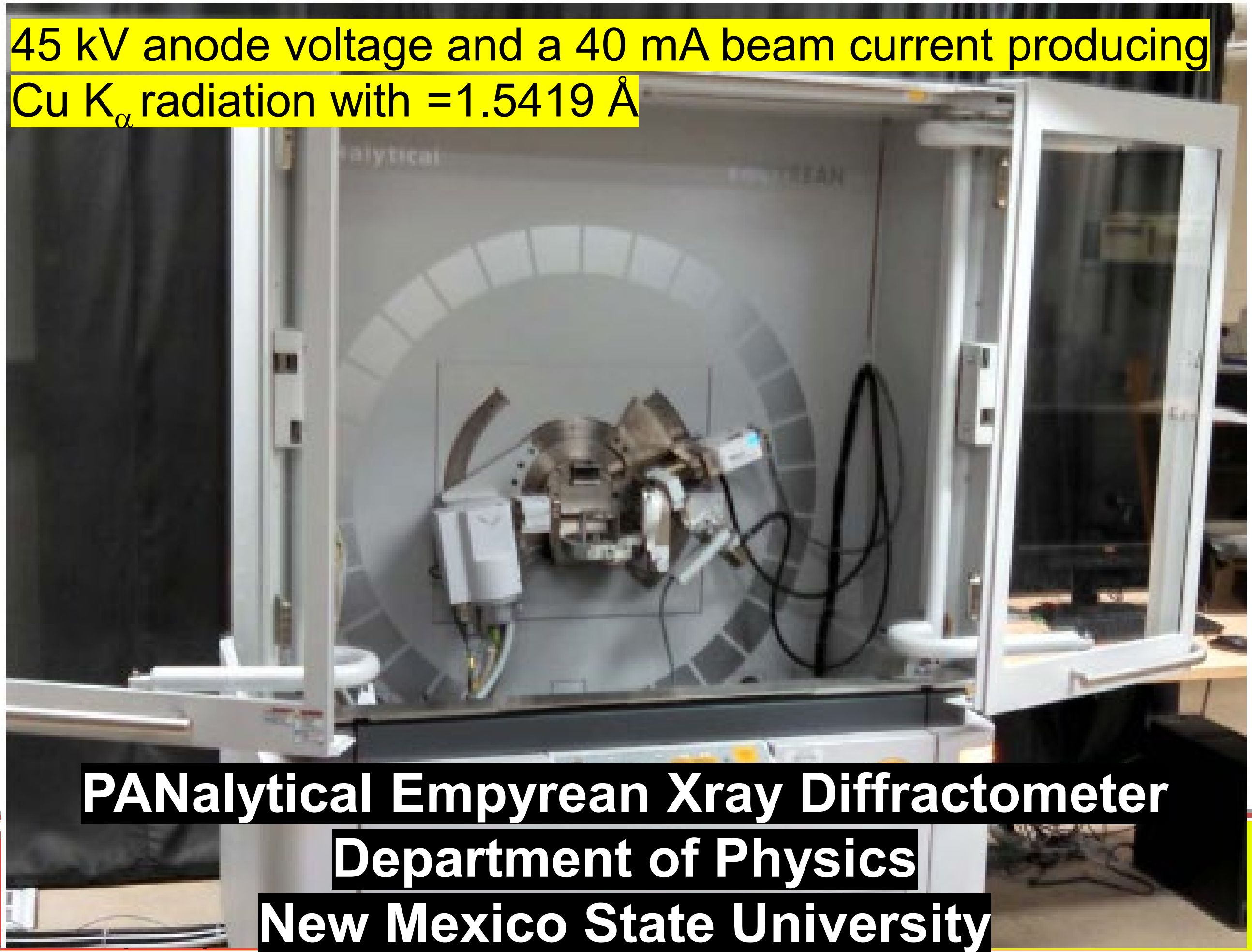
- Conclusions

How thick is my film?

- ☐ **Physicist**: Use optical interference techniques: Spectroscopic ellipsometry (optical, IR/VIS/UV), X-ray reflectance (XRR:more accurate than electron microscopy)
  - Sometimes ellipsometry cannot determine both the optical constants and the thickness of ultrathin layers or may not be able to detect thin interfacial layers, surface roughness, or density variations.



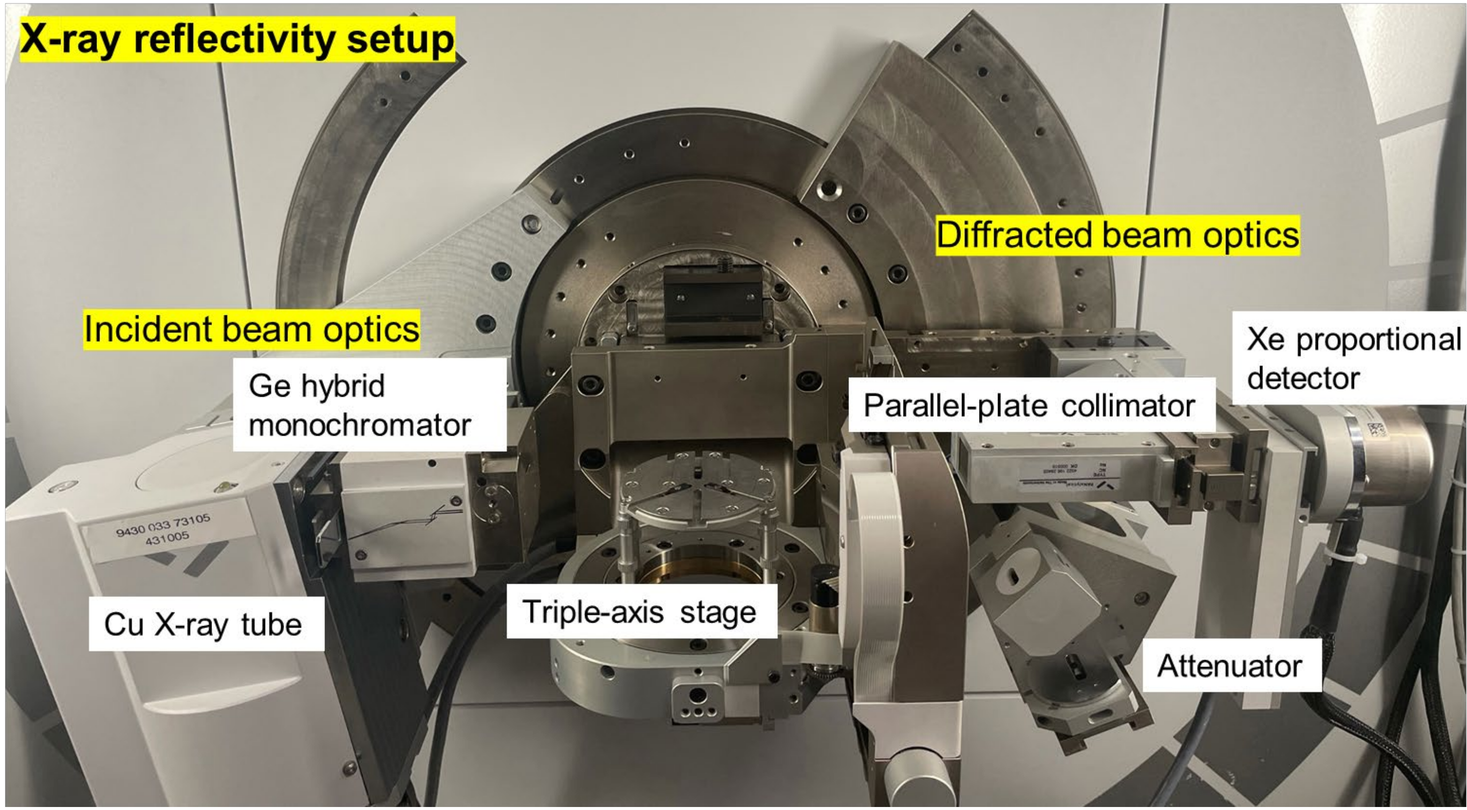
45 kV anode voltage and a 40 mA beam current producing Cu K_α radiation with =1.5419 Å

PANalytical Empyrean Xray Diffractometer
Department of Physics
New Mexico State University

- ☐ **X-Ray Reflectance (XRR)**
- ☐ Powder X-Ray Diffraction (XRD)
- ☐ High Resolution X-Ray Diffraction (HRXRD)
- ☐ Preferred orientation (Pole figure) etc.…

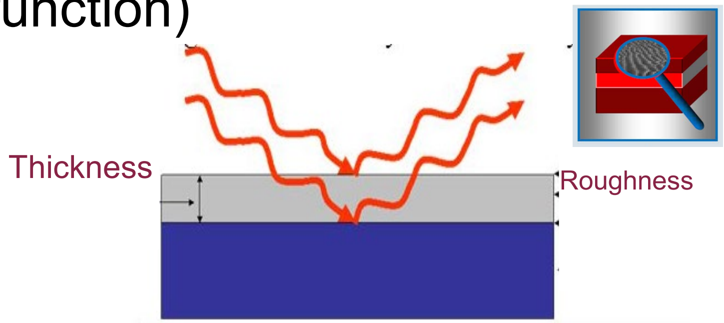
Instrumentation I: X ray diffractometer

X-ray reflectance (XRR)



What x-ray reflectivity reveals:

- **Film thickness** (5 Å to 1000 Å)
- **Surface and interface roughness**
  → (quality of the thin film)
- **Electron density (ED) profile**
  (ED can change the dielectric function)



☐ Incident beam optics: Ge (220) two-bounce hybrid monochromator, a fixed 1/32°divergence slit, and a 4 mm beam mask to produce a parallel beam.

☐ Diffracted beam optics: 0.27° parallel-plate collimator, a 0.04 rad soller slit, a programmable beam attenuator with a 0.125 mm Ni foil, Xe proportional detector.

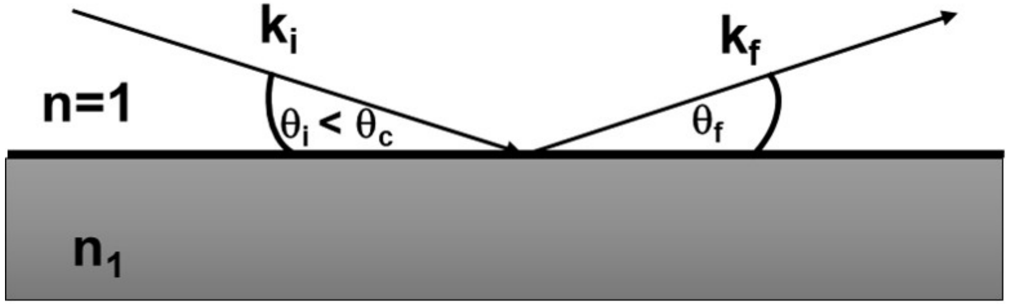
Instrumentation I: X ray diffractometer

X-ray reflectance (XRR)

Refractive index: $n_1 = 1 - \delta + i\beta$

☐ $\delta = \frac{\lambda^2 r_e}{2\pi}\rho_e$ ☐ $\beta = \frac{\lambda}{4\pi}\mu$

$r_e = 2.8*10^{-15}$ m: classical electron radius
λ: X-ray wavelength
ρ_e: electron density
μ: linear absorption coefficient.

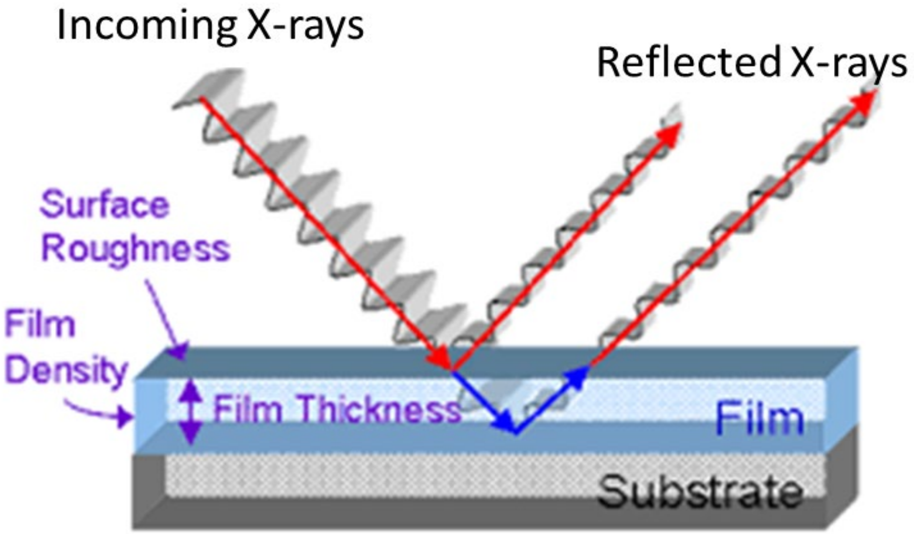


Case I. IF θ_i<θ_c

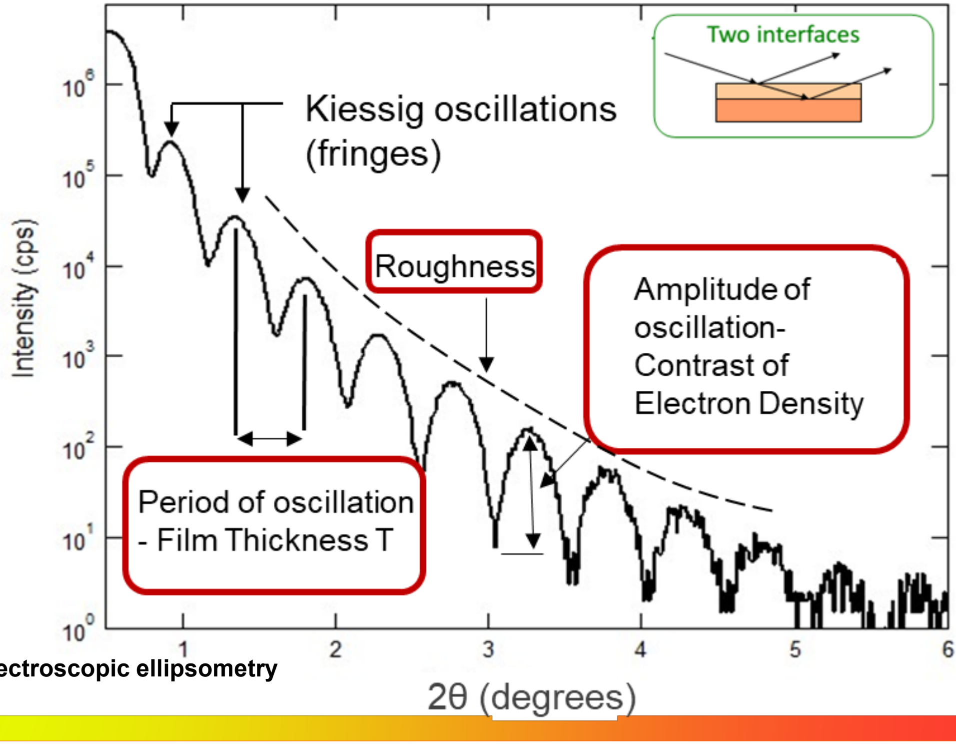
Total external reflection

$$\theta_c = \sqrt{2\delta}$$

Case II. IF θ_i>θ_c

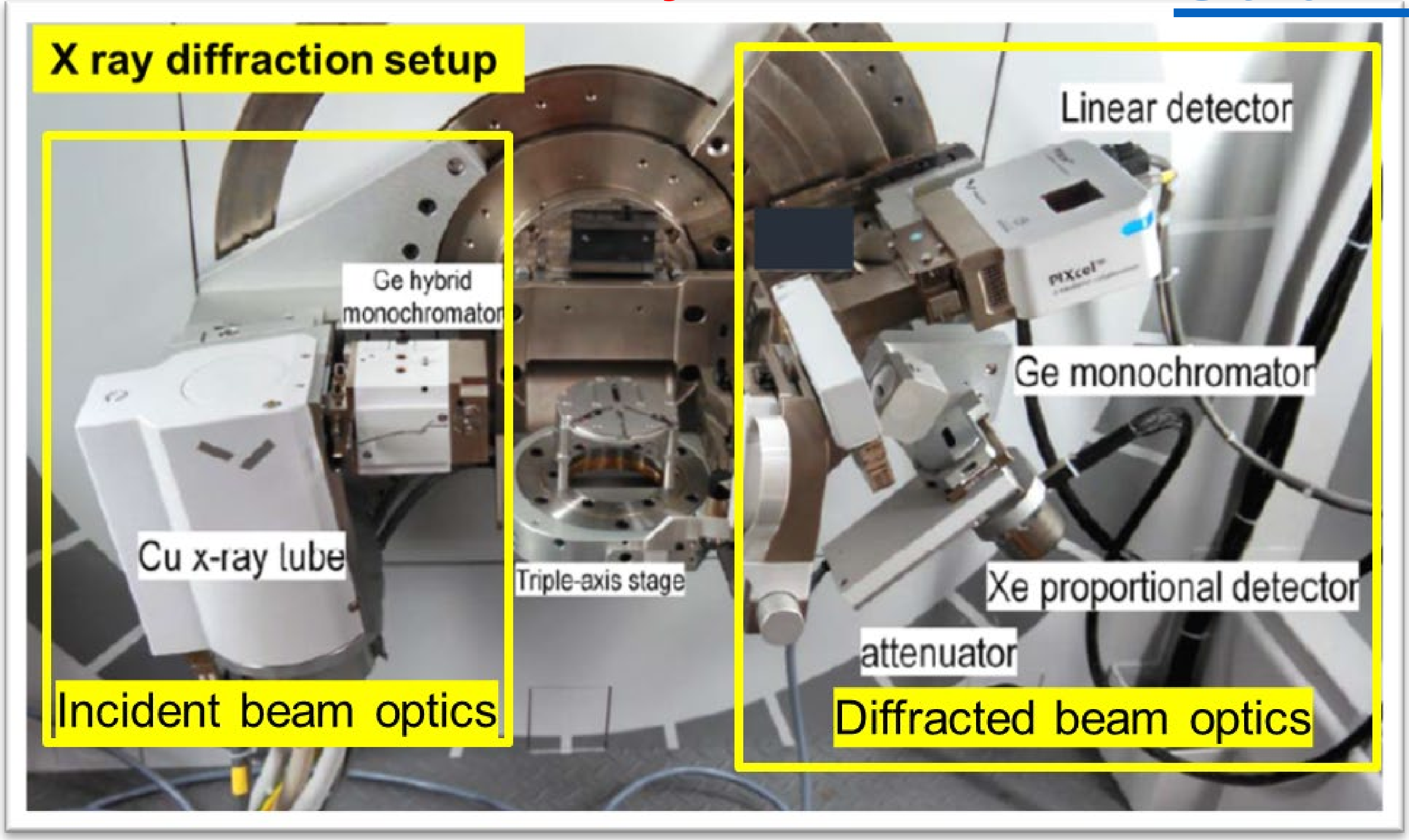


http://physics.valpo.edu/staff/arichter/XRR.htm



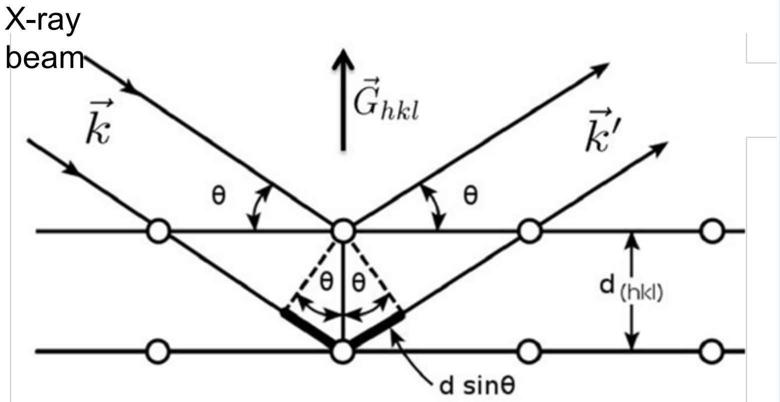
Instrumentation I: X ray diffractometer

Strain and Crystallinity



What x-ray diffraction reveals:

- Distances between atoms
- Lattice mismatch (**strain**)
- Grain size



$2d_{hkl}Sin\theta = n\lambda$ Bragg's Law

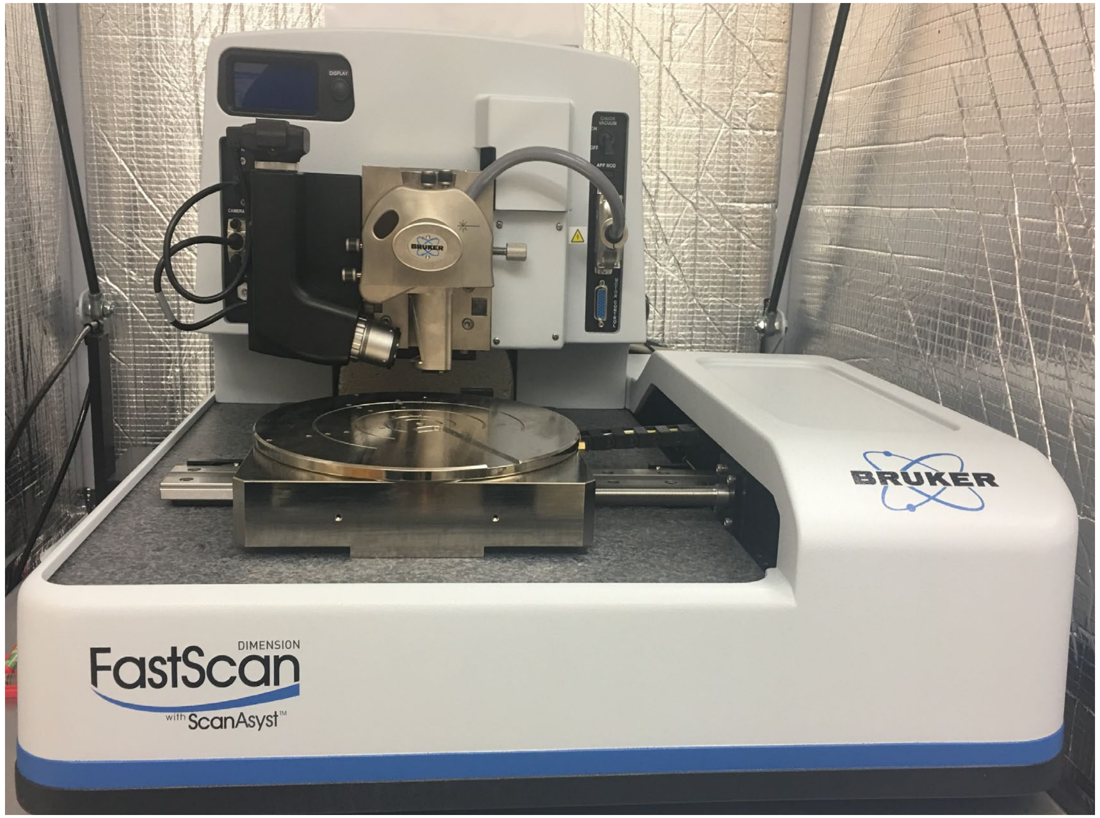
$$where\ \ d_{hkl} = a_{\perp}/\sqrt{h^2+k^2+l^2}$$

https://en.wikipedia.org/wiki/File:Bragg_diffraction.png

- ☐ Incident beam optics: fixed divergence slit, 4 mm beam mask, 0.04 rad soller slits, and a fixed anti-scatter slit
- ☐ Diffracted beam optics: programmable anti-scatter slit, 0.04 rad soller slits, and a 0.02 mm thick Ni filter (to block the K_β radiation).
- ☐ The diffracted intensity was measured with a PIXcel1D detector.

Instrumentation II: Atomic Force Microscope (AFM)

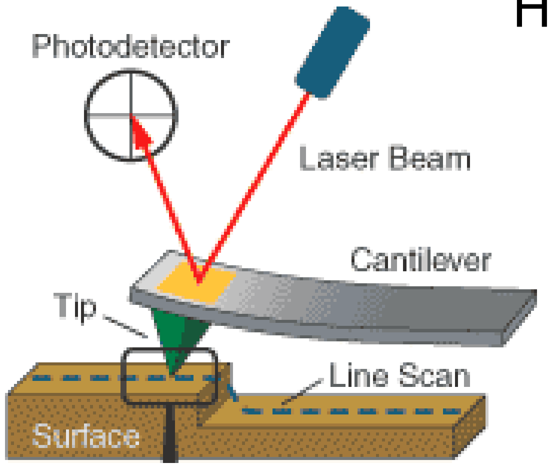
- ❑ The surface morphologies of ZnO films were examined by atomic force microscopy (AFM)



Surface Morphology

What atomic force microscope reveals:

- Surface roughness
- A Bruker FastScan Dimension AFM -TESPA probe in noncontact tapping mode
- Across a 10*10 μm^2 area of the samples



Hooke's law $F = -kx$

* F: force between the sample surface and the probe

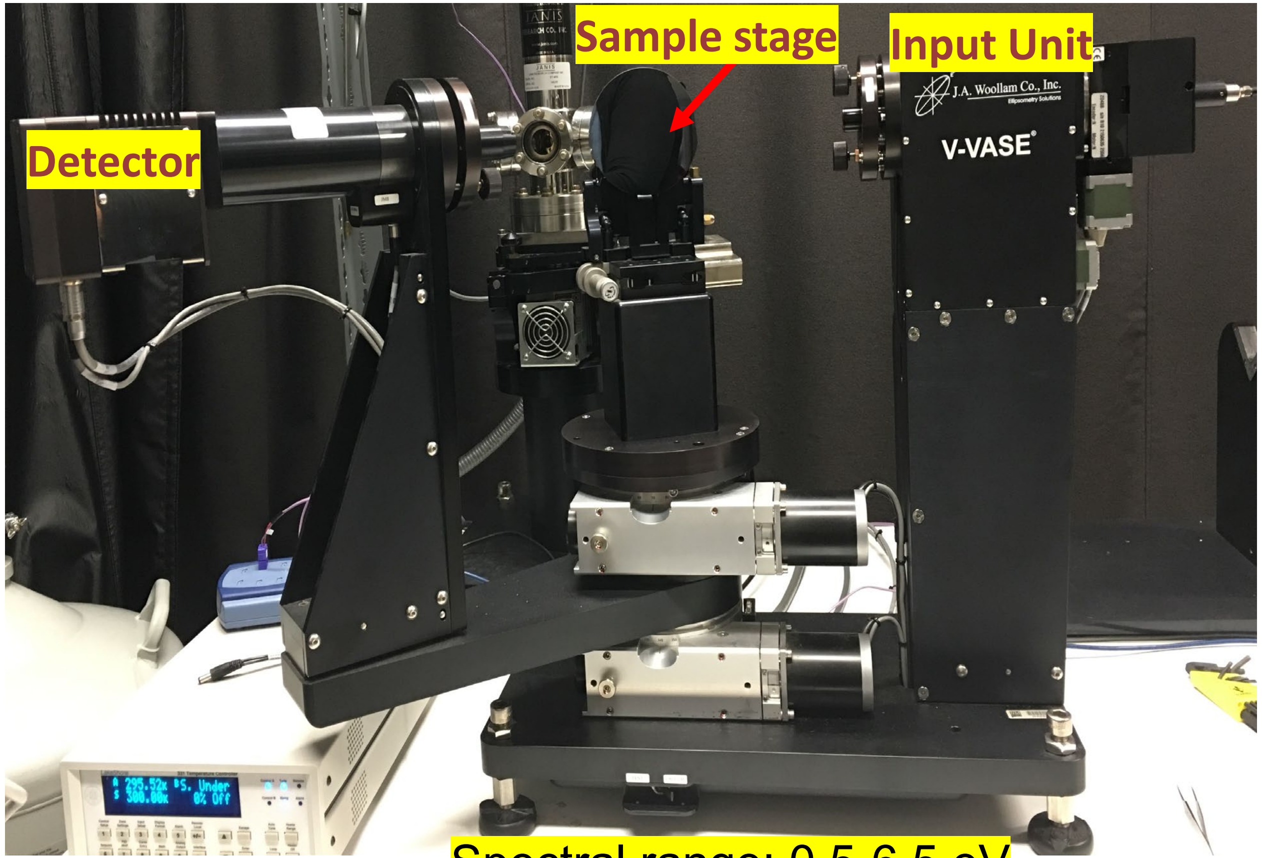
* k: spring constant

* x: cantilever deflection.

D. H. Agarwal, P. M. Bhatt, and A. M. Pathan, AIP Conference Proceedings **1447**, 531 (2012).

Instrumentation III: UV-Spectroscopic Ellipsometer

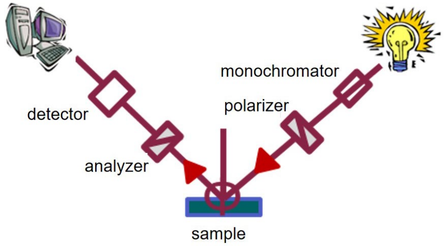
- Optical measurement technique. Spectroscopic Ellipsometry measures a change in polarization as light reflects or transmits from a material structure.
- Widely used optical metrology technique in the semiconductor industry
- Use with all types of materials: semiconductors, dielectrics, polymers, metals, multi-layers, and more



Spectral range: 0.5-6.5 eV

What spectroscopic ellipsometry (UV-VASE) reveals:

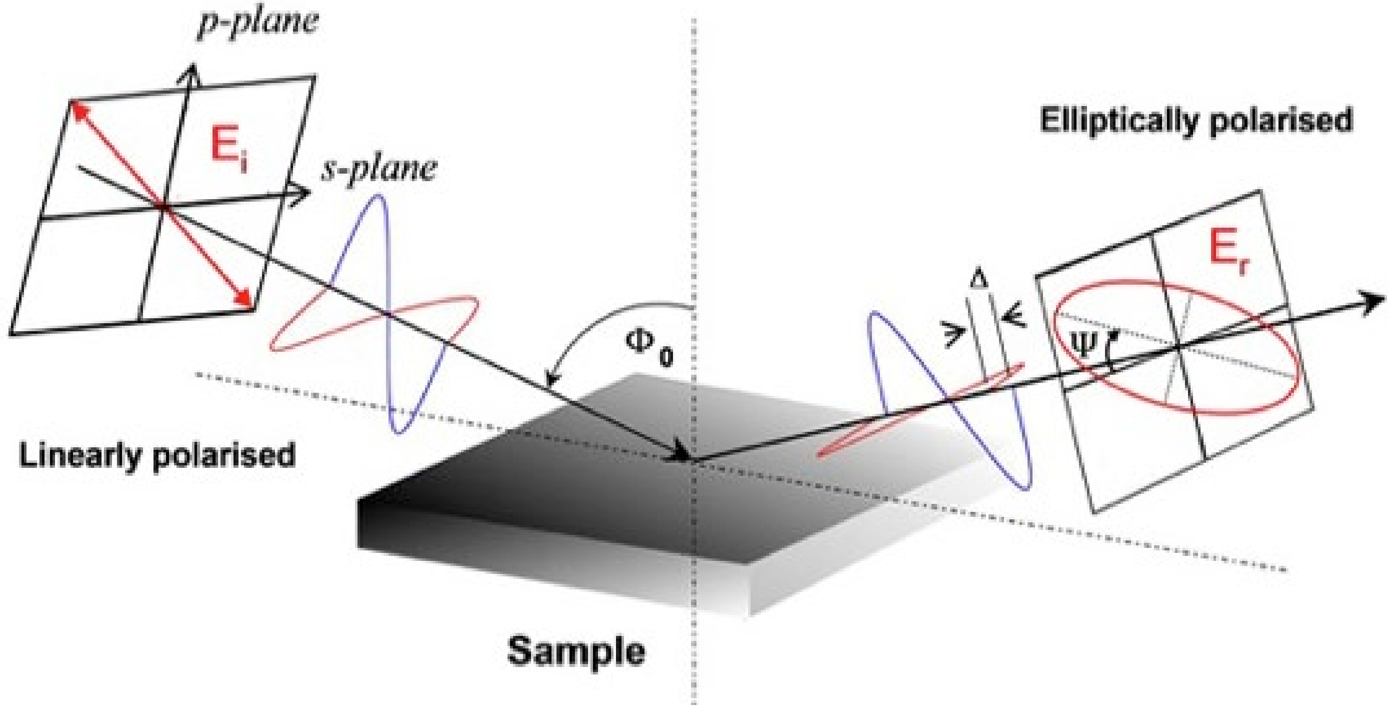
- Thickness (100 Å to 10000 Å)
- Excitonic absorption near band gap
- Optical constants (n and k)
- Dielectric properties
- Surface and interfacial layers
- Doping concentration
- Material composition (alloy fraction)
- Free carrier absorption



Instrumentation III: UV-Spectroscopic Ellipsometer

- Spectroscopic Ellipsometry measures the change of polarization as light is reflected or transmitted from a material structure.

- The polarization change is represented as an amplitude ratio Ψ and a phase difference Δ (ellipsometric angles)



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

Angle of incidence

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

$$\tilde{n} = n + ik$$

Complex refractive index $\tilde{n}$ consists of the index (n) and extinction coefficient (k):

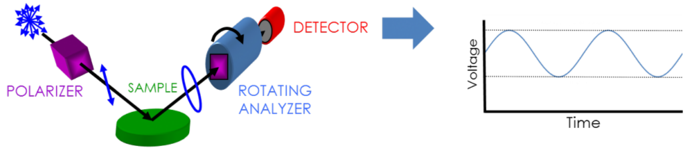
$$n, k :$$

Optical properties can be represented as the complex dielectric function

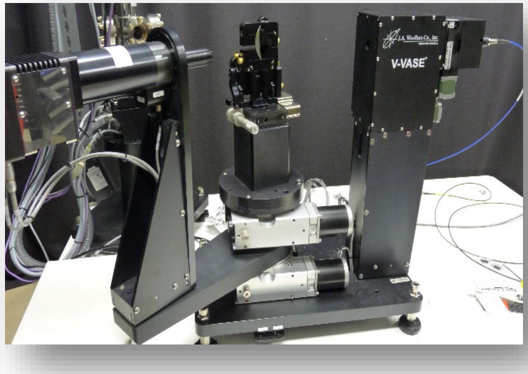
$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$

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

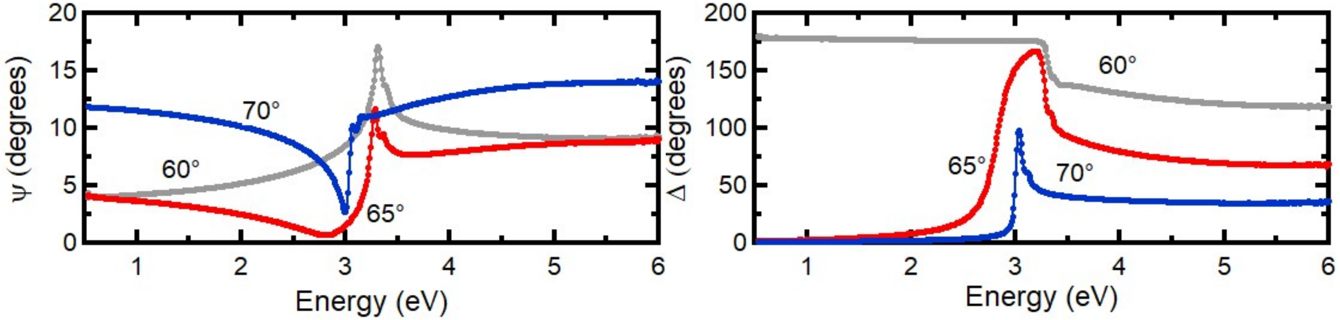
$$\varepsilon_2 = 2nk$$



Instrumentation III: Spectroscopic Ellipsometer_Data Analysis

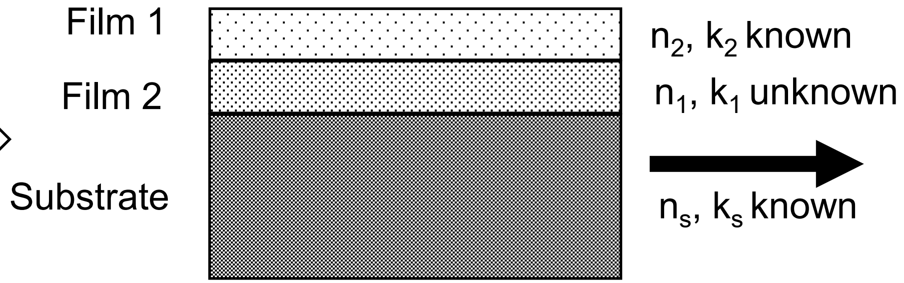


Measurement



Ellipsometric angles Ψ and Δ

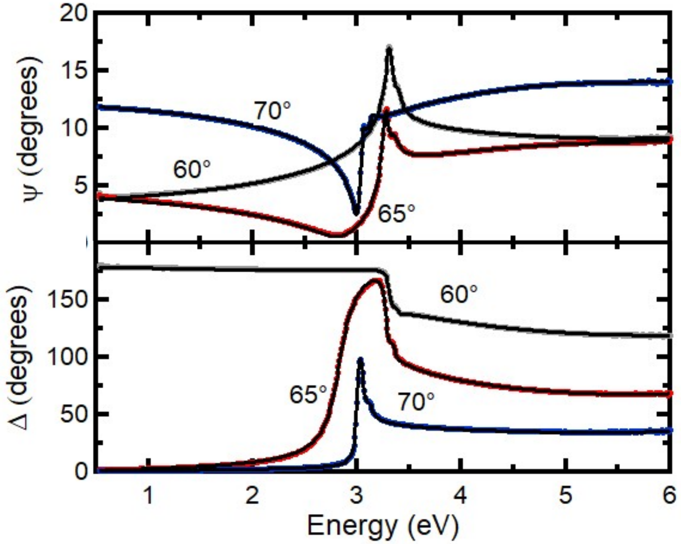
Model

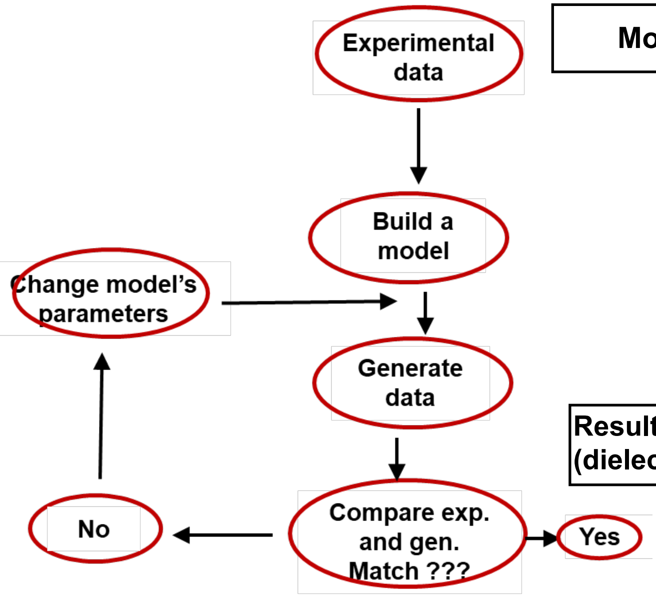


n_2, k_2 known

n_1, k_1 unknown

n_s, k_s known





Experimental data

Build a model

Change model's parameters

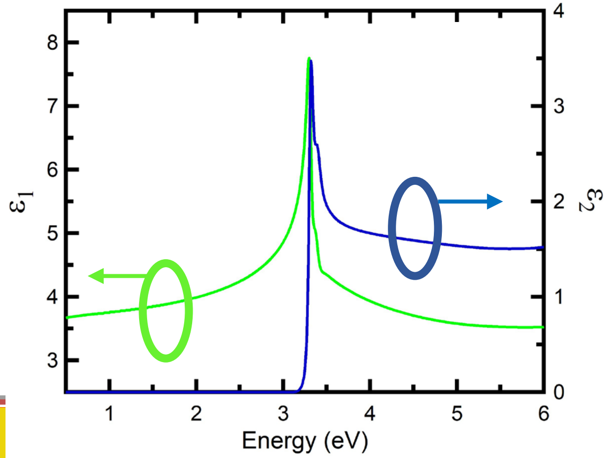
Generate data

Compare exp. and gen. Match ???

No

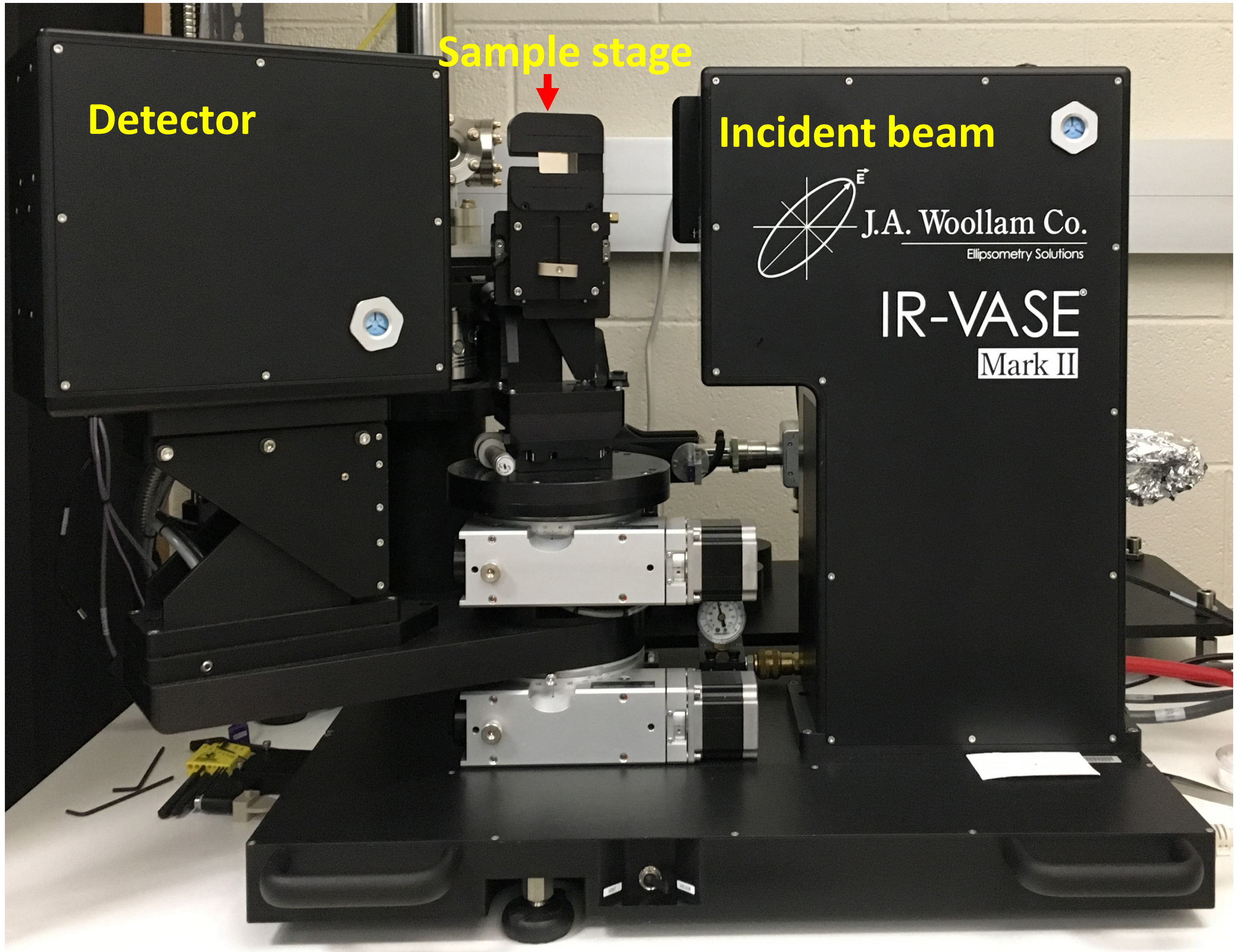
Yes

Results (dielectric function)

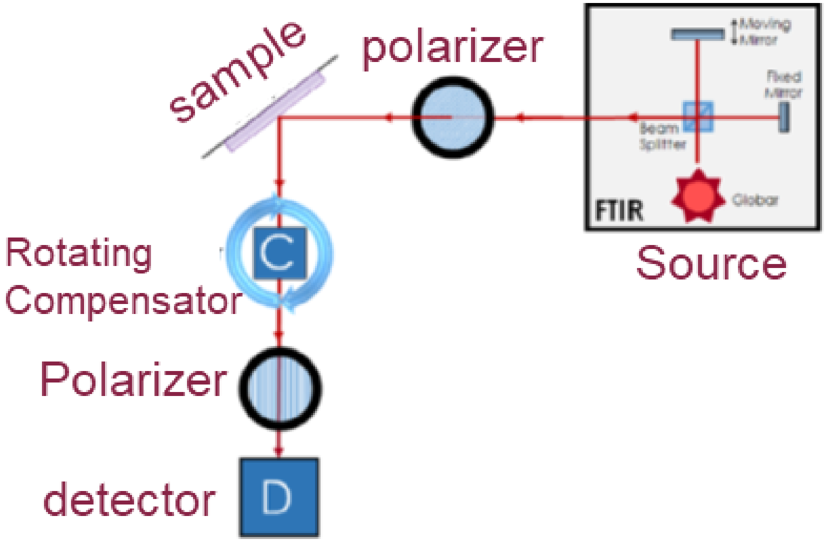


Instrumentation IV: IR Spectroscopic Ellipsometer

- The knowledge of vibrational structure changes (understand the energies and activity of the lattice vibrations) is valuable for microelectronic devices.



- Spectral range: 0.03-0.8 eV
- Angle of Incidence: 32° to 90°
- User-specified resolution from 1 to 64 cm^{-1}



☐ Introduction-part I

- Zinc Oxide (ZnO:II-VI compound semiconductor) for optoelectronic industry
- Role of ZnO film thickness for optoelectronic and photonic devices

☐ Sample characterization

- Optical Characterization: Spectroscopic Ellipsometer (IR-VASE, UV-VASE)
- Structural Characterization: X-ray diffraction (XRD), X-ray reflectivity (XRR), Atomic force microscope (AFM)

☐ **Results: Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition (ALD)**

[**Nuwanjula S. Samarasingha**, Stefan Zollner, Dipayan Pal, Rinki Singh, and Sudeshna Chattopadhyay, Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition, J. Vac. Sci. Technol. B **38**, 042201 (2020)]

☐ Introduction-part II

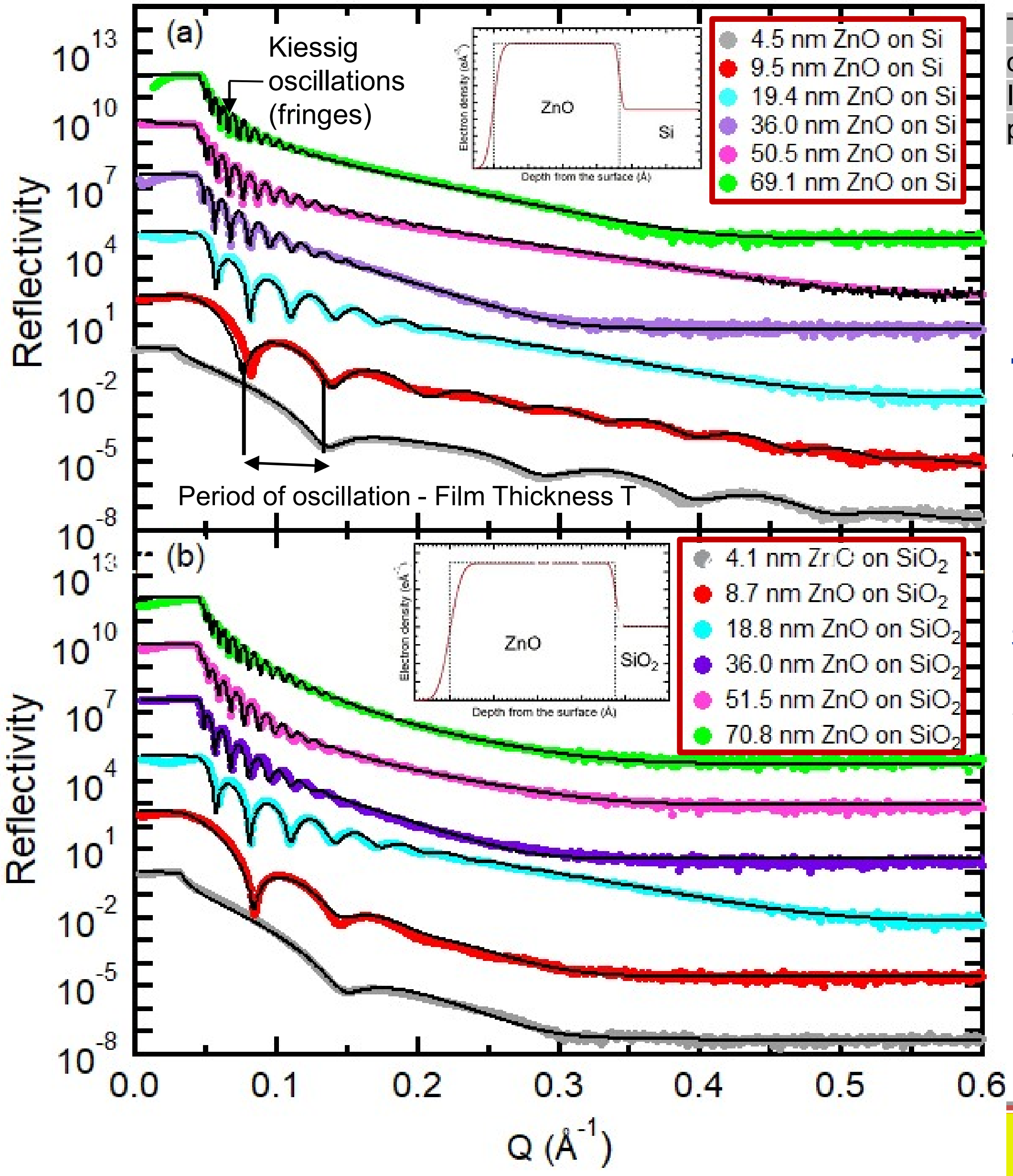
- Gallium Phosphide (GaP:III-V compound semiconductor) for optoelectronic industry
- Why we study temperature dependence of lattice vibration in GaP

☐ Results: Temperature dependence of the optical phonon reflection band in GaP

[[Nuwanjula Samarasingha and Stefan Zollner, Temperature dependence of optical phonon reflection bands in GaP, J. Vac. Sci. Technol. B (under review) arXiv:2105.06662, (2021)]

☐ Conclusions

Results I: X ray reflection (XRR) How thick is my film?



The data were analyzed using the Parrat formalism (L. G. Parrat, Surface studie of solids by total reflection of x-rays, Phys. Rev. 95, 359, 1954). We used the MotoFit program (http://motofit.sourceforge. net) in an Igor Pro (Wavemetrics, Inc., Lake Oswego, OR USA) environment to fit our XRR data and determine the fit parameters.

1) The agreement between data and fit is excellent using our model

➤ **high level of confidence in the accuracy of our layer thicknesses and densities.**

2) The drop of reflectance versus Q (scattering vector) is relatively slow

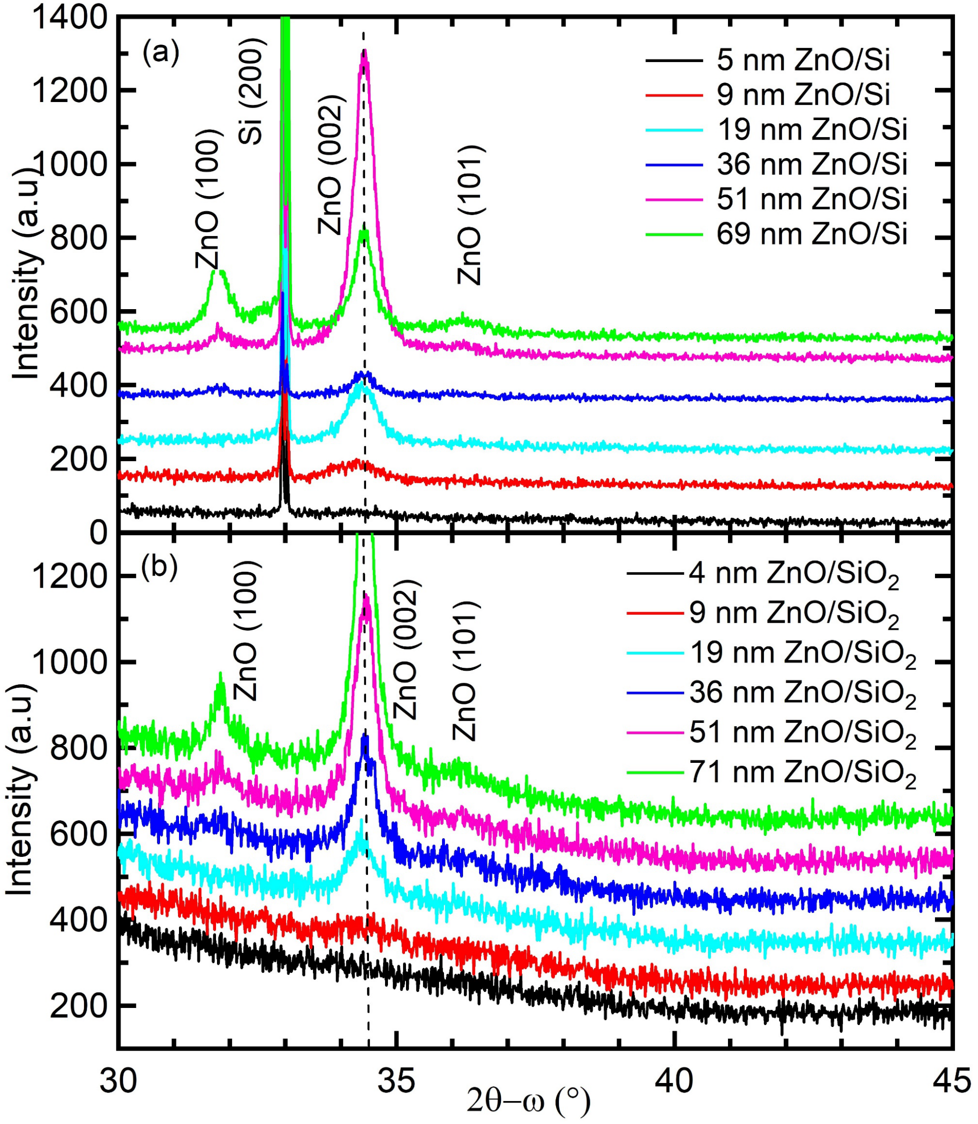
➤ **the surface roughness for our ZnO layers is rather small.**

3) The critical angle given by the sharp drop of the reflectance is nearly the same

➤ **nearly constant electron density (independent of layer thickness).**

High-quality pinhole-free ZnO films with very low surface and interface roughness

Results II: X ray diffraction (XRD) Crystallinity and Strain



1) X ray diffraction pattern matches with the **standard diffraction pattern** of hexagonal ZnO.

2) ZnO (002) peak is the strongest peak. ➤ **Preferred orientation (texture) of the ZnO is along <002>** direction with c axis perpendicular to the substrate surface.

3) 36 nm ZnO/Si film has more crystallinity than ZnO/SiO_2 ➤ The role of the substrate (Si or quartz) is very important.

4) Strain ($\varepsilon_\perp$) is small (0.01%-0.10%) and not even the sign of the strain can be determined with certainty.

Bragg's Law

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

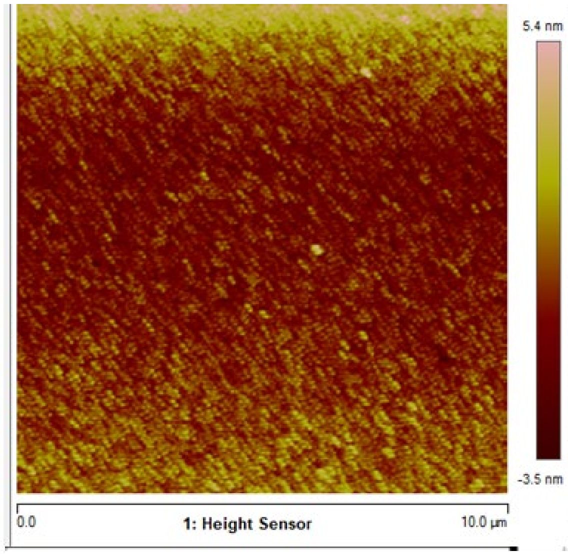
$$where \ \ d_{hkl} = a_\perp/\sqrt{h^2+k^2+l^2}$$

$$\varepsilon_\perp = \frac{a_\perp}{a_0} - 1$$

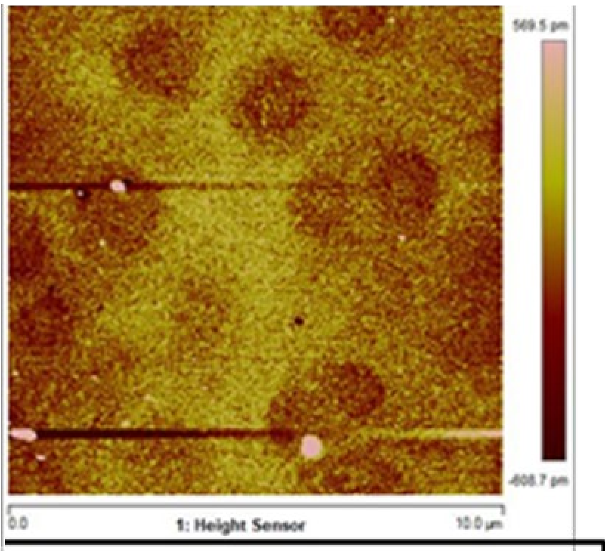
a_0 is the lattice constant of bulk ZnO crystal

Results III: Atomic Force Microscope (AFM)

Surface Roughness



69 nm ZnO/Si



5 nm ZnO/Si

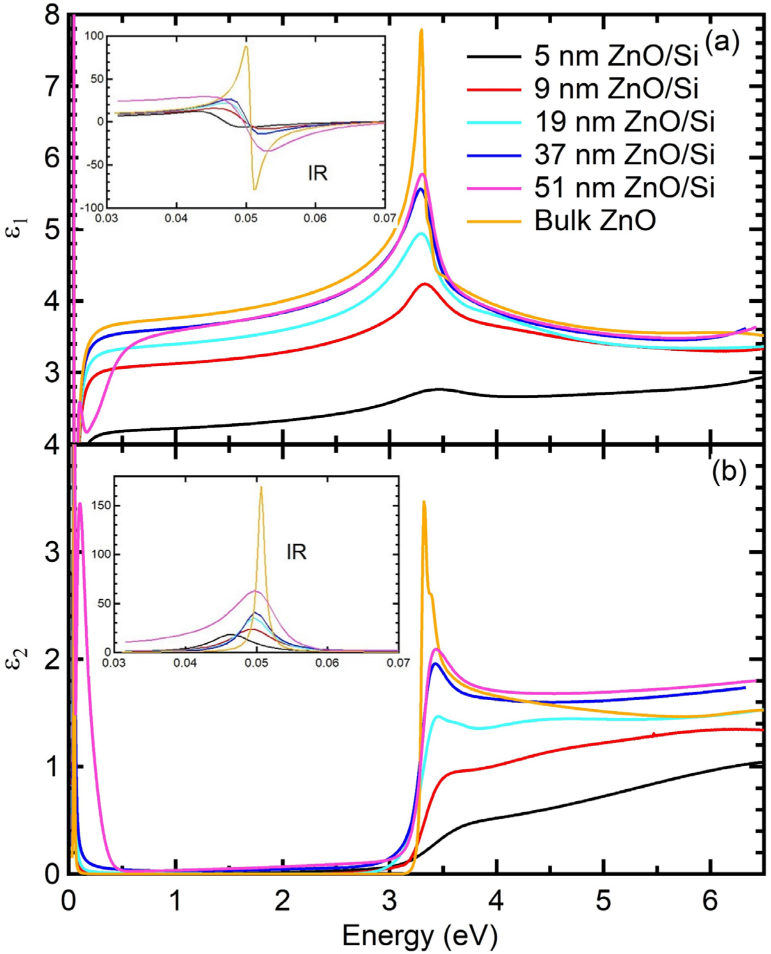
☐ The RMS surface roughness

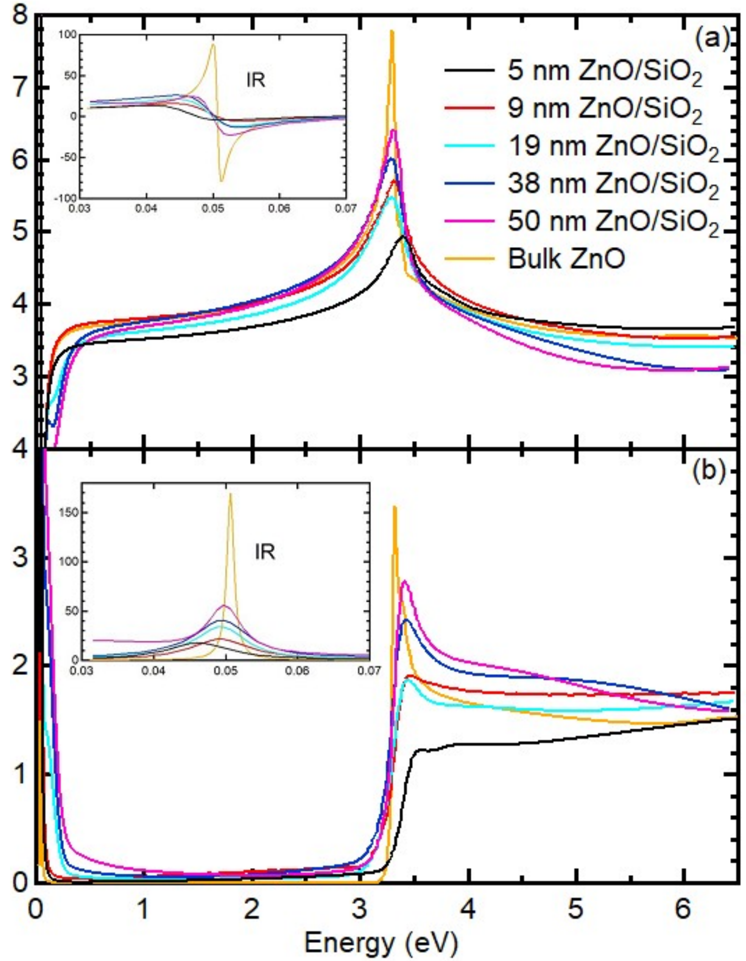
- Data Analysis: Bruker NanoScope analysis software
- Averaged over several sites.

The surface roughness measured by XRR for the ZnO films on Si and SiO_2 substrates is in good agreement with the AFM RMS roughness.

Results IV: Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition

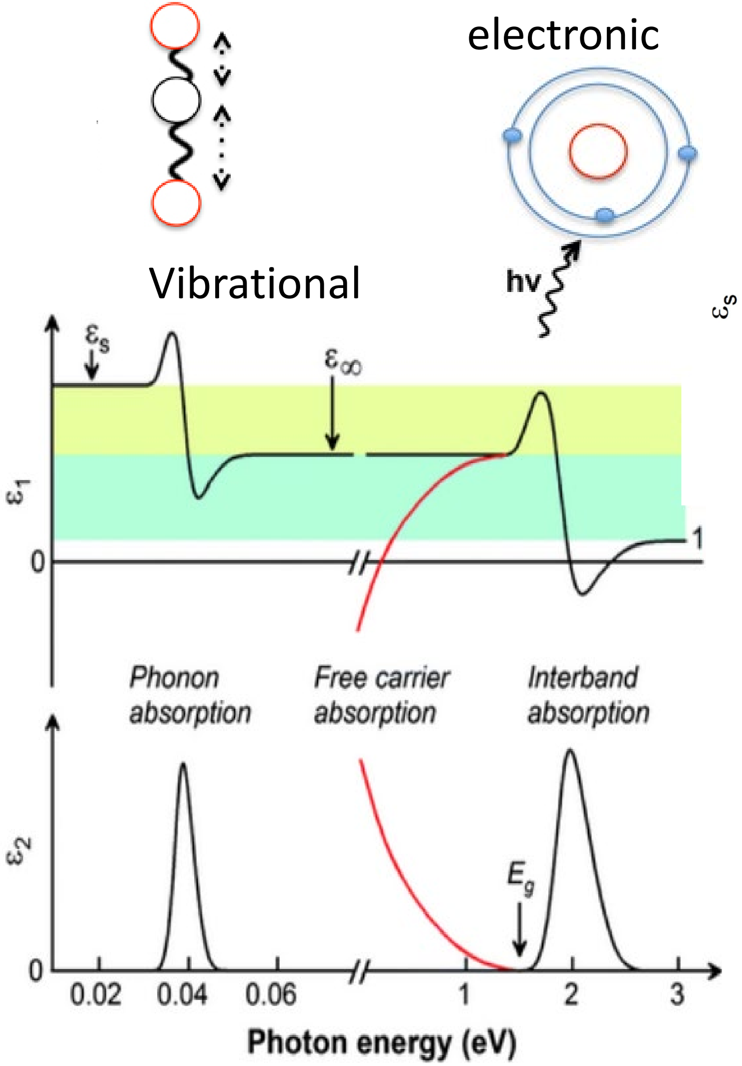
- ❑ Measured ZnO from the midinfrared (0.03 eV) to the deep ultraviolet (6.6 eV).
  - variability of the DF and the influence of electronic and **vibrational structure changes**. **This knowledge is valuable for microelectronic devices.**

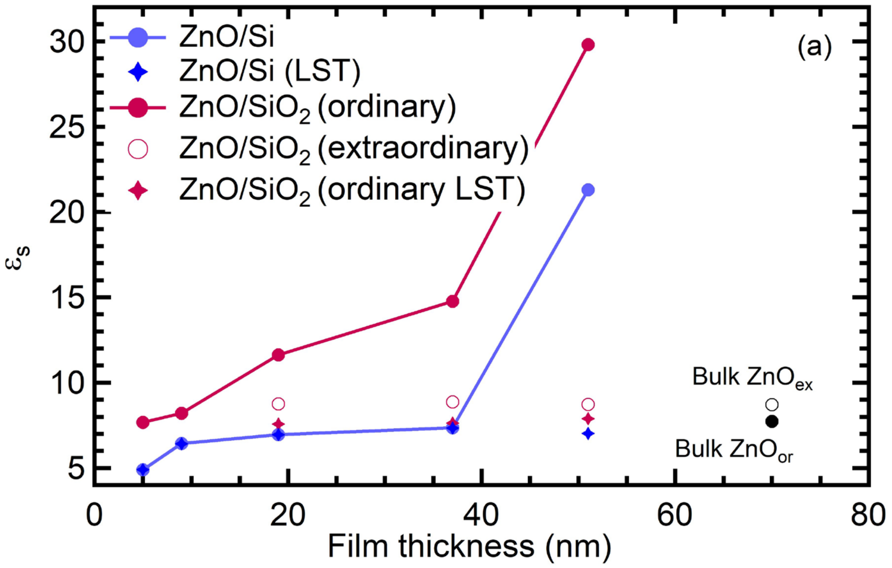


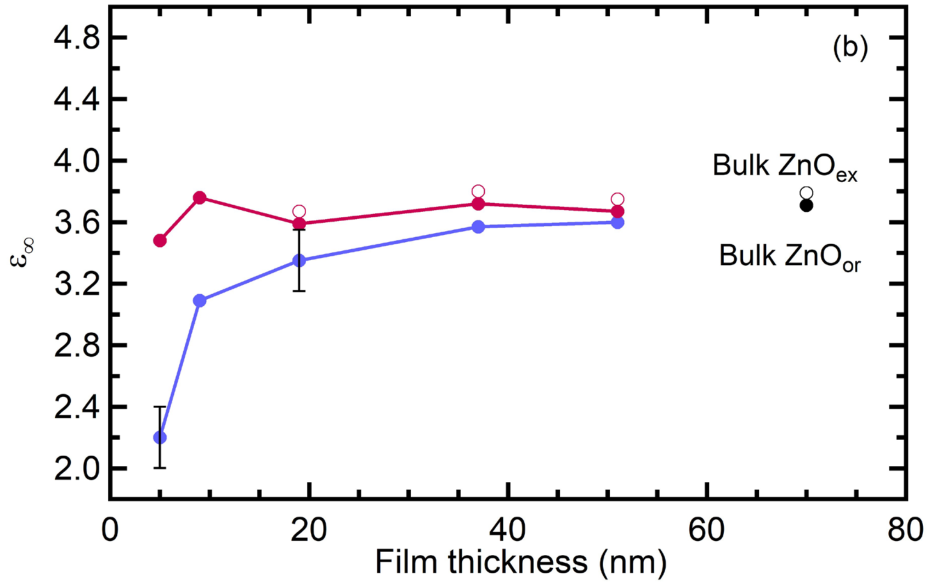


- ❑ How the dielectric functions $(\widetilde{\varepsilon})$ of semiconductors depend on
  - **Film thickness • Substrate material • Excitonic effects (bound electron – hole pair)??**
- ❑ Significant variations of the optical constants of ZnO as a function of thickness.
- ❑ Both ϵ_1 and ϵ_2 show significant variations with thickness over the complete spectral range, regardless of the substrate.
- ❑ For ZnO on Si, the absorption above the bandgap (say, at 4 eV) increases monotonically with the layer thickness.
- ❑ There is a drastic reduction in the excitonic effects near the bandgap, especially for thin ZnO on Si.

Results V: Thickness dependence static (ε_s) and high (ε_∞) frequency dielectric constant







Lyddane Sachs Teller relation (LST relation)

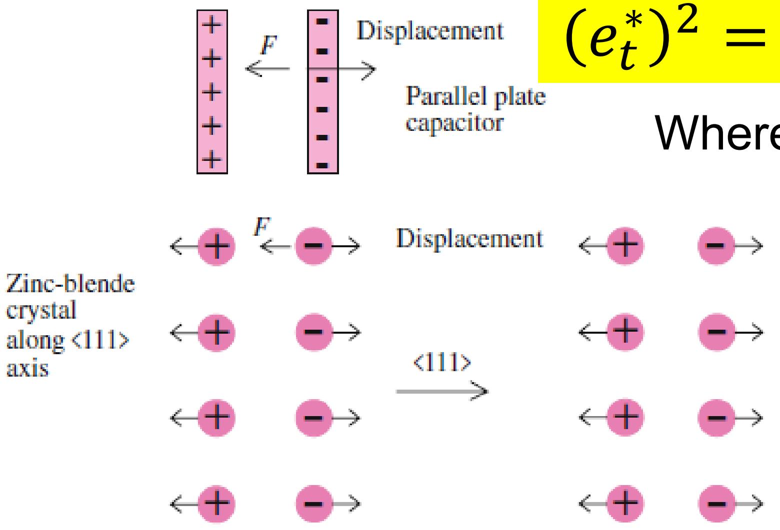
$$\boxed{\varepsilon_s = \varepsilon_\infty \frac{\omega_{LO}^2}{\omega_{TO}^2}}$$

($\boldsymbol{\omega_{LO,TO}}$: longitudinal and transverse optical phonon frequencies)

- 40% reduction of the high-frequency dielectric constant ε_∞ in thin layers on Si
- ZnO on SiO$_2$: high-frequency dielectric constant ε_∞ is nearly independent of thickness
- ZnO on Si/SiO$_2$: ε_s increasing with increasing film thickness

Results V: Thickness dependence “Born Effective Charge”

Coupling between optical phonons and electric fields is quantified by the Born effective charge



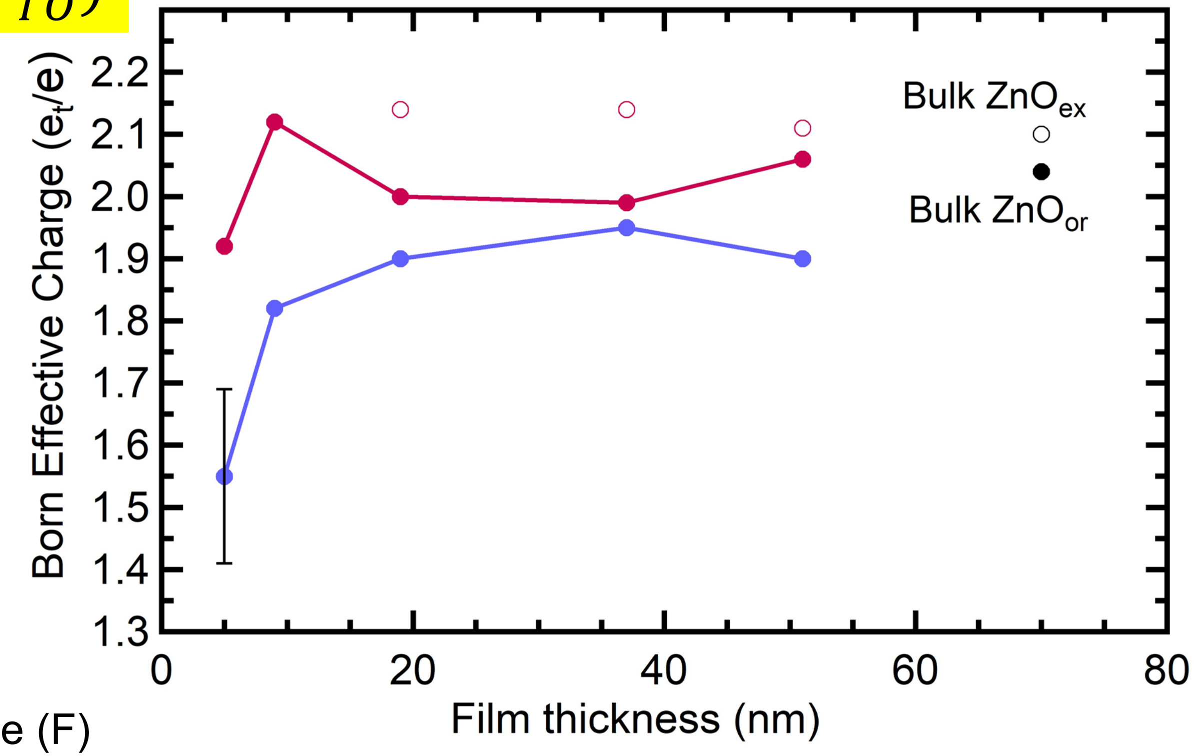
$$(e_t^*)^2 = 4\pi^2 V\mu\varepsilon_0\varepsilon_\infty(\nu_{LO}^2 - \nu_{TO}^2)$$

Where V : volume

μ : reduced mass

ε_0 : vacuum permittivity

- ➢ TO propagating along [111] direction
- ➢ ⊕ and ⊖ ions planes ⊥ [111] axis ⟶ ↑⊕ $\xrightarrow{k}$ ⊖↓
- ➢ LO mode ⊕ ⊖ (← LO →) ⟶ additional Coulombic restoring force (F)
- ➢ Additional force then leads to the frequency change

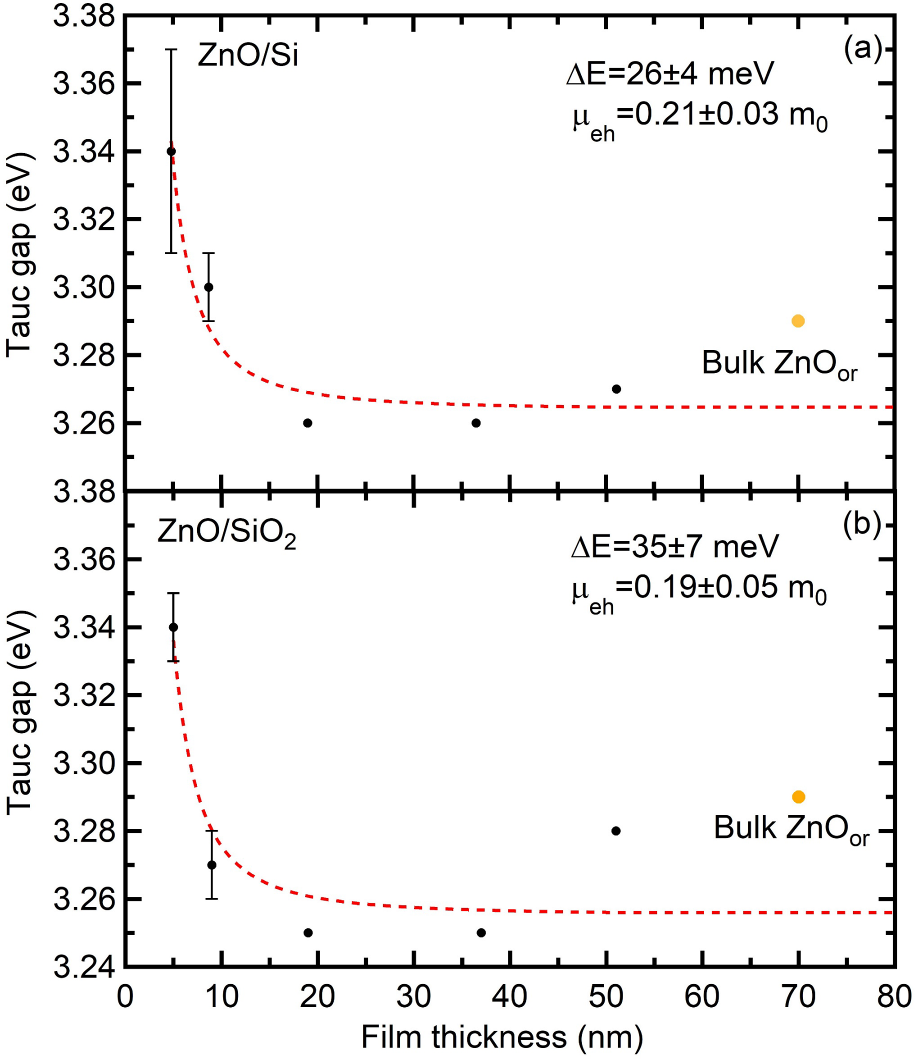


- ➢ ZnO/Si: Born Effective Charge decreasing with decreasing film thickness (by about 20%).
- ➢ ZnO/SiO$_2$: nearly independent of thickness.

Manuel Cardona, and Peter Y. Yu, *Fundamentals of Semiconductors: Physics and Materials Properties,* Philadelphia, 1995.
Reparaz, J. S., et al., *Applied Physics Letters* 96.**23** (2010)

Results VI: Thickness dependence of the band gap

- ☐ **Band gap is a major factor determining the electrical conductivity.**



energy increases

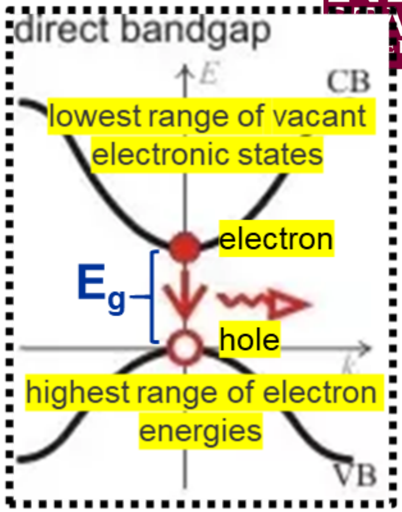
- ☐ Small blueshift of the band gap (80 meV) with decreasing layer thickness due to quantum confinement.
- ☐ Quantum confinement

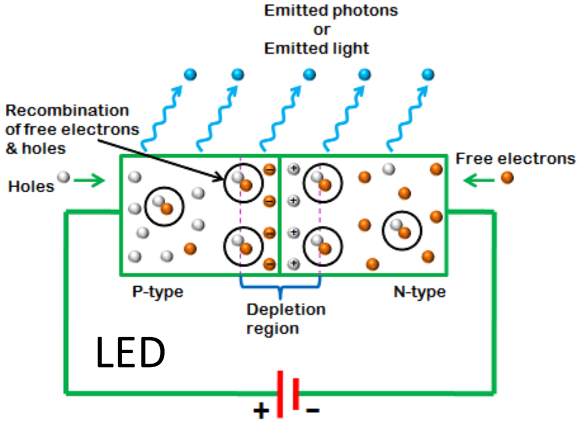
$$E_g(\mathrm{t}) = E_{g,bulk} + \frac{F}{t^2}\text{-}\Delta\mathrm{E}$$

where $E_{g,bulk}$ =3:29 eV

t is the layer thickness

F is the confinement factor (F=$\frac{\hbar^2\pi^2}{2\mu_{eh}}$, μ_{eh} is the electron-hole reduced effective mass), and ΔE is a thickness-independent difference between the bulk and layer Tauc gap.





Conclusion I

High quality, smooth, ZnO thin films with varying film thickness, from ~5 nm to ~50 nm, were characterized by IR/UV Spectroscopic Ellipsometer, X-ray reflectance (XRR), X-ray diffraction (XRD), and Atomic force microscope (AFM).

❑ Thickness confirmed by X ray reflectance.

❑ Electron density of ZnO films is close to that of bulk ZnO and does not vary considerably with film thickness.

➤ **High-quality pinhole-free ZnO films**

❑ 36 nm ZnO/Si film has more crystallinity than ZnO/SiO_2 ➤ The role of the substrate (Si or quartz) is very important

❑ Significant variations of the optical constants of ZnO as a function of thickness.

❑ Both ϵ_1 and ϵ_2 show significant variations with thickness over the complete spectral range

- ZnO on Si: excitonic enhancement disappears in thin films
- ZnO on SiO_2: excitonic enhancement reduced with decreasing thickness

❑ Strain ($\varepsilon_\perp$) is very small. Therefore, the variations of the dielectric function are more likely to be a function of thickness rather than a function of strain

❑ Small blueshift of the band gap with decreasing layer thickness due to quantum confinement

- ☐ Introduction-part I
  - Zinc Oxide (ZnO:II-VI compound semiconductor) for optoelectronic industry
  - Role of ZnO film thickness for optoelectronic and photonic devices
- ☐ Sample characterization
  - Optical Characterization: Spectroscopic Ellipsometer (IR-VASE, UV-VASE)
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[Nuwanjula S. Samarasingha, Stefan Zollner, Dipayan Pal, Rinki Singh, and Sudeshna Chattopadhyay, Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition, J. Vac. Sci. Technol. B 38, 042201 (2020)]

- ☐ **Introduction-part II**
  - Gallium Phosphide (GaP:III-V compound semiconductor) for optoelectronic industry
  - Why we study temperature dependence of lattice vibration in GaP
- ☐ Results: Temperature dependence of the optical phonon reflection band in GaP

[[Nuwanjula Samarasingha and Stefan Zollner, Temperature dependence of optical phonon reflection bands in GaP, J. Vac. Sci. Technol. B (under review) arXiv:2105.06662, (2021)]

- ☐ Conclusions

Gallium Phosphide (GaP: III-V compound semiconductor)

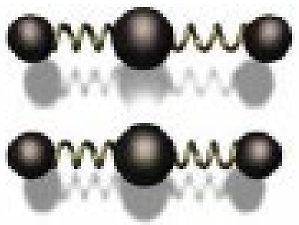
Excellent semiconductor for optoelectronic and photonic applications

☐ Thermally stable semiconductor material

☐ Application: Light-emitting diodes (LEDs), detectors, solar cells, and high-temperature transistors.

❯ **Important to study the optical properties of this semiconductor, including the effects of cryogenic and elevated temperatures**

Temperature dependence of the optical phonon bands in GaP



☐ Optical phonons are vibrations of the atom in a crystal.

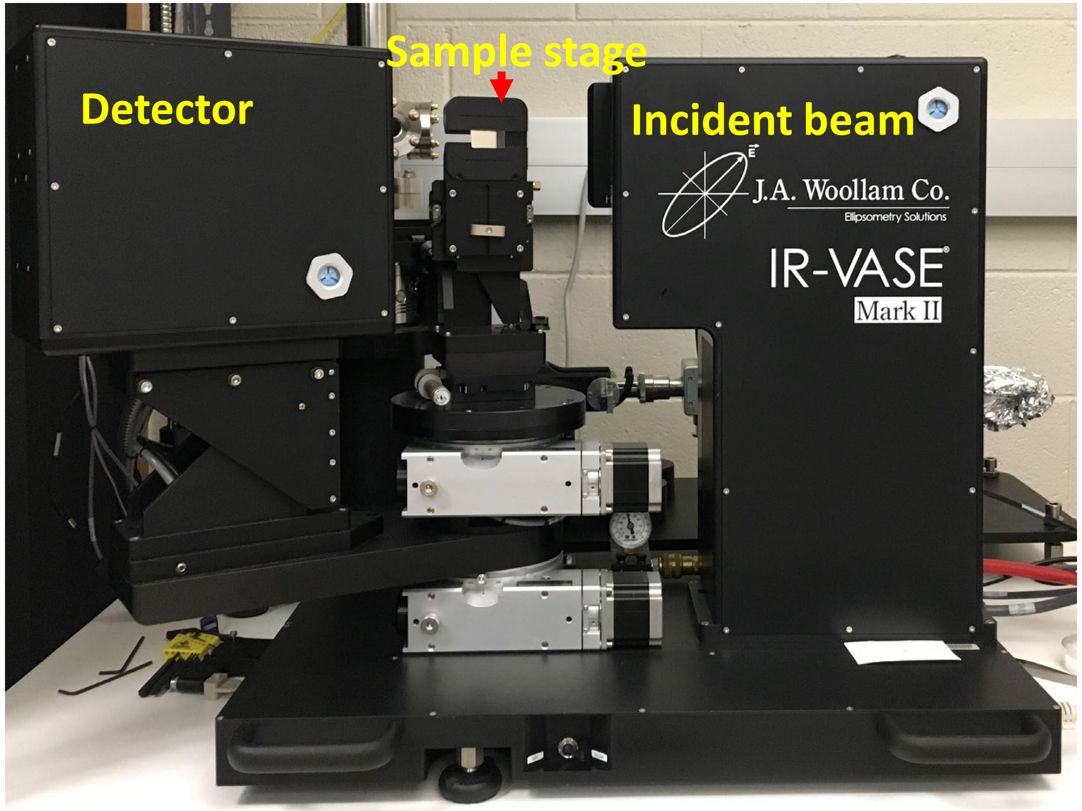
Why this knowledge is valuable for microelectronic devices?

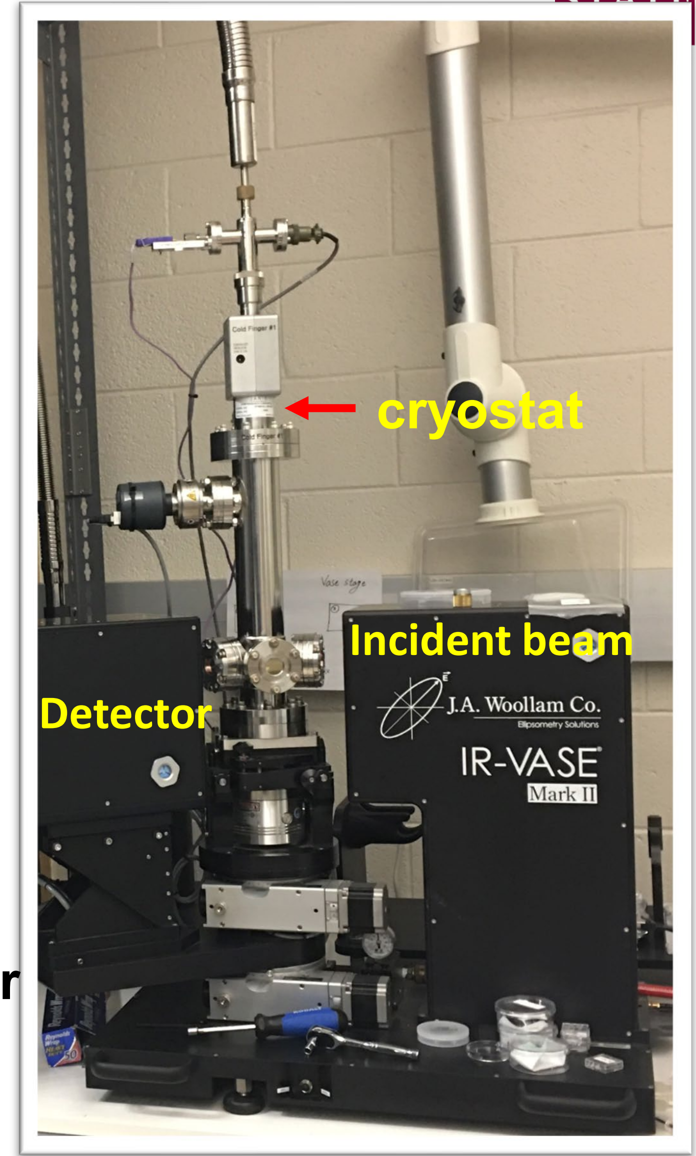
Ex: ▪ Electrons ⓔ move through a transistor channel (interface between Si and gate oxide) ❯ if this ⓔ collide with the nucleus of an atom ❯ oscillate ❯ this absorbs energy from the electron and contributes to **increased power consumption** by the device.

Therefore, it is very important to study the behavior of these lattice vibrations not only at the room temperature but also at cryogenic and elevated temperatures.

Instrumentation: IR Spectroscopic Ellipsometer with ST-400 ultra high vacuum (UHV) cryostat

- ❑ The knowledge of vibrational structure changes (understand the behavior of lattice vibrations) is valuable for microelectronic devices.





- Temperature range:80 K (liquid nitrogen) to 800 K
- UHV pressure: 10^{-8}-10^{-9} Torr

☐ Introduction-part I

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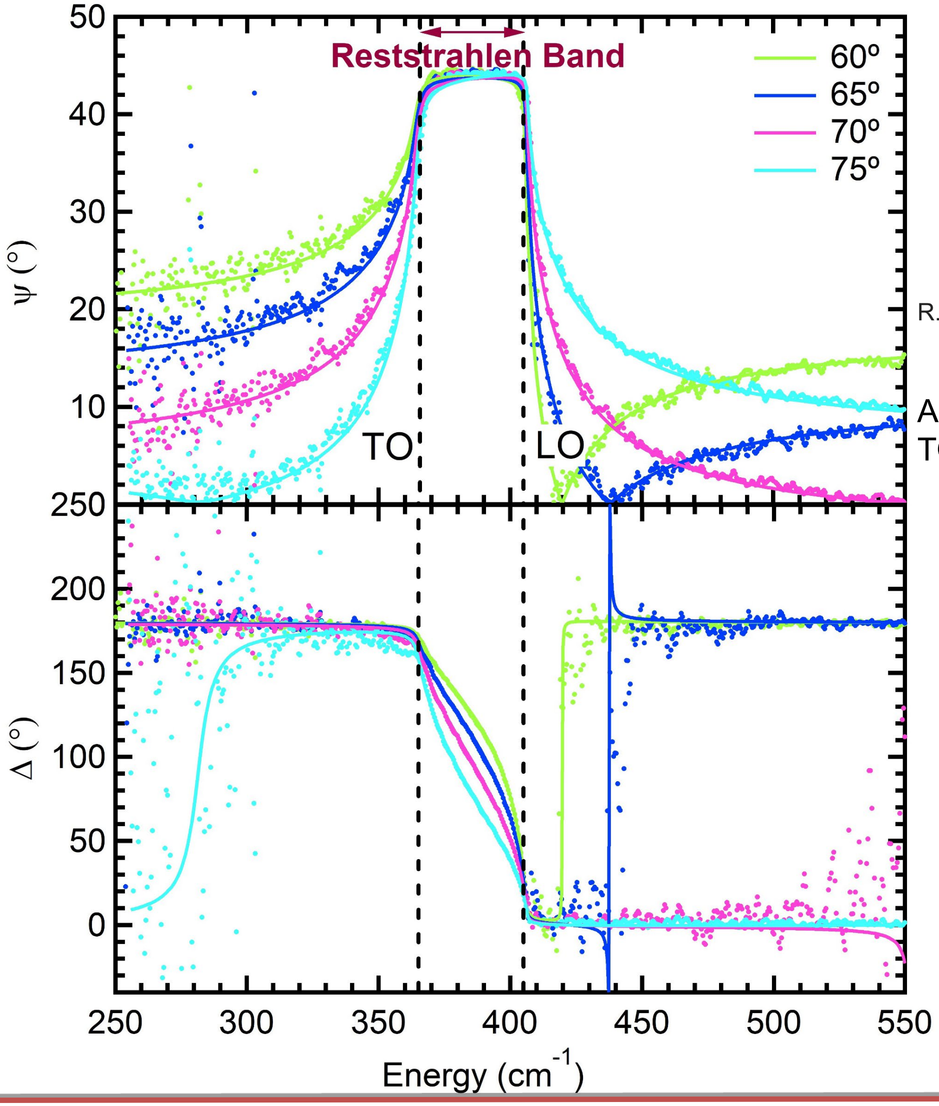
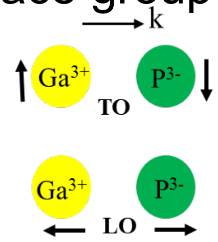
First temperature dependence published work using our J. A. Woollam IR-VASE Mark II Spectroscopic Ellipsometer.

Results I: GaP: Infrared Lattice Vibrations (room temperature)



GaP space group: T_d^2

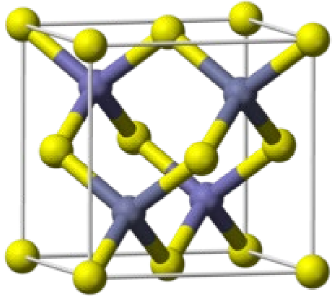


R. P. Lowndes, Physical Review **B 1.6**, 2754, 1970.

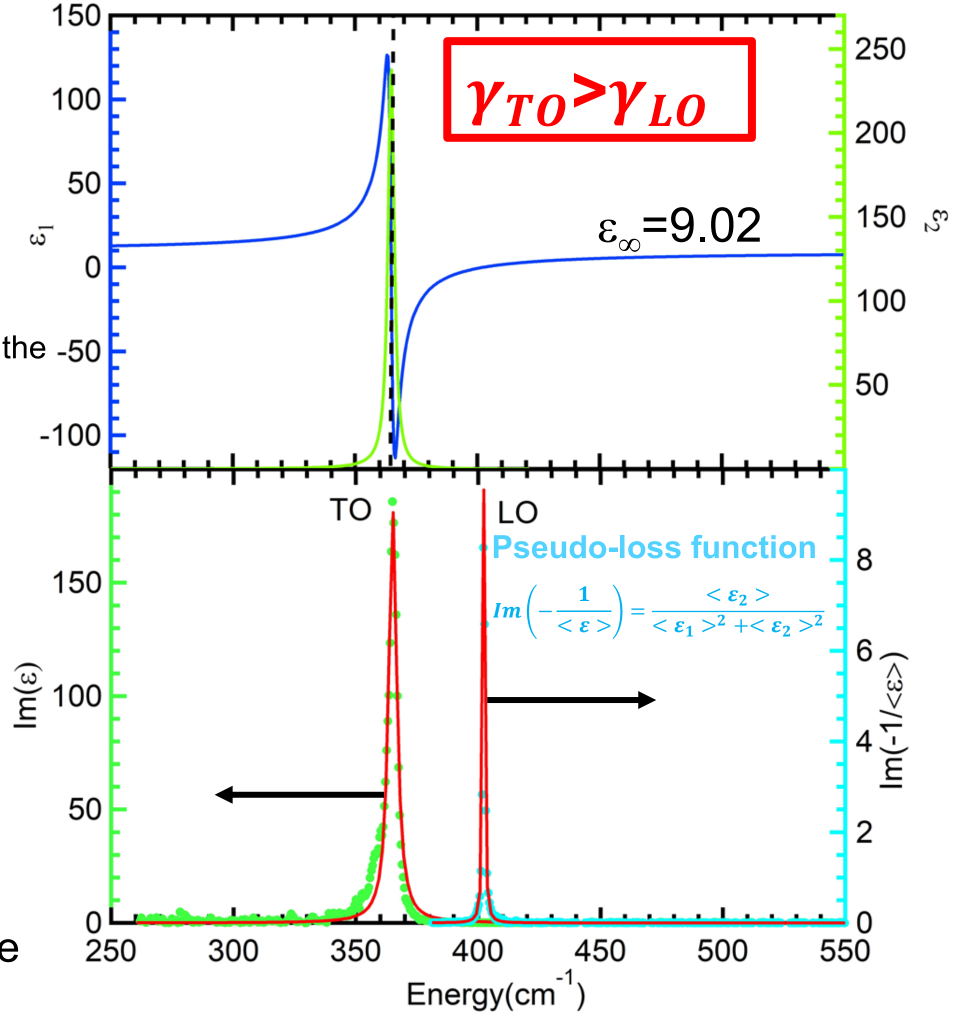
Lowndes model (TOLO):

Applies two different broadening parameters to the TO and LO phonons

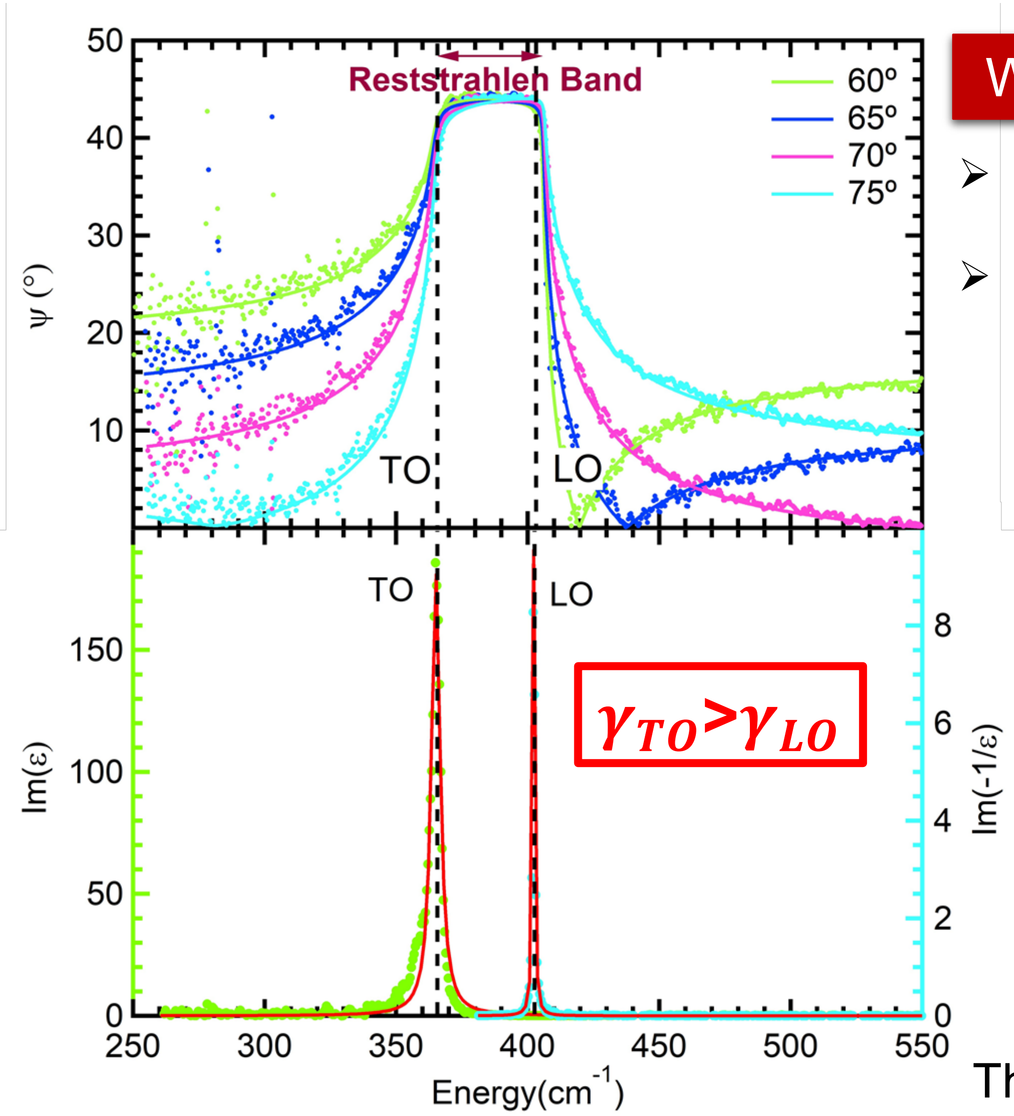
$$\varepsilon(\omega)=\varepsilon_\infty \frac{\omega_{LO}^2-\omega^2-i\gamma_{LO}\omega}{\omega_{TO}^2-\omega^2-i\gamma_{TO}\omega}$$



- ➢ ε_2: peak near TO frequency
- ➢ Loss function: Im(–1/<ε>):
  - ▪ Very symmetric lineshape
  - ▪ peak near LO frequency

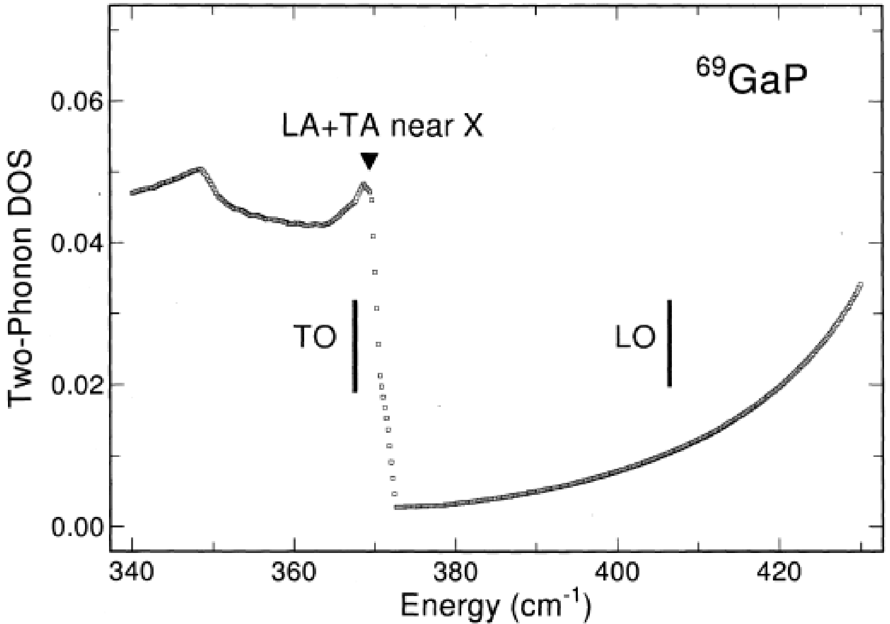


Results I: GaP: Infrared Lattice Vibrations (room temperature)



Why $\gamma_{TO}>\gamma_{LO}$ and asymmetric reststrahlen line shape ?

- Zinc blende semiconductors: Lifetime broadenings
  - decay of optical phonons into acoustic phonons.
- GaP: The two-phonon density of state is larger for the decay of TO phonons than for LO phonons ➡ the decay of TO phonons into two acoustic phonons is very fast.



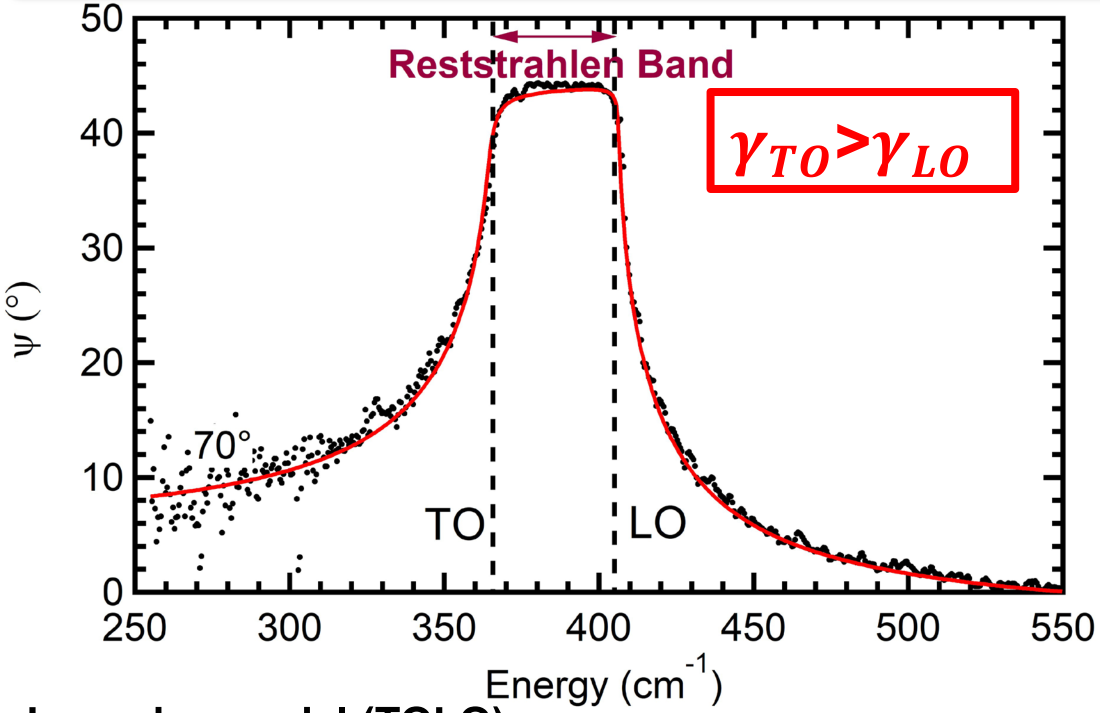
S. Ves , I. Loa, K. Syassen, F. Widulle, and M. Cardona , *physica status solidi (b)* **223.1**, 241-245 (2001).

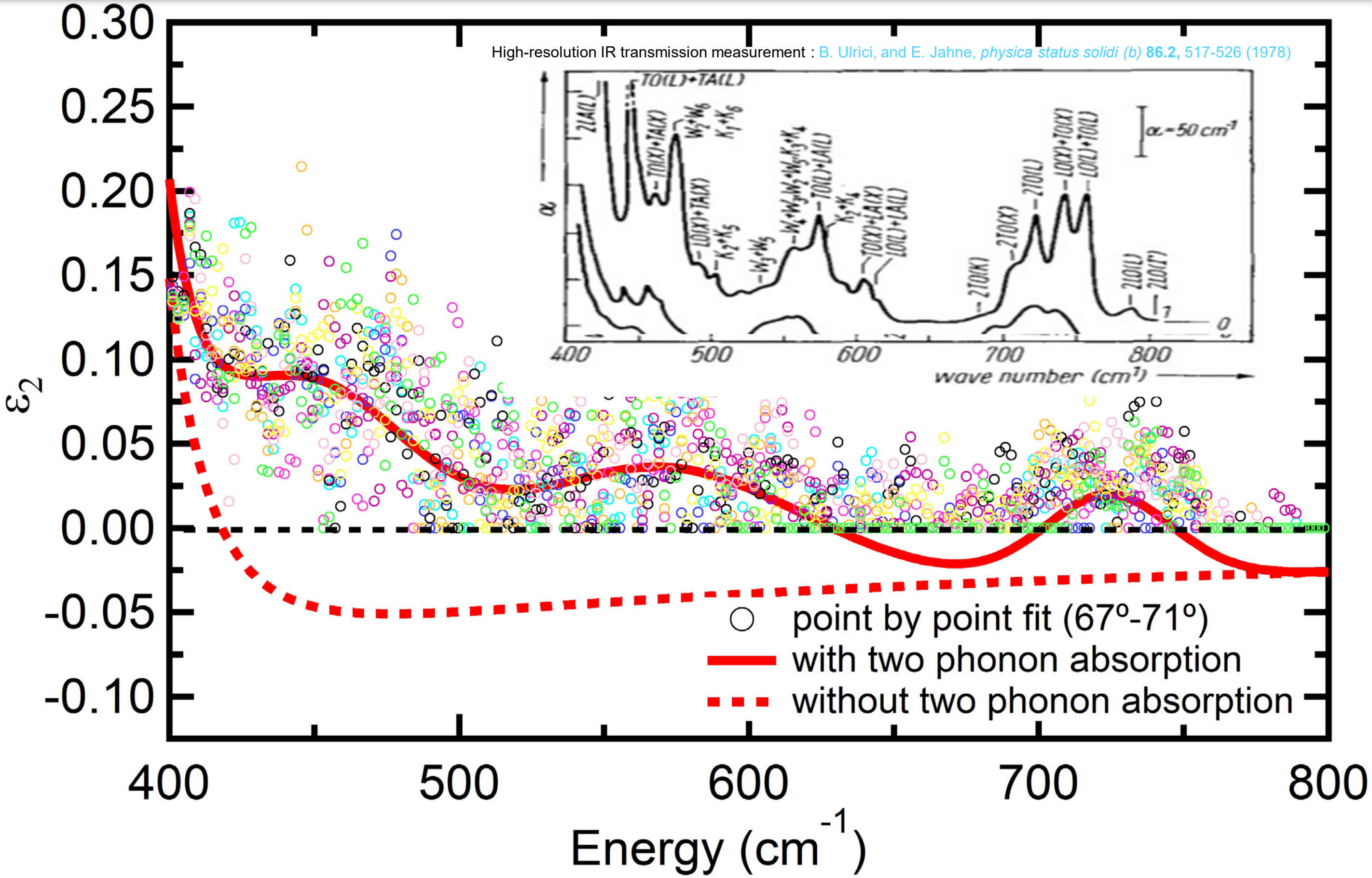
⬇

This leads to a negative dielectric constant (ε_2) just above the LO phonon.

GaP: Two-phonon absorption

Negative dielectric constant (ε_2) and two-phonon absorption




High-resolution IR transmission measurement : B. Ulrici, and E. Jahne, *physica status solidi (b)* **86.2,** 517-526 (1978)

Lowndes model (TOLO):

$$\varepsilon(\omega)=\varepsilon_\infty \frac{\omega_{LO}^2-\omega^2-i\gamma_{LO}\omega}{\omega_{TO}^2-\omega^2-i\gamma_{TO}\omega}\text{: } \gamma_{LO}<\gamma_{TO} \Rightarrow \varepsilon_2<0$$

Problem: ε_2 is negative just above E_{LO}: $\varepsilon_2=-0.05$, $\alpha=-60$ cm^{-1}.

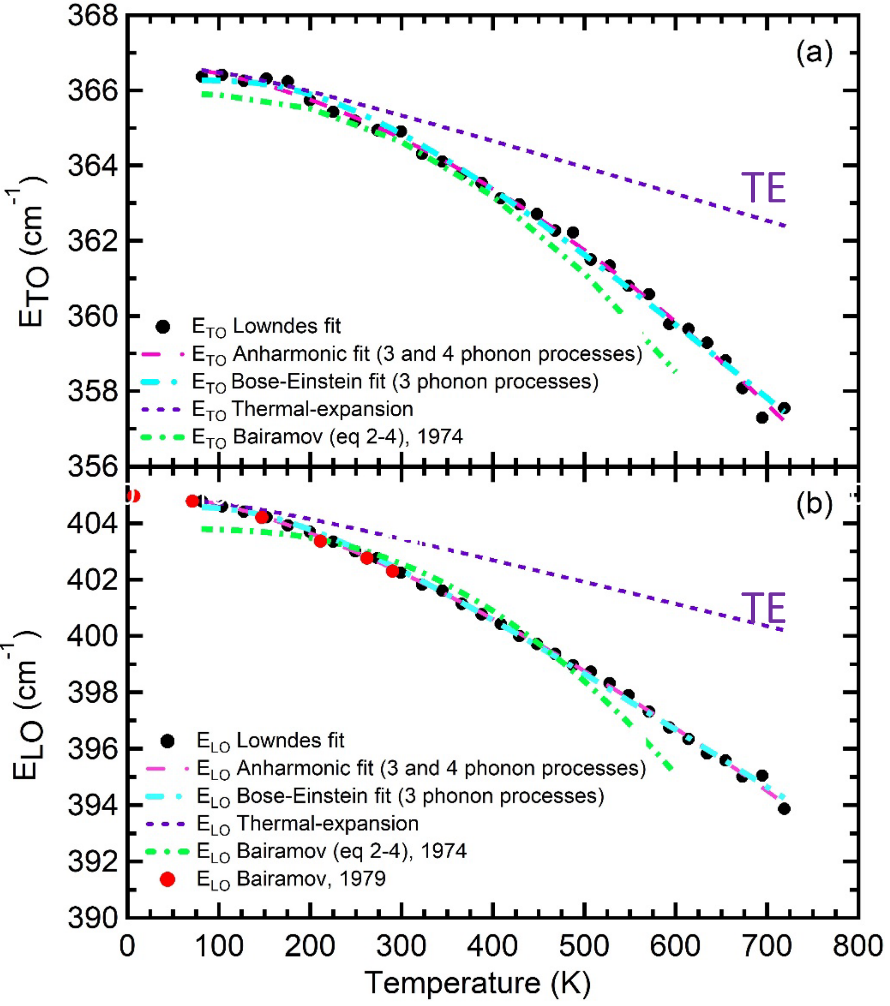
Solution: Two-phonon absorption can be added in the model to avoid a negative ε_2.

Two phonon absorption: Ellipsometry (FTIR-VASE) data agree with the high-resolution IR transmission measurement.

Results II: Temperature dependence of TO/LO phonon energy

energy decreases

E_{TO} /E_{LO}: Redshift with increasing temperature



The temperature dependence of the optical phonon energies due to thermal expansion (TE):

J. Menéndez, and M. Cardona, *Physical Review B* **29.4,** 2051 (1984).

$$\Omega_{TE}(T) = \omega_0 exp\left[-3\gamma\int_0^T \alpha_l(\theta)d\theta\right]$$ γ: Grüneisen parameter

Coefficient of linear thermal expansion: $\alpha_l(\theta)=\alpha_{l\infty}D(\frac{\theta_D}{T})$ ➤ $\alpha_l(\theta)=3\alpha_{l\infty}\left(\frac{T}{\theta_D}\right)^3\int_0^{\frac{\theta_D}{T}}\frac{\xi^4 e^\xi}{(e^\xi-1)^2}d\xi$

B. Kh. Bairamov, Yu. E. Kitaev, V. K. Negoduiko, and Z. M. Khashkhozhev, Sov. Phys. Solid State **16**, 1323 (1974).
R. Roucka, Y.-Y. Fang, J. Kouvetakis, A. V. G. Chizmeshya, and J. Menéndez, Physical Review B **81,** 245214 (2010).

The temperature dependence of the optical phonon energies due to three and four phonon process:

Anharmonic Fit: Three and four phonon process M. Balkanski, R. F. Wallis, and E. Haro, Phys. Rev. B **28**, 1928 (1983).

$$\Omega(T) = \omega_0 - C\left[1+\frac{2}{e^x-1}\right] - D\left[1+\frac{3}{e^y-1}+\frac{3}{(e^y-1)^2}\right]$$

$x=\frac{\hbar\omega_0}{2k_BT}$ and $y=\frac{\hbar\omega_0}{3k_BT}$

ω_0 : unrenormalized phonon frequency

2 variables: C and D

Bose-Einstein Fit: Temperature dependence due to three phonon processes.

L. Vina, S. Logothetidis, and M. Cardona., *Physical Review B* **30**, 1979 (1984).

$$\Omega\,(T) = \omega_0 - C\left[1+\frac{2}{e^{\frac{\theta_B}{T}}-1}\right]$$ ➤ Effective phonon energy $\omega_{eff}=\theta_B k_B$

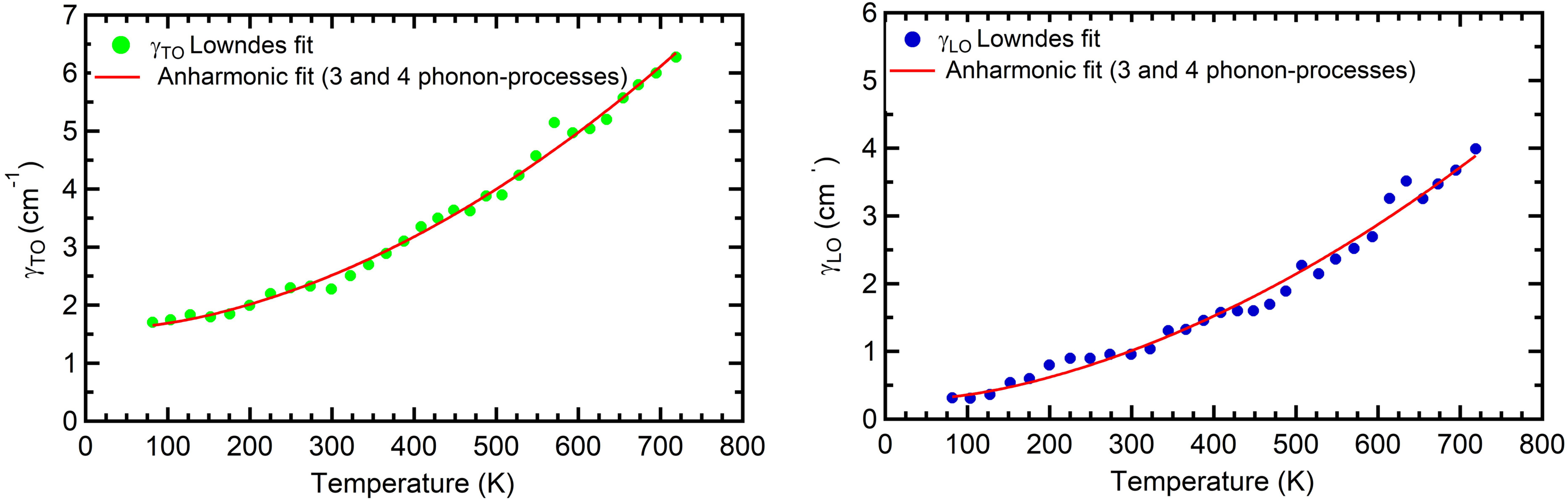
Results III: Temperature dependence of phonon broadening

Phonon broadening (PHONON LIFETIME: decay of optical phonons into acoustic phonons)

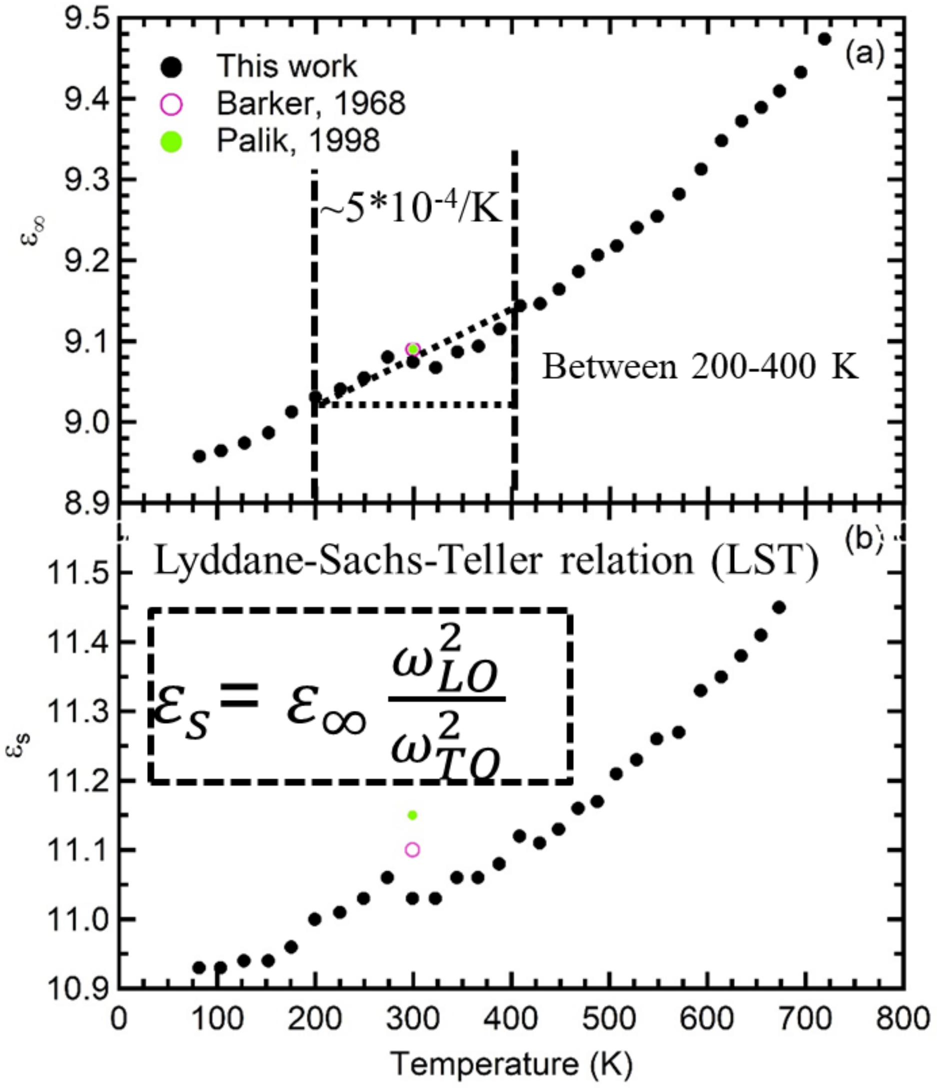
γ_{TO}/γ_{LO}: Increasing broadening with increasing temperature

$$\gamma(T) = \gamma_0 + A\left[1 + \frac{2}{e^x - 1}\right] + B\left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2}\right]$$ Three and four phonon process

2 renormalization parameters: depending on whether the phonon decays in to 2 or 3 acoustic phonons $x = \frac{\hbar\omega_0}{2k_B T}$ and $y = \frac{\hbar\omega_0}{3k_B T}$



Results IV: Temperature dependence of High-frequency dielectric constant (ε_∞)



$$\boxed{\varepsilon_s = \varepsilon_\infty \frac{\omega_{LO}^2}{\omega_{TO}^2}}$$

$$\varepsilon_\infty = 1 + \left(\frac{E_p}{E_{\mathrm{Penn}}}\right)^2$$ E_p: Unscreened plasma energy of the valence electron

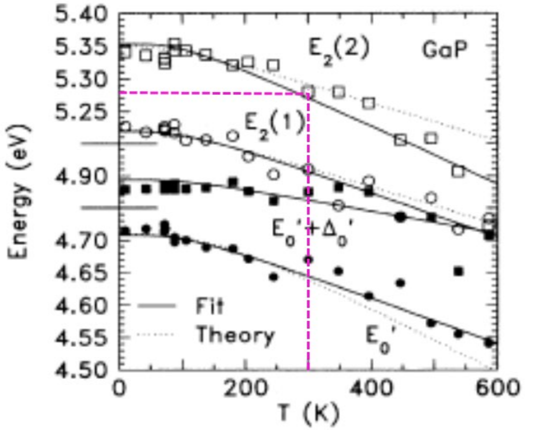
$E_{\mathrm{Penn}} \approx E_2(2) \approx$ 5.28 eV: because the oscillator strength at the E_2 transition is strong

$$E_p^{\,2} = \frac{\hbar^2 N e^2}{m_0 \varepsilon_0}$$ N: density of valence electrons per unit volume

$$\boxed{\frac{d\varepsilon_\infty}{dT} = \underbrace{-3\alpha(\varepsilon_\infty\text{-}1)}_{\text{Thermal expansion term}} \underbrace{-2(\varepsilon_\infty-1)\frac{1}{E_2}\frac{dE_2}{dT}}_{\text{Temperature dependence of the Penn gap}}}$$

Between 200-400 K: Theory $\boxed{\left.\frac{d\varepsilon_\infty}{dT}\right|_{T=300\ \mathrm{K}} = 6*10^{-4}/\mathrm{K}}$

Between 200-400 K: Measurement $\boxed{\sim 5*10^{-4}/\mathrm{K}}$



S. Zollner, M. Garriga, J. Kircher, J. Humlíček, M. Cardona, and G. Neuhold, *Physical Review B* **48**.11 (1993).

ε_∞: Increasing with increasing temperature (Thermal expansion + Temperature dependence of the Penn gap).

C. M. Nelson, M. Spies, L. S. Abdallah, and S. Zollner, J. Vac. Sci. Technol. A **30**, 061404 (2012).
A. S. Barker, Phys. Rev. **165**, 917 (1968).
A. Borghesi and G. Guizetti, in Handbook of Optical Constants of Solids, edited by E. D. Palik (Academic, New York, 1998).
D. F. Parsons and P. D. Coleman, Appl. Opt. **10**, 1683 (1971).

- ☐ Introduction-part I
  - Zinc Oxide (ZnO:II-VI compound semiconductor) for optoelectronic industry
  - Role of ZnO film thickness for optoelectronic and photonic devices
- ☐ Sample characterization
  - Optical Characterization: Spectroscopic Ellipsometer (IR-VASE, UV-VASE)
  - Structural Characterization: X-ray diffraction (XRD), X-ray reflectivity (XRR), Atomic force microscope (AFM)
- ☐ Results: Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition (ALD)

[**Nuwanjula S. Samarasingha**, Stefan Zollner, Dipayan Pal, Rinki Singh, and Sudeshna Chattopadhyay, Thickness dependence of infrared lattice absorption and excitonic absorption in ZnO layers on Si and SiO_2 grown by atomic layer deposition, J. Vac. Sci. Technol. B 38, 042201 (2020)]

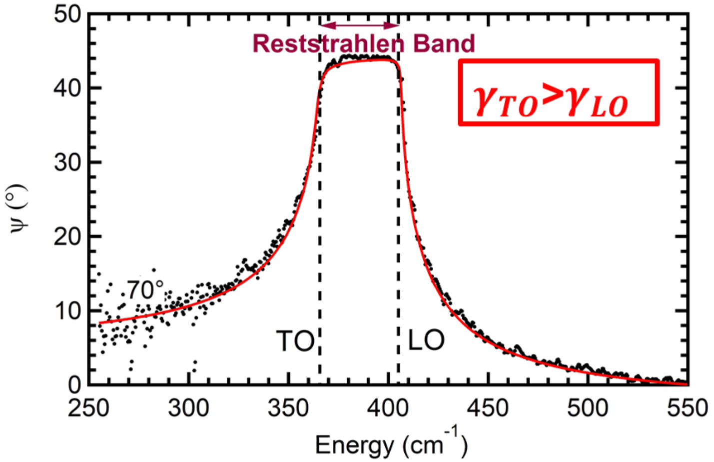
- ☐ Introduction-part II
  - Gallium Phosphide (GaP:III-V compound semiconductor) for optoelectronic industry
  - Why we study temperature dependence of lattice vibration in GaP
- ☐ Results: Temperature dependence of the optical phonon reflection band in GaP

[[Nuwanjula Samarasingha and Stefan Zollner, Temperature dependence of optical phonon reflection bands in GaP, J. Vac. Sci. Technol. B (under review) arXiv:2105.06662, (2021)]

- ☐ Conclusions

Conclusion II

- Explore the effect of temperature on the frequency and linewidth of transverse (TO) and longitudinal (LO) optical phonons.



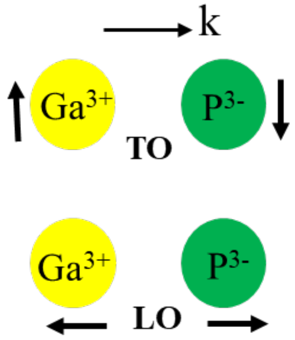
- The two-phonon density of state (TP-DOS) is larger for the decay of TO phonons than for LO phonons. ➡ large TO phonon broadening and an asymmetric reststrahlen line shape ➡ negative dielectric constant (ε_2).

- Multi-phonon absorption can be added in the model to avoid this negative ε_2.

- Transverse (TO) and longitudinal (LO) optical phonons:
  - TO and LO energy: redshift with increasing temperature
  - Broadening with increasing temperature

Anharmonic phonon-phonon decay (described by three and four phonon decay processes)

- $\varepsilon_s/\varepsilon_\infty$: increase with increasing temperature (thermal expansion and the temperature dependence of the Penn gap).



Future Work

- Analyze the dependence of the excitonic Tanguy parameters on ZnO film thickness and substrate material.
    - Fit our ellipsometric spectra with the Elliot–Tanguy theory model.
- Model our ellipsometric spectra including excitonic effects and exciton-phonon complexes.
- Temperature dependent optical properties of ZnO thin films.
- Measure GaP in far-infrared region.
- Study the frequency dependent scattering rate with a better signal-to-noise ratio.

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