Ellipsometric Study of Simple and Complex Oxides from the Mid Infrared to the Near Ultraviolet

Masters Thesis Defense of T. Nathan Nunley

Advisor: Dr. Stefan Zollner

Department of Physics, New Mexico State University, Las Cruces, NM

Vita

- Professional Societies
  - American Physical Society
  - American Association of Physics Teachers
  - Sigma Pi Sigma
- Publications
  - T. N. Nunley, T. I. Willett-Gies, J. A. Cooke, F. S. Manciu, P. Marsik, C. Bernhard, S. Zollner *In Review, Journal of Vacuum Science and Technology A* (2016)
  - T. N. Nunley, N. S. Fernando, N. Samarasingha, J. M. Moya, C. M. Nelson, A. A. Medina, S, Zollner *In Review, Journal of Vacuum Science and Technology B* (2016)
  - S. Zollner, T. N. Nunley, D. P. Trujillo, L. G. Pineda, L. S. Abdallah *In Review, Applied Surface Science* (2016)
  - A. O’Hara, T.N. Nunley, A.B. Posadas, S. Zollner, and A.A. Demkov, J. Appl.Phys. 116, 213705 (2014).

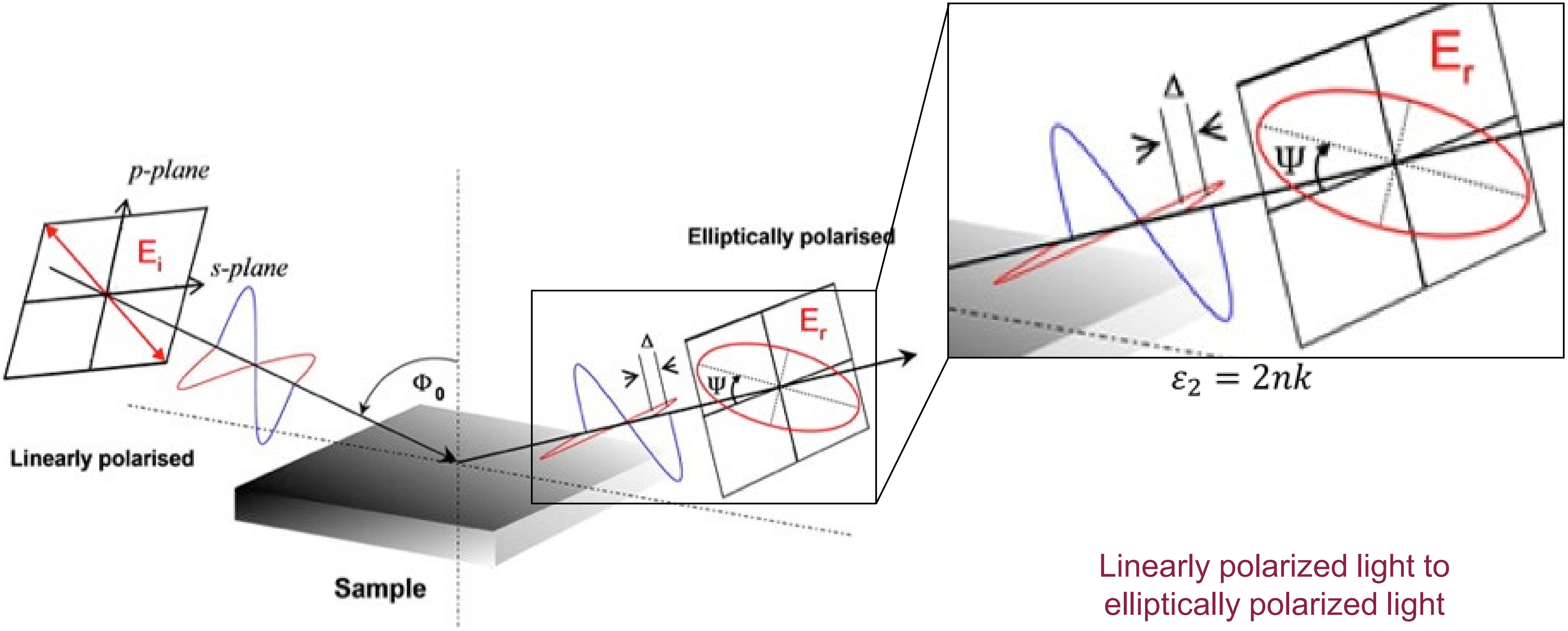
Vita

- Recent Presentations at
  - 7th International Conference on Spectroscopic Ellipsometry
  - American Vacuum Society New Mexico Chapter Meeting 2016
  - American Physical Society 4 Corners Section Meeting

Outline

- Experimental Methods
- LSAT
  - Near IR to Near UV Analysis
  - Infrared Analysis
- Thermal Ge Oxide and Ge
  - Preparation
  - Analysis
- Temperature Dependence of Ni Optical Constants
- Conclusions

Spectroscopic Ellipsometry: Theory

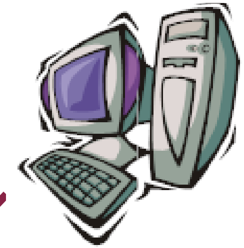


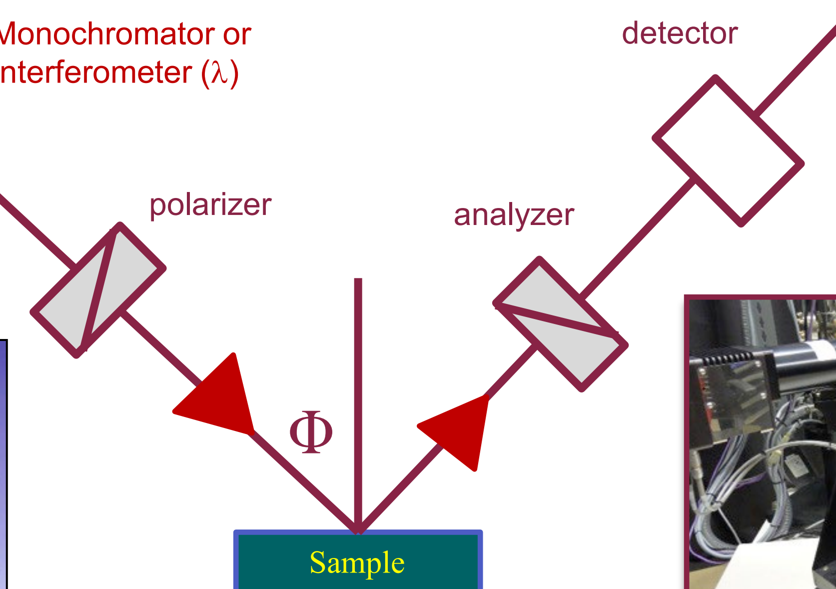
$\varepsilon_2 = 2nk$

Linearly polarized light to elliptically polarized light

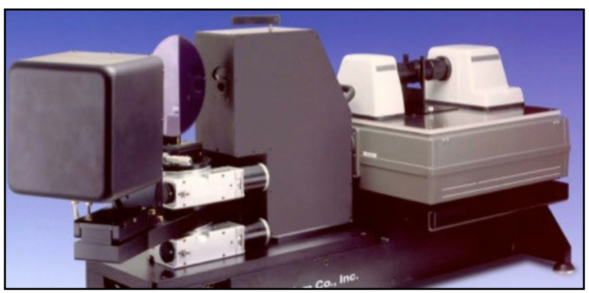
Ellipsometry: How does it work ?

We measure the change in the polarization state of light, when it is reflected by a flat surface.

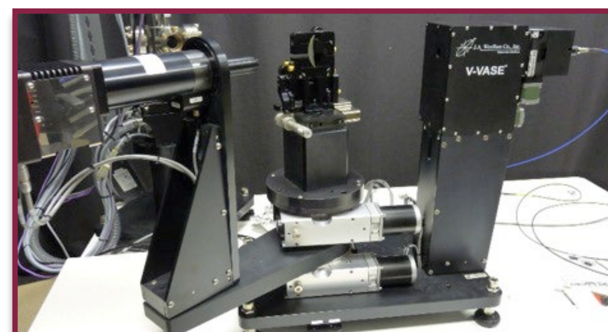




CINT

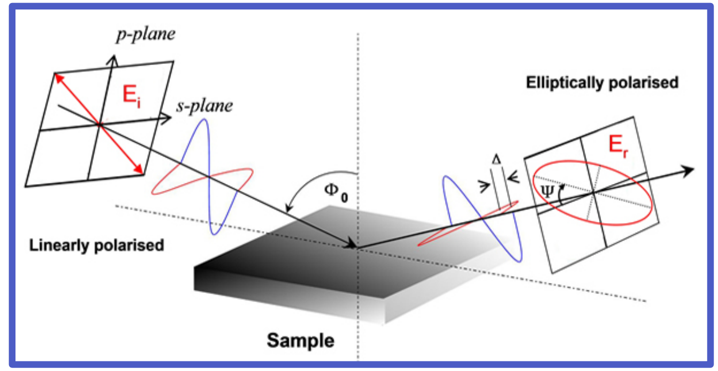


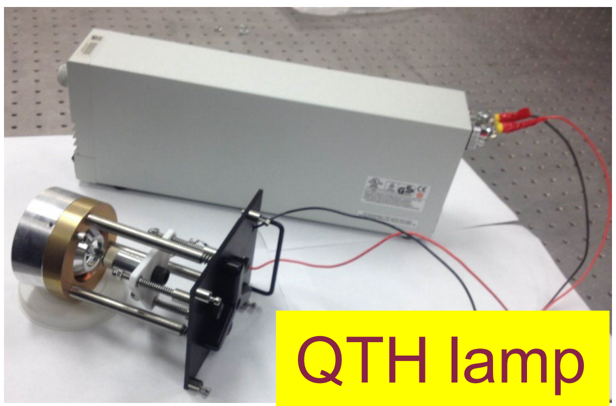
NMSU



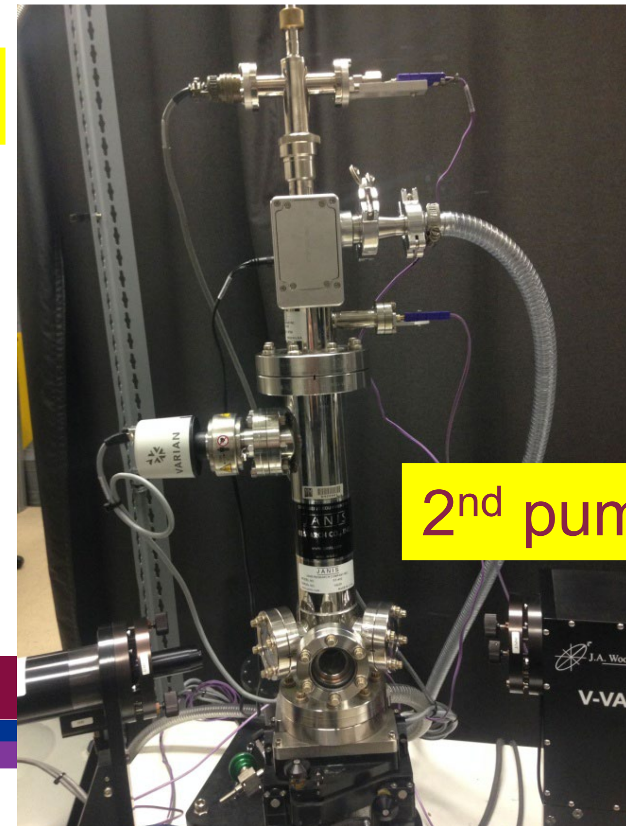
Ellipsometry: How does it work ?

- Modified HS-190 monochromator: Quartz-tungsten-halogen lamp (avoid IR spikes from Xe lamp)
- Modified detector electronics to reject black body IR spectrum (800 K).



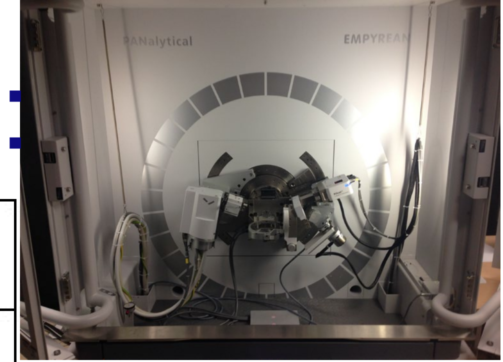


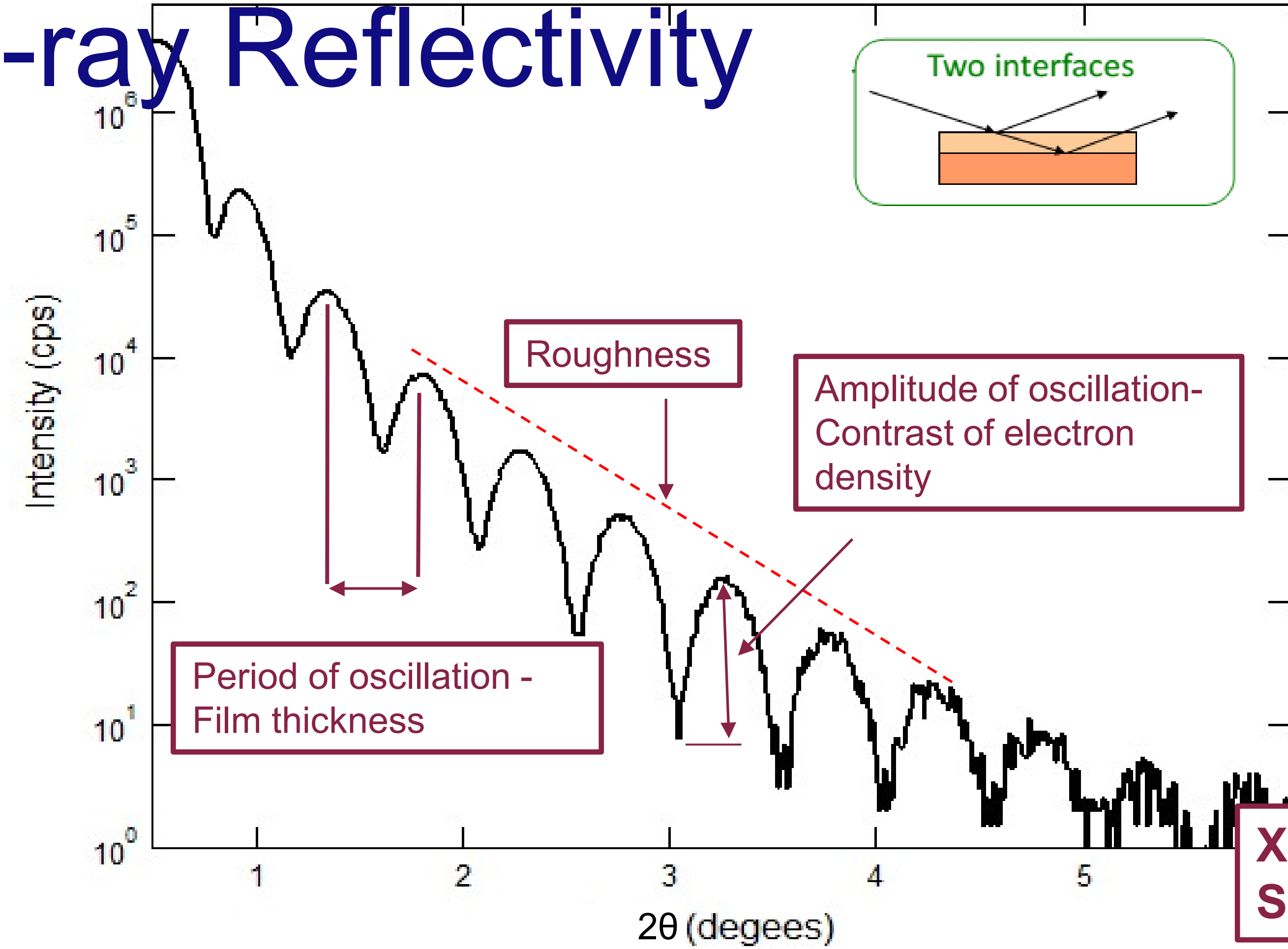
2nd thermocouple



- Janis cryostat (80 to 800 K)
- Pump on LN_2 space during heating.
- Add second thermocouple in UHV space

Characterization Technique: X-ray Reflectivity





XRR Spectra of a $SrTiO_3$ film

Film Thickness

$$T = \frac{2\pi}{\Delta Q}$$

$$Q = \frac{4\pi \sin\vartheta}{\lambda}$$

Outline

- Experimental Methods
- **LSAT**
  - Near IR to Near UV Analysis
  - Infrared Analysis
- Thermal Ge Oxide and Ge
  - Preparation
  - Analysis
- Temperature Dependence of Ni Optical Constants
- Conclusions

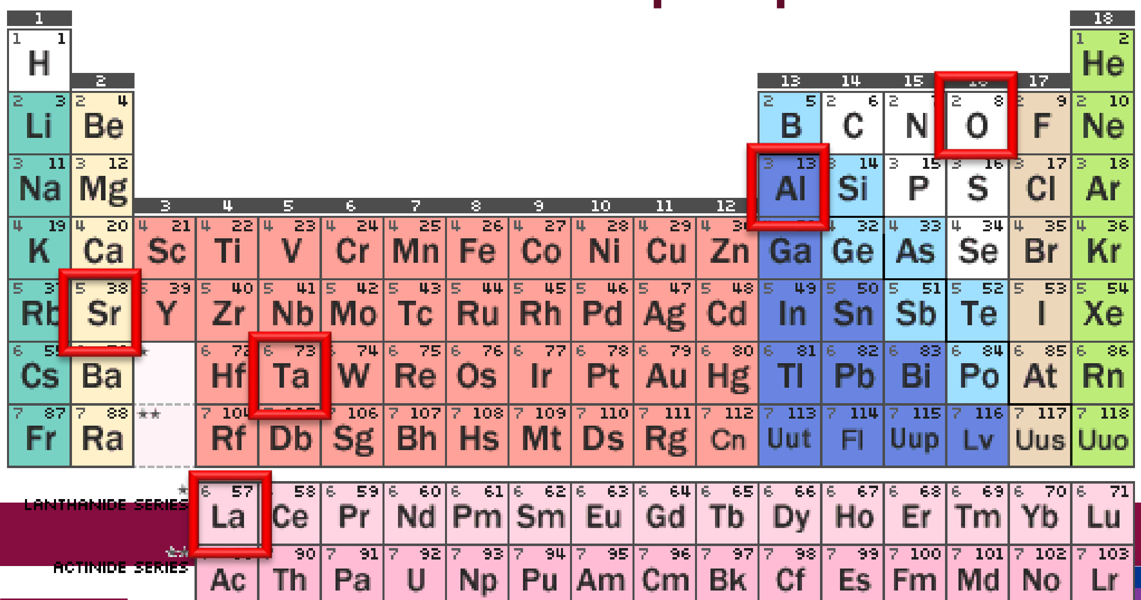
Ellipsometric Study of LSAT

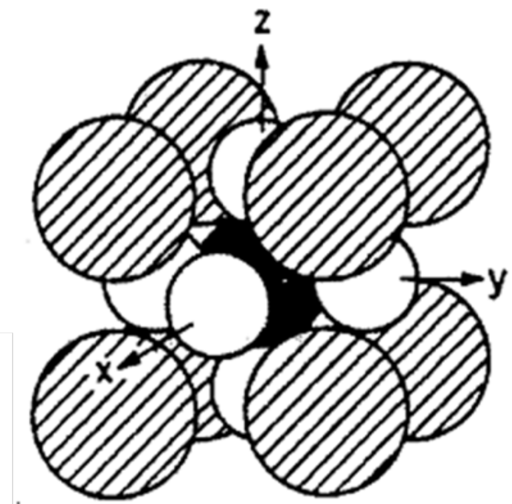
T. Nathan Nunley[1], Travis I. Willett-Gies[1], Jacqueline A. Cooke[1], Felicia S. Manciu[2], Premysl Marsik[3], Christian Bernhard[3], Stefan Zollner[1],

1. Dept. of Physics, New Mexico State University, Las Cruces, NM
2. Department of Physics, University of Texas at El Paso, El Paso, TX
3. Department of Physics and Fribourg Center for Nanomaterials, University of Fribourg, Chemin du Musee 3, CH-1700 Fribourg, Switzerland

LSAT, the substrate of interest

- $(LaAlO_3)_{0.3}\ (Sr_2AlTaO_6)_{0.35}$
- Insulating perovskite
- Good substrate properties



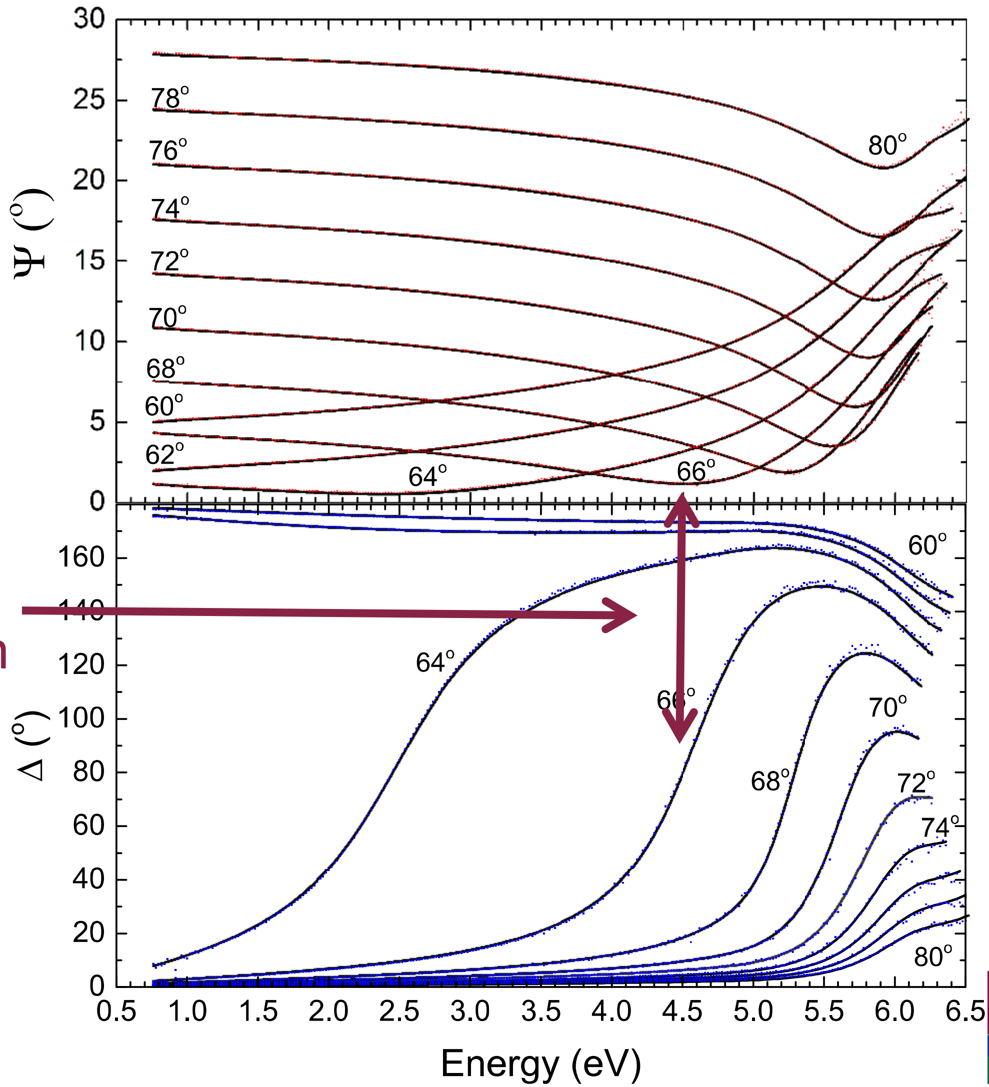


LSAT Ellipsometric Angles

This is a very simple spectra, we only see large dispersion at the highest energies.

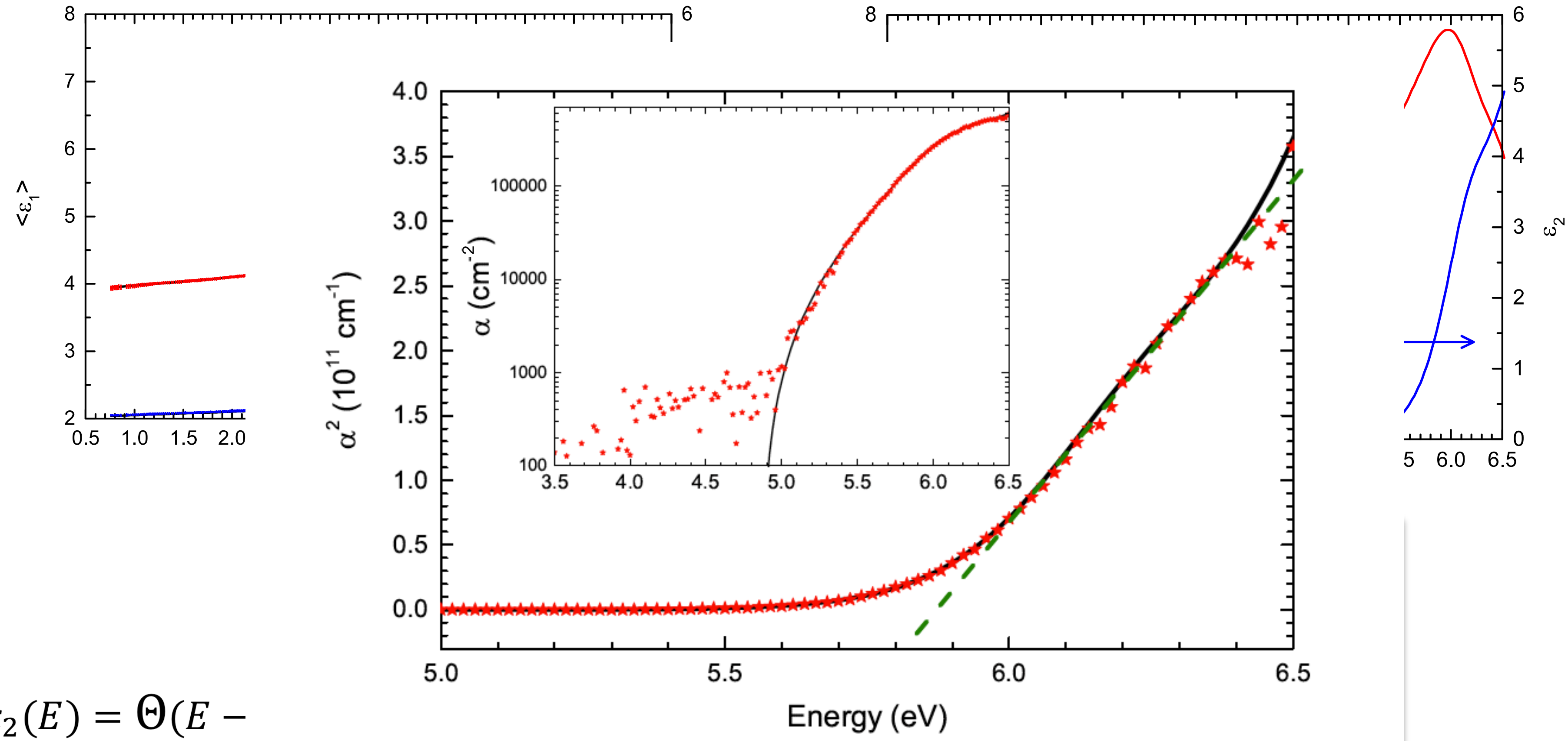
This material is transparent in the visible range.

We can see the Brewster angle change as a function of energy in Δ, with corresponding minima in Ψ.



New Mexico State University
All About Discovery!
nmsu.edu

LSAT Model



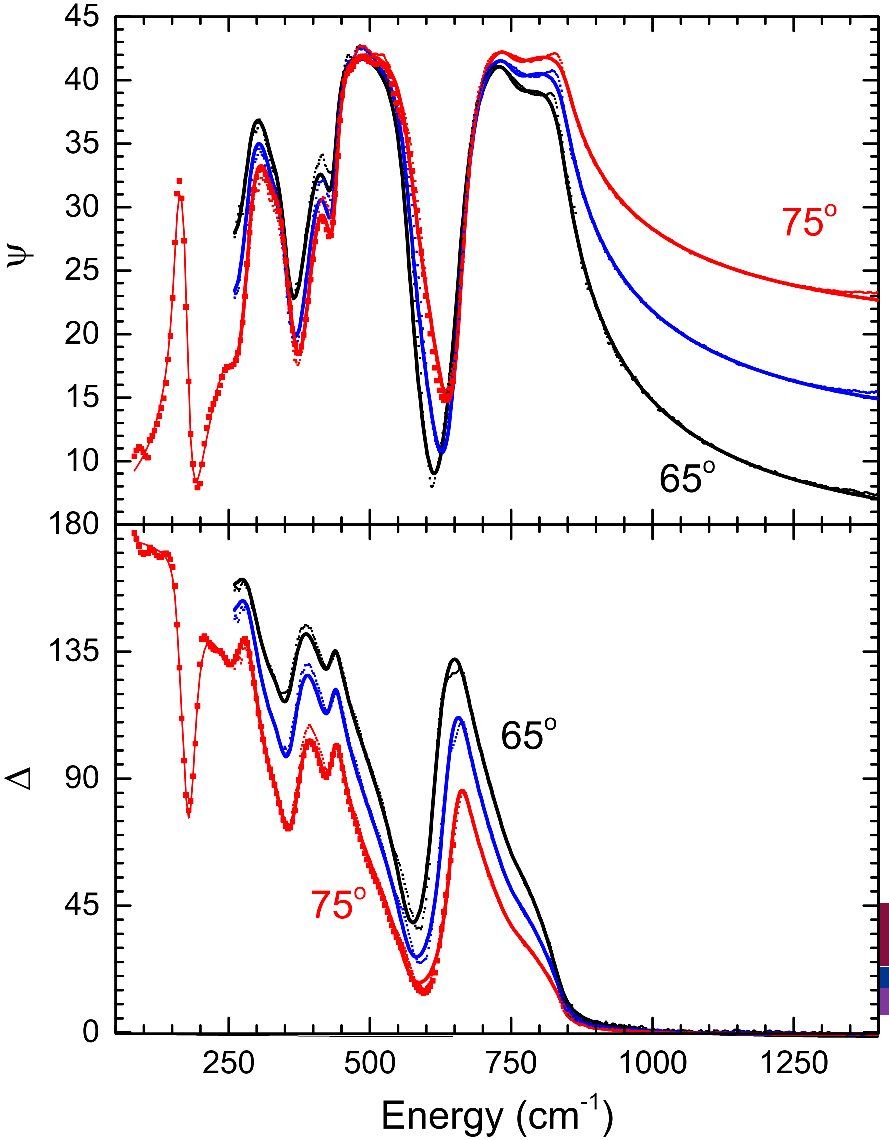
$\varepsilon_2(E) = \Theta(E -$

TL1	6.14(2)	53(6) eV	0.84(3)	4.87(1)
TL2	6.67(4)	38(7) eV	0.7(1)	same
UV pole	11.56(4)	289(2) eV²		
IR pole	0.08(f)	0.027(1) eV²		

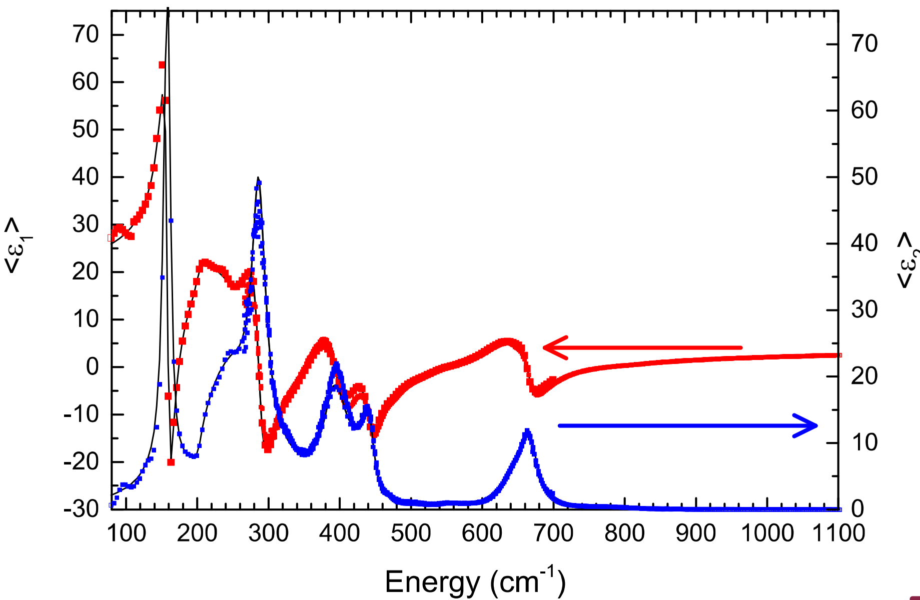
LSAT Infrared Ellipsometric Angles

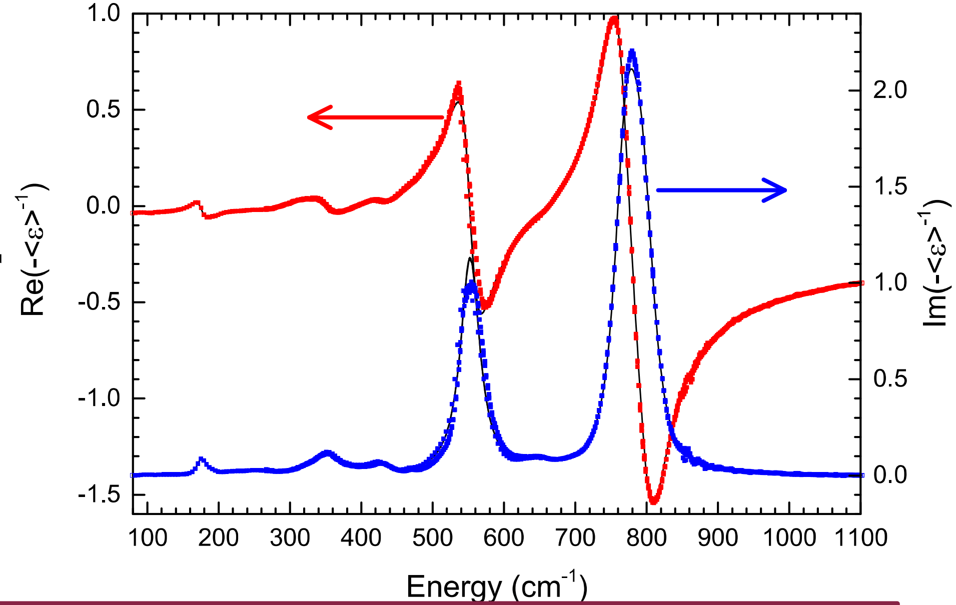
This is very similar to the IR reflectivity results. We see restrahlen bands in Ψ.

There is much more complexity in the infrared spectra.



LSAT IR Dielectric Phonons





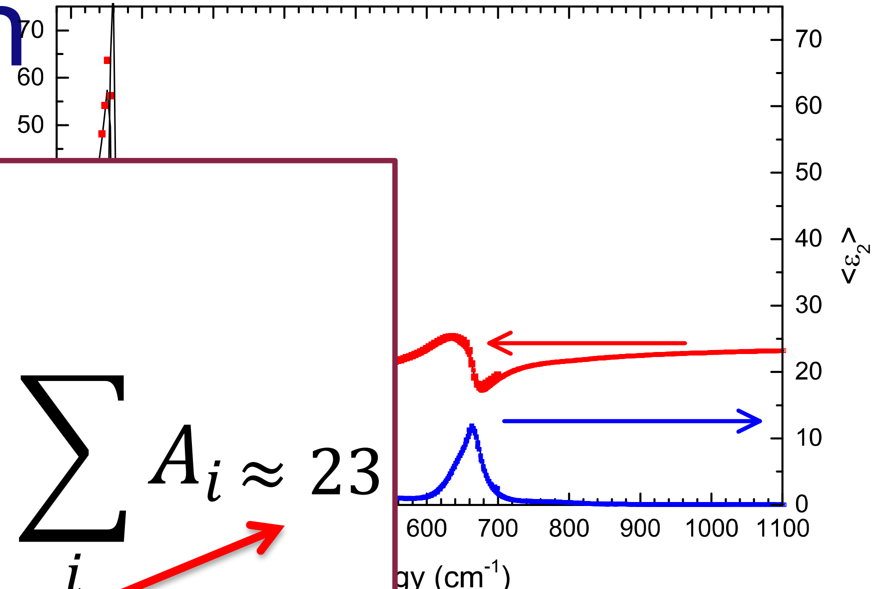
The dielectric spectra gives the positions of optically active phonons

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

$$A_i = \varepsilon_\infty \frac{E_{iLO}^2 - E_{iTO}^2}{E_{iTO}^2} \prod_{j \neq i} \frac{E_{jLO}^2 - E_{iTO}^2}{E_{jTO}^2 - E_{iTO}^2}$$

Phonon Designation

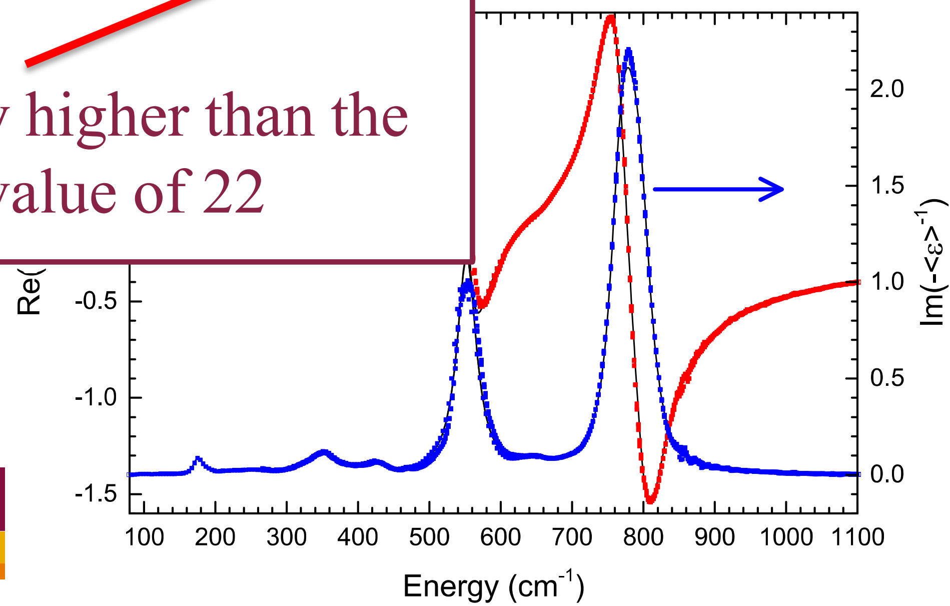
No.	A (cm⁻¹)	E_{TO}	Γ_{TO} (cm	E_{LO}	Γ_{LO}	assignment
L1	6.30(4)	156.9(1)	12.8			
L2	1.5(4)	222(2)	35(			
L3	2.6(5)	248(1)	42(			
L4	4.3(2)	285.9(3)	28(			
L5	0.46(8)	330(2)	46(			
L6	1.89(4)	395.0(2)	44(			
L7	0.51(2)	436.4(2)	18.6			
L8	0.646(2)	659.8(1)	36.5			
L9	0.0045(6)	787(1)	26(			
1	5.58	158.1(1)	10.7			
2	2.35	286.3(2)	22.8			
3	1.56	392.3(3)	40.5			
4	0.43	442.1(2)	22.4			
5	0.11	632(1)	46(			
6	0.49	666.2(3)	32.4(5)	766.8(8)	45.7(2)	B-O stretch
7	0.01	789(2)	74(5)	800(1)	48(2)	two-phonon
8	−0.74	201.7(5)	23(1)	199(1)	23(1)	
9	9.50	251(1)	115(3)	277(1)	57(2)	



$$\varepsilon_\infty = 3.96$$

$$\varepsilon_{stat} = \varepsilon_\infty + \sum_i A_i \approx 23$$

This is slightly higher than the experimental value of 22



Outline

- Experimental Methods
- LSAT
  - Near IR to Near UV Analysis
  - Infrared Analysis
- **Thermal Ge Oxide and Ge**
  - Preparation
  - Analysis
- Temperature Dependence of Ni Optical Constants
- Conclusions

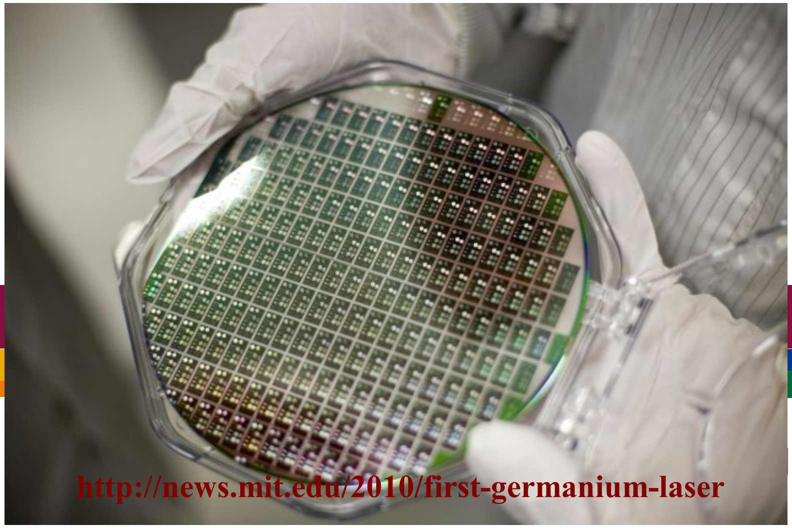
Growth and Characterization of Ge Thermal Oxides

T. Nathan Nunley, Nalin Fernando, Nuwanjula Samarasingha, Jaime Moya, Cayla M. Nelson, Amber A. Medina, Stefan Zollner

Department of Physics, New Mexico State University, Las Cruces, NM

We want to integrate and improve electronics and photonics.

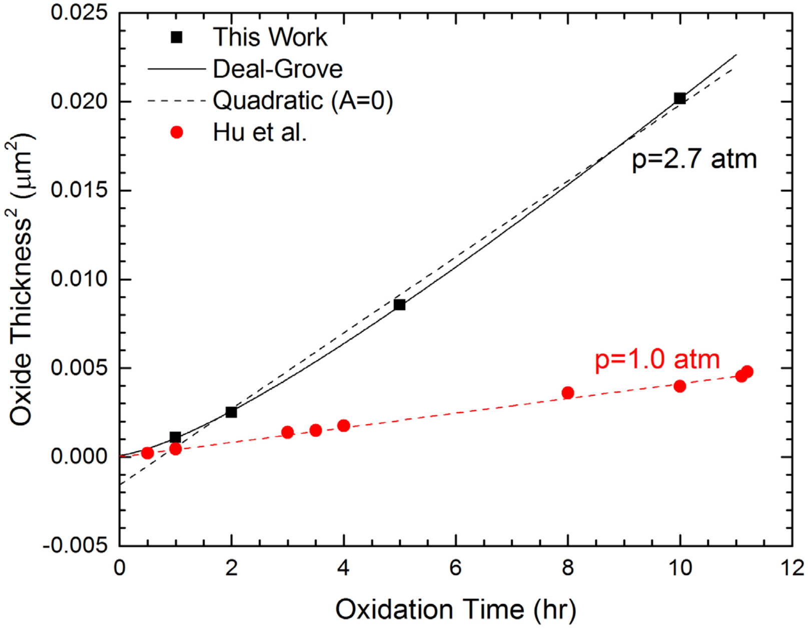
- Ge is of interest because of bipolar and MOSFET technologies.
- Optical constants aren't as well known as Si.
- We want films like high-κ oxides (e.g. HfO_2).
- GeO_2 is always present.

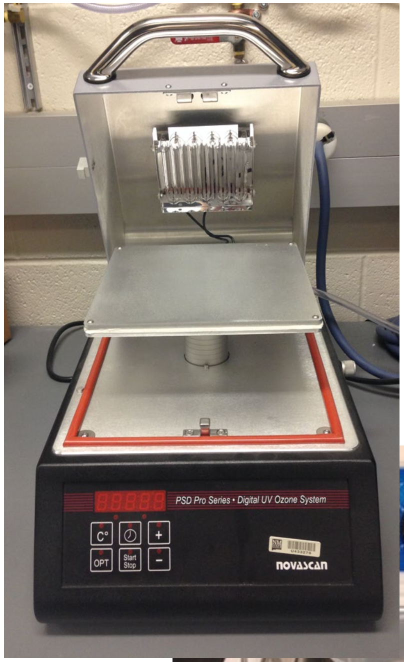


http://news.mit.edu/2010/first-germanium-laser

Preparation: Thermal Oxidation

- UV-O_3 clean at 150ºC for 90 min.
- Ultrasonic clean - Water and Isopropanol, 20 min each.
- Anneal in ultra pure O_2 at 1.7 atm gauge 1 L/min flow at 550ºC.





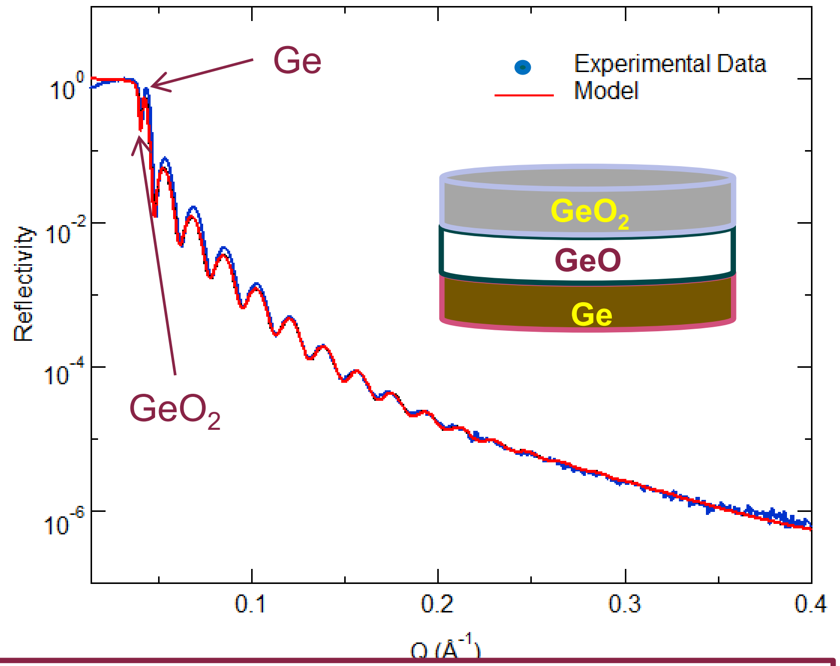
$$d^2 + Ad = B(t + \tau)$$

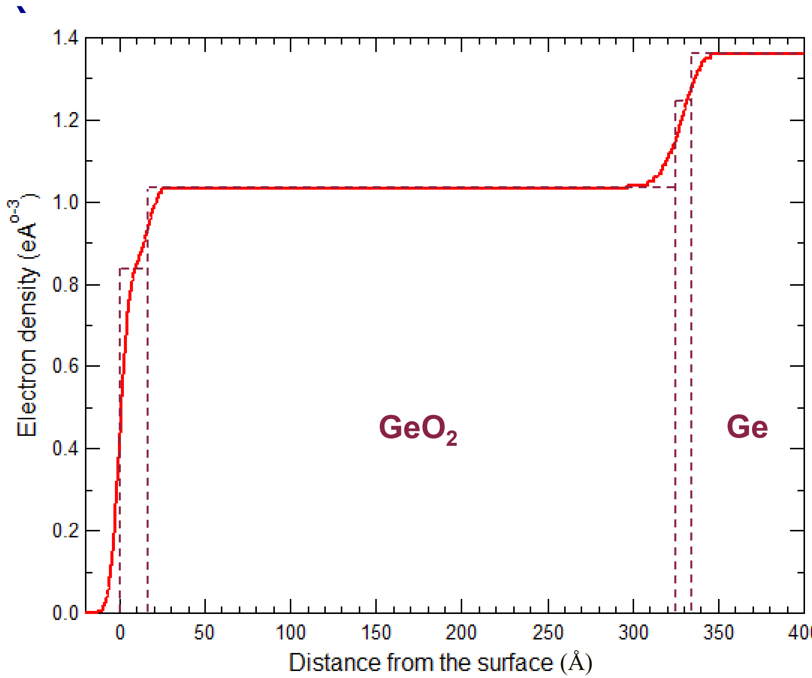
T (°C)	p (kPa)	A (nm)	B (nm^2/hr)	τ (hr)
550	100	0	432	0
550	270	97	3300	0.28

B.E. Deal and A.S. Grove, J. Appl. Phys. **36**, 3770 (1965)

Hu *et al.* Appl. Phys. Lett. **61** (9) (1992)

X-ray Reflectance of Typical Sample 550ºC, 1 hr, 33nm





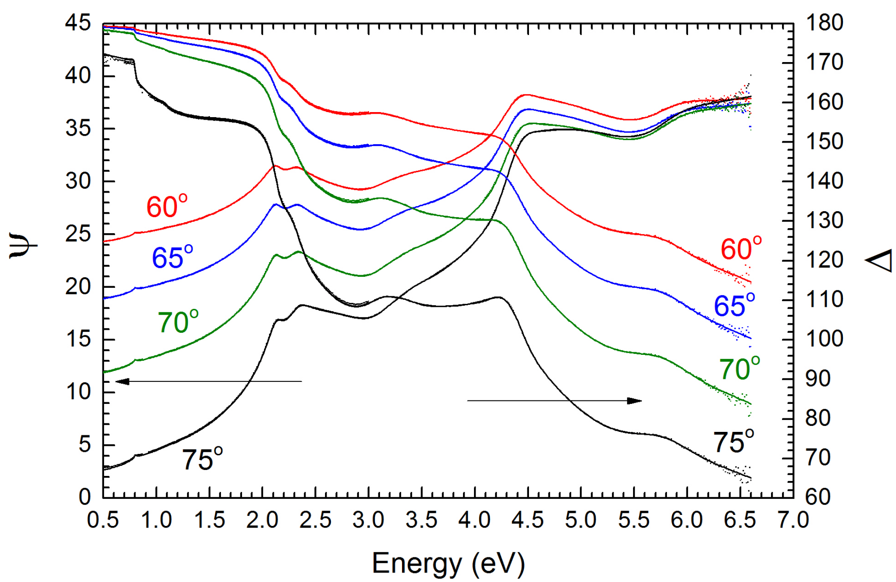
XRR has shown the samples to have similar electron densities. This is important for our analysis

Layer	Electron Density (eÅ^{-3})	Bulk Electron Density (eÅ^{-3})	Thickness (nm)	Roughness (nm)
GeO2	0.84	1.14	1.67	0.4429
GeO_2	1.03	1.14	30.8	0.4734
GeO	1.24		0.79	0.9723
Ge	1.36	1.36	Substrate	0.6906

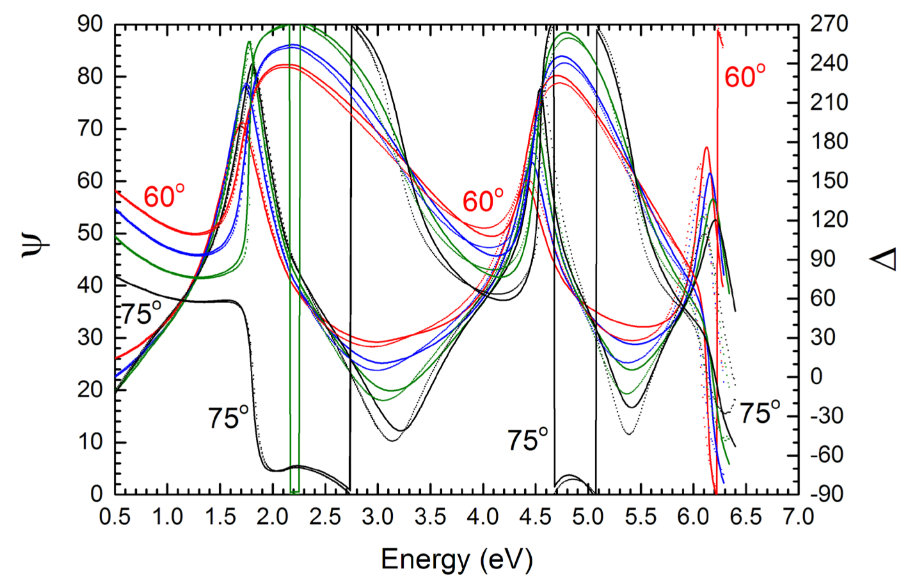
Data: Initial Assumptions

- Initial basic assumption: The **SAME** oxide is present
  - → The only difference is the thickness
    - → Thickness is fit by the interference fringes

Ellipsometric Angles of Native oxide ~20 Å



Ellipsometric Angles of 10 hour anneal ~1400 Å



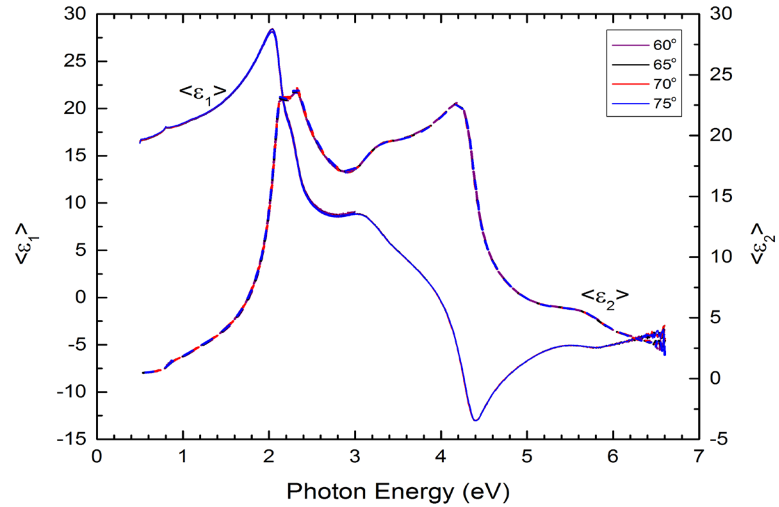
Samples were measured with a Woollam RAE V-VASE with 2 lamps.

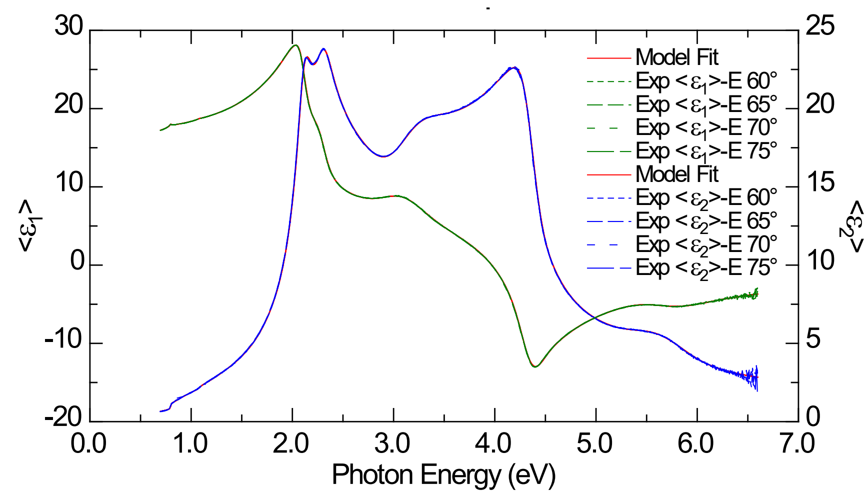
Model

1	GeO_2	variable
0	Ge	1 mm

- Fit 5 data sets simultaneously
- Thickness variation allowed for layer decoupling

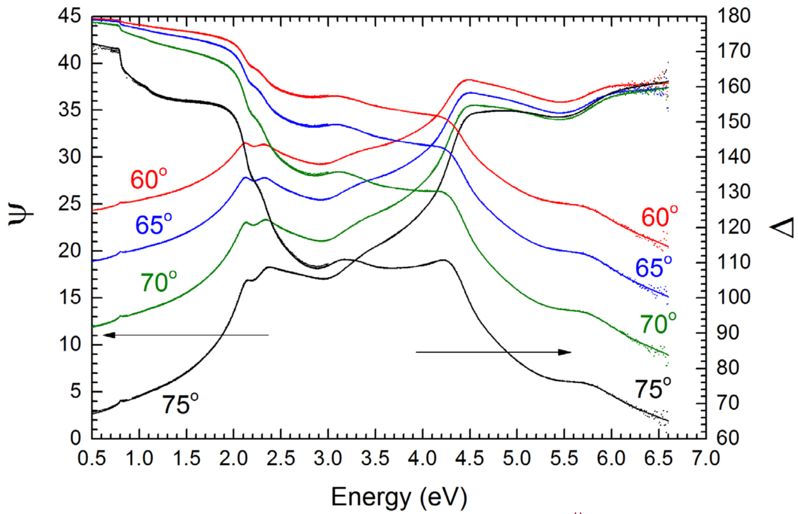
1	GeO_2	23.14 Å
0	Ge	1 mm



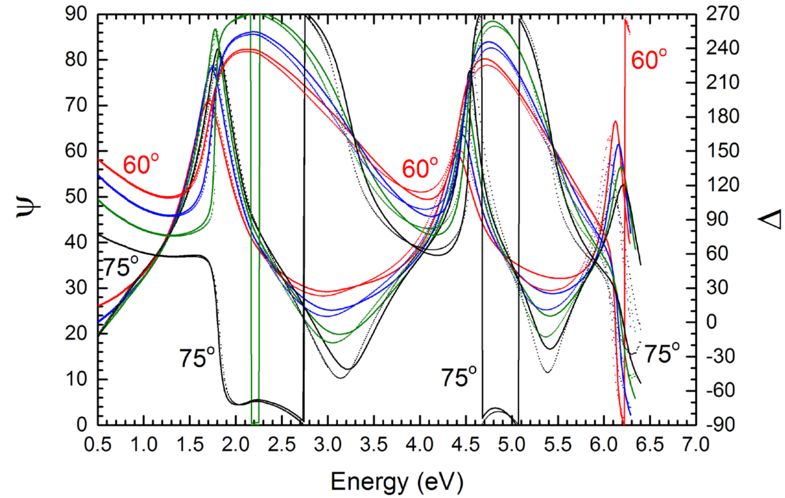


Model

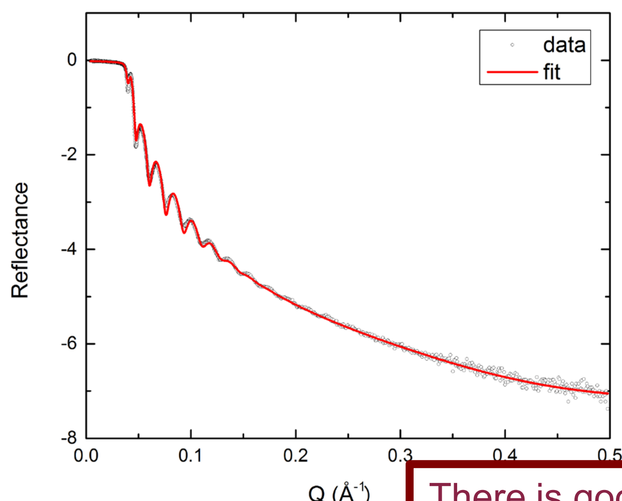
Native oxide ~20 Å



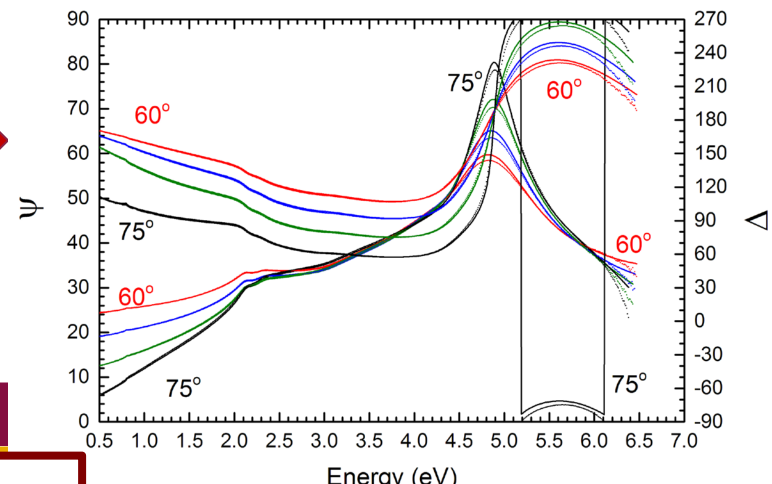
10 hour anneal ~1400 Å



1hour anneal ~330 Å



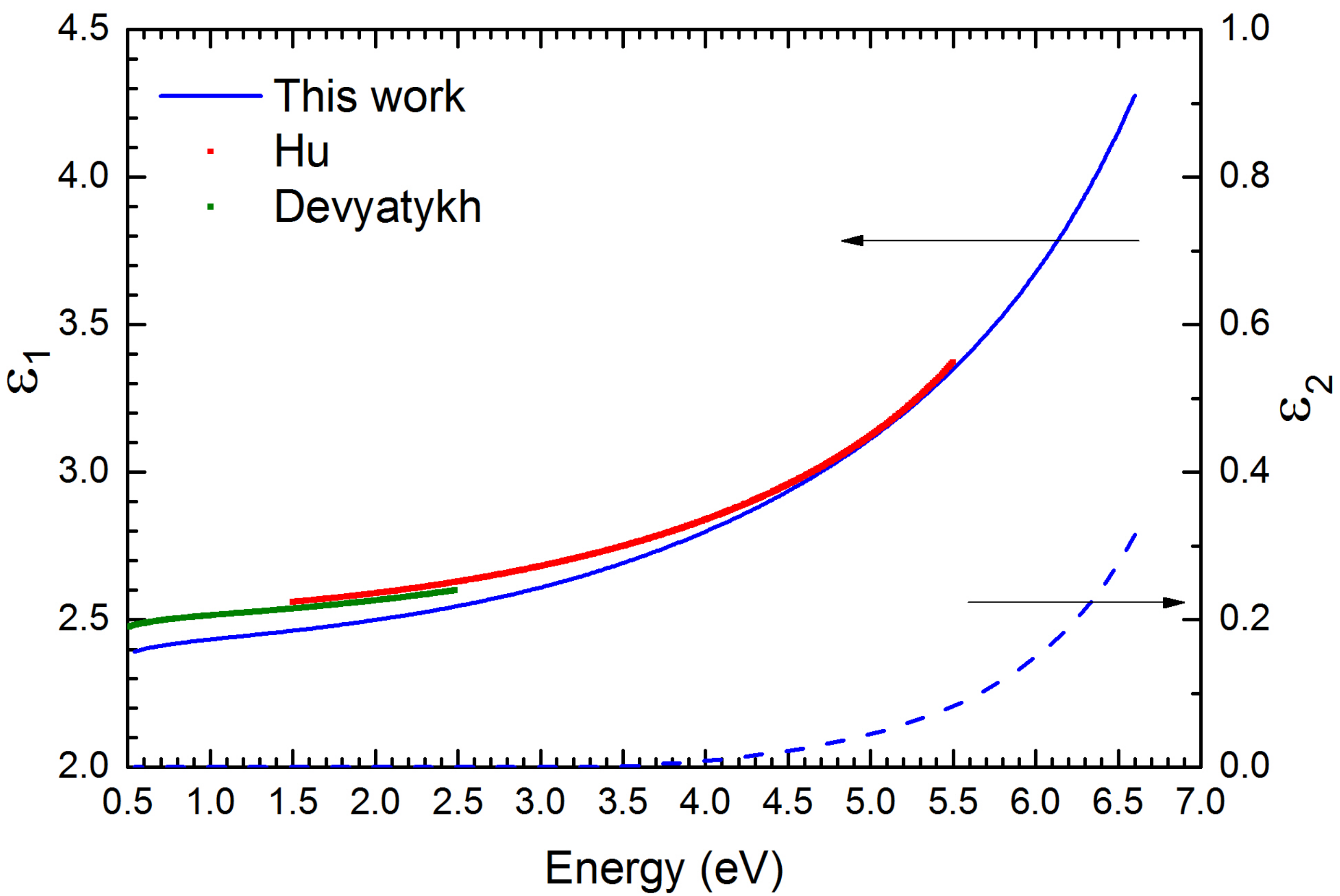
1 hour anneal ~340 Å



There is good agreement between XRR and Ellipsometric model thicknesses

New Mexico State University
All About Discovery!
nmsu.edu

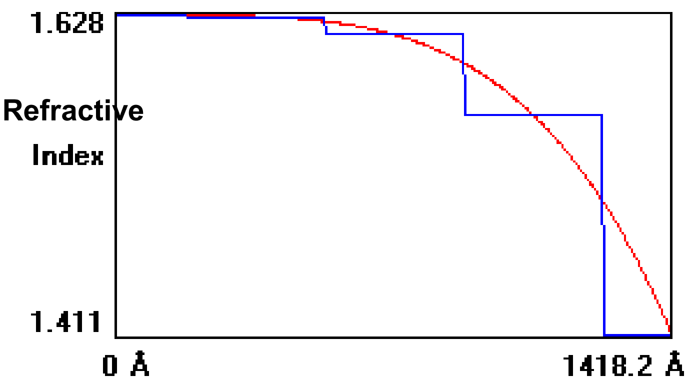
Comparison to Previous Work (GeO_2)

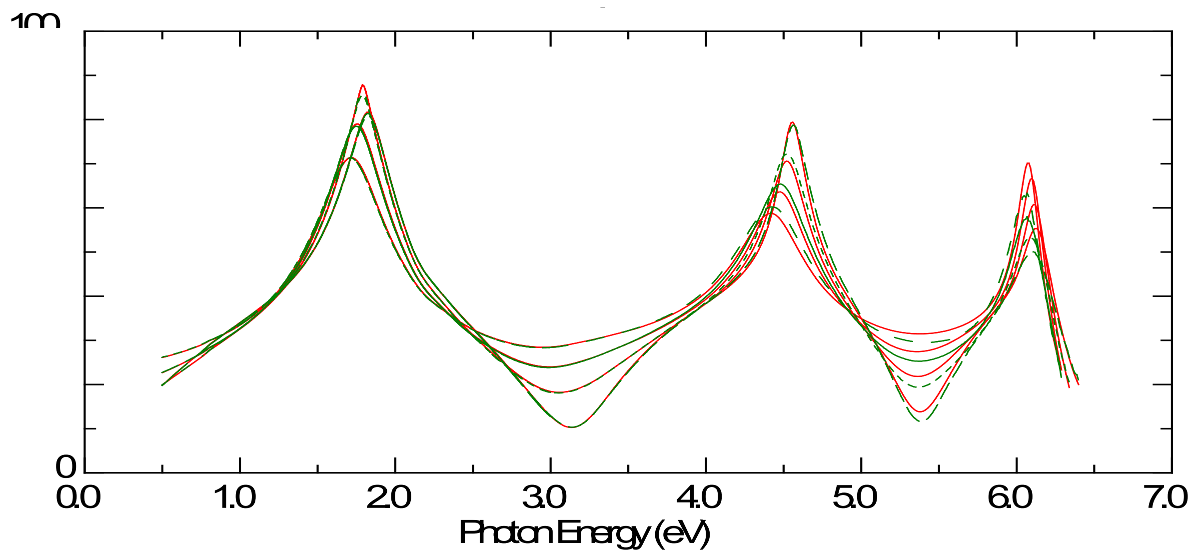


New Mexico State University
All About Discovery!
nmsu.edu

Graded Layer Model

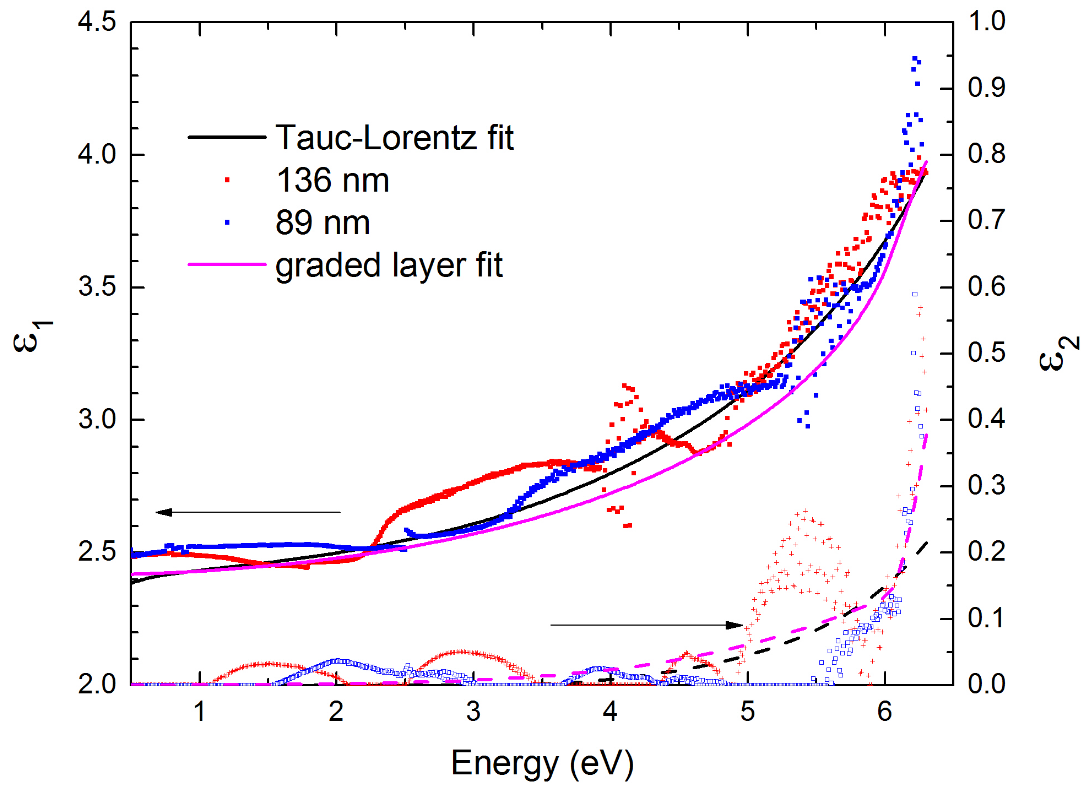
- For the thicker films, the higher energies were hard to fit.
- A graded layer for the thickest film better describes the data.
- The Ge model wasn't modified.



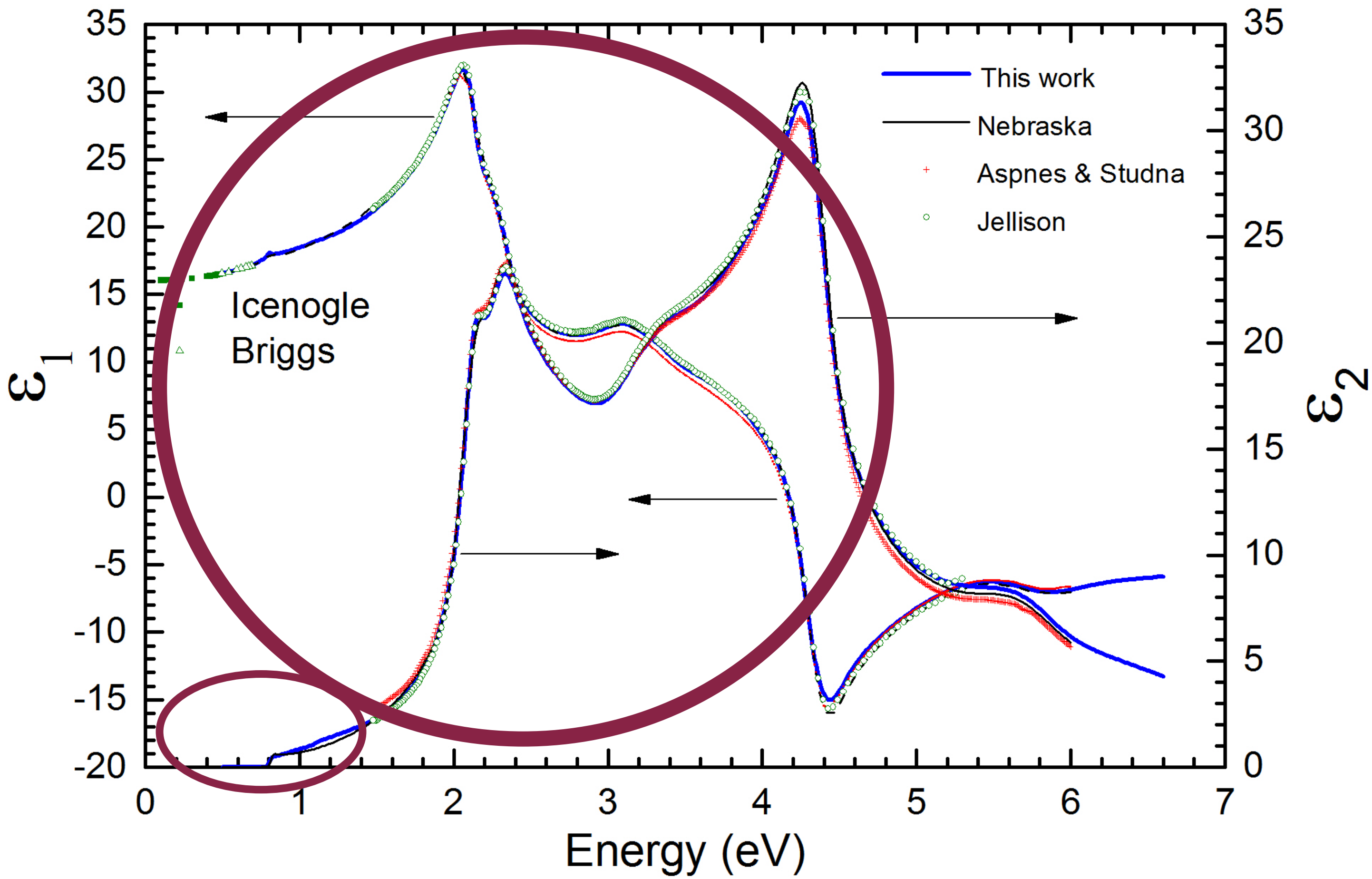


Results

- The GeO_2 layer was fit with an oscillator model and a graded layer model, results shown.
- The Ge layer was fit with a semi-conductor parametric model during the Tauc-Lorentz fit.
- All of the models should give the same constants.
- This gives us an estimate of our accuracy.



Comparison to Previous Work (Ge)



Outline

- Experimental Methods
- LSAT
  - Near IR to Near UV Analysis
  - Infrared Analysis
- Thermal Ge Oxide and Ge
  - Preparation
  - Analysis
- **Temperature Dependence of Ni Optical Constants**
- Conclusions

Ellipsometric Study of Nickel as a Function of Temperature

Stefan Zollner, **T. Nathan Nunley**, Dennis P. Trujillo, Laura G. Pineda, Lina S. Abdallah

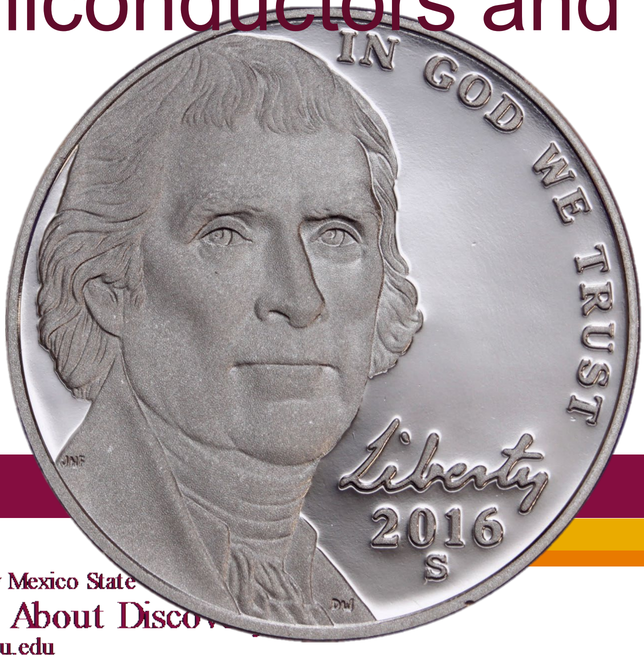
Department of Physics, New Mexico State University, Las Cruces, NM

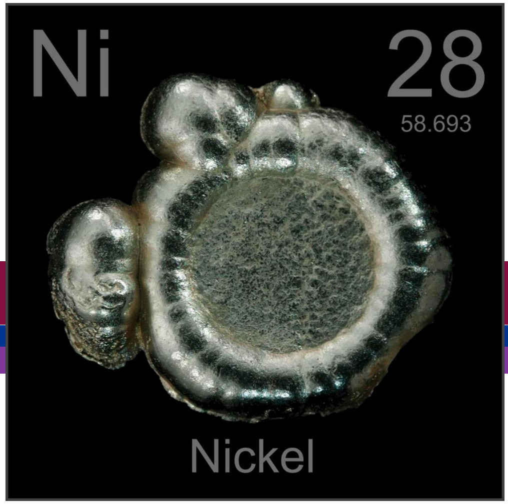
New Mexico State University
All About Discovery!
nmsu.edu

New Mexico State University
All About Discovery!
nmsu.edu

Motivation

- Nickel and Nickel based materials are important in CMOS application
- The dielectric functions of metals are much less understood than classical semiconductors and insulators.

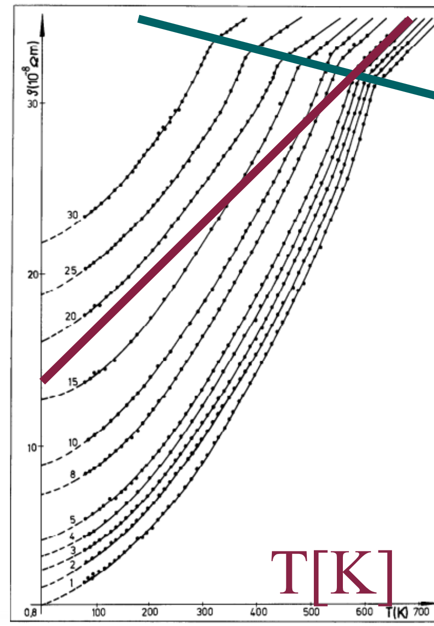




Motivation Continued

- Litschel *et al.* and Ornstein *et al.* measured the DC resistivity (top) and reflectance at 1.9 eV (bottom) near the Curie temperature of Ni (T_c=627 K).
- We expect a discontinuity in the dielectric function near T_c analogous to reflectance.
- The dielectric function for metals includes contributions from interband transitions (Lorentz) and free carriers (Drude), as described in the Drude-Lorentz model.

Litschel and Pop, J. Phys. Chem. Solids **46**, 1421 (1985)



Resistivity versus temperature for $Ni_{1-x}Pt_x$ alloys

Ornstein & Koefoed, *Physica* **5**, 175 (1938)

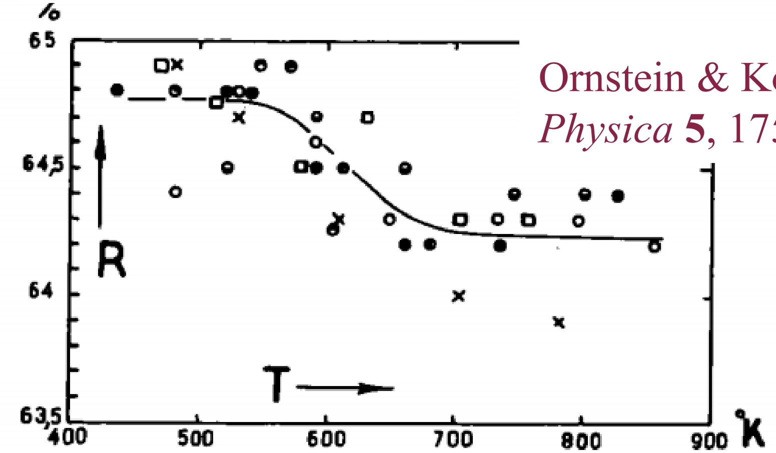
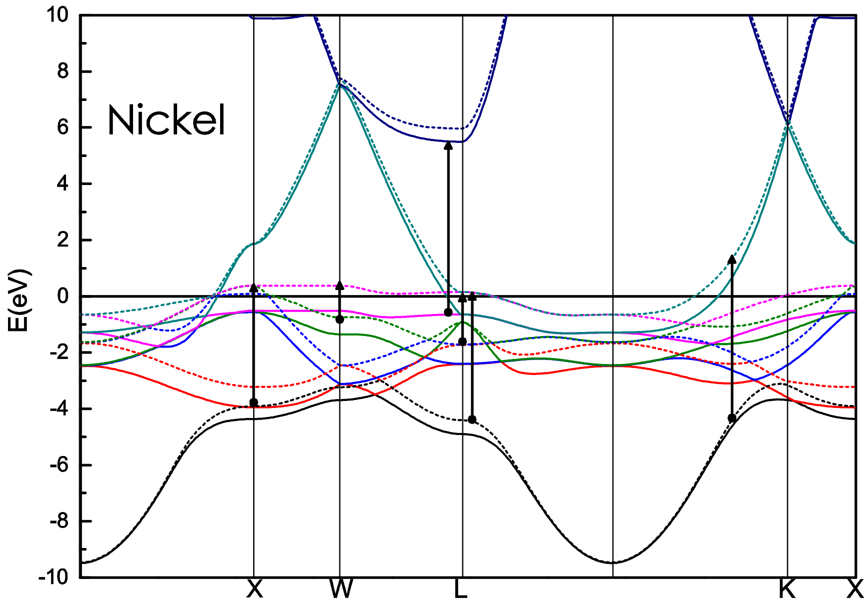
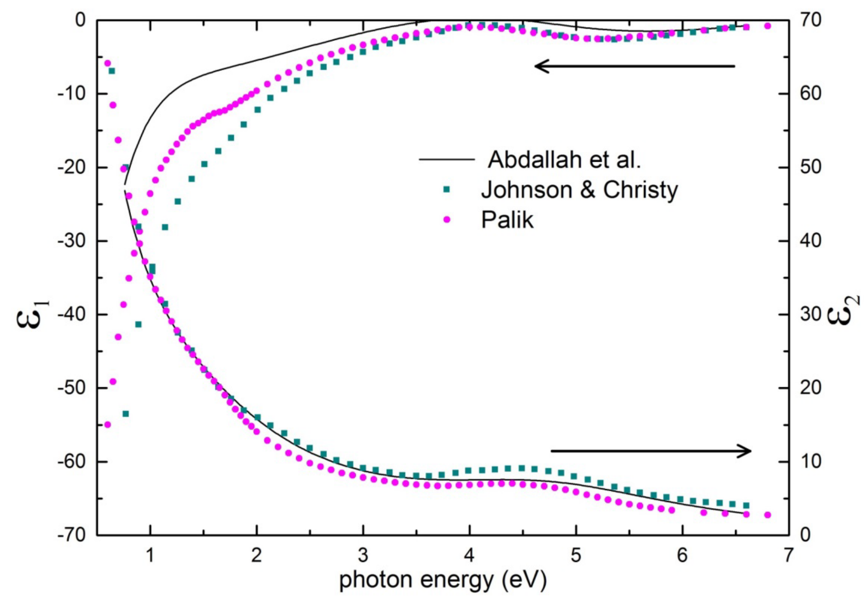


Fig. 1. Reflectivity of Nickel near the Curie-point.

What is Nickel?



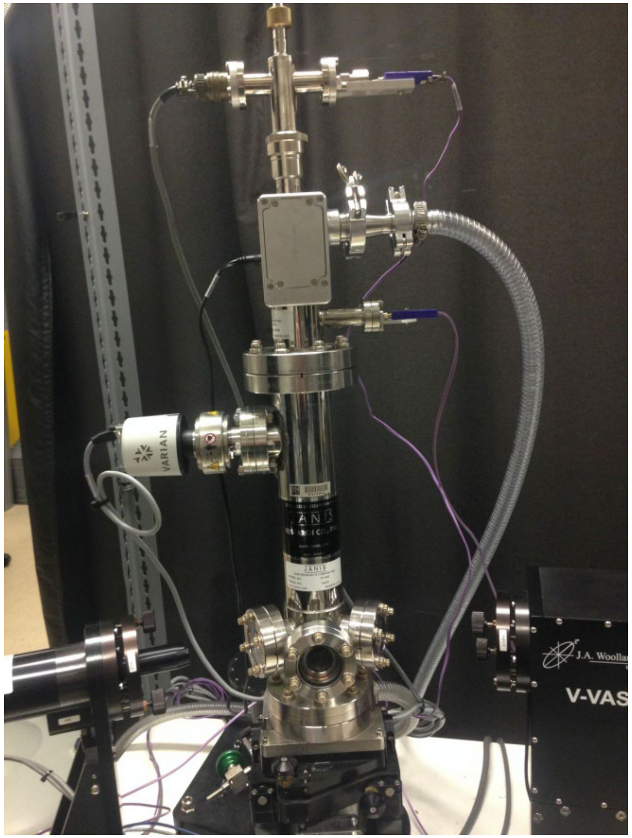
- Transition metal
- No band gap
- Ferromagnetic at room temperature



Abdallah, AIP Advances **4**, 017102 (2014)

Experimental Setup

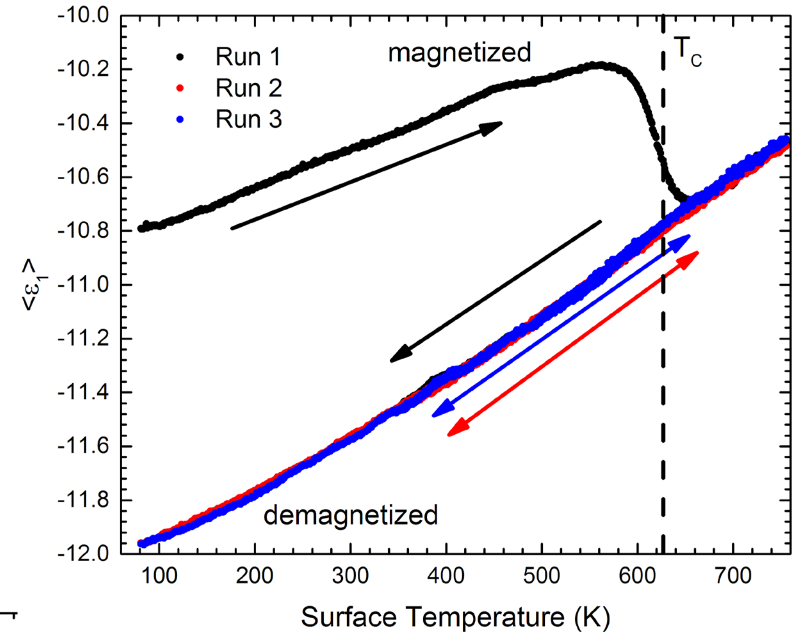
- Measurements performed on bulk polycrystalline sample in UHV (10^{-8} Torr).
- A single wavelength was used, 1.96 eV (the HeNe Laser wavelength).
- The sample temperature spanned 80-760 K.
- The measurements were taken every half minute, every 5-10 s in temperature.

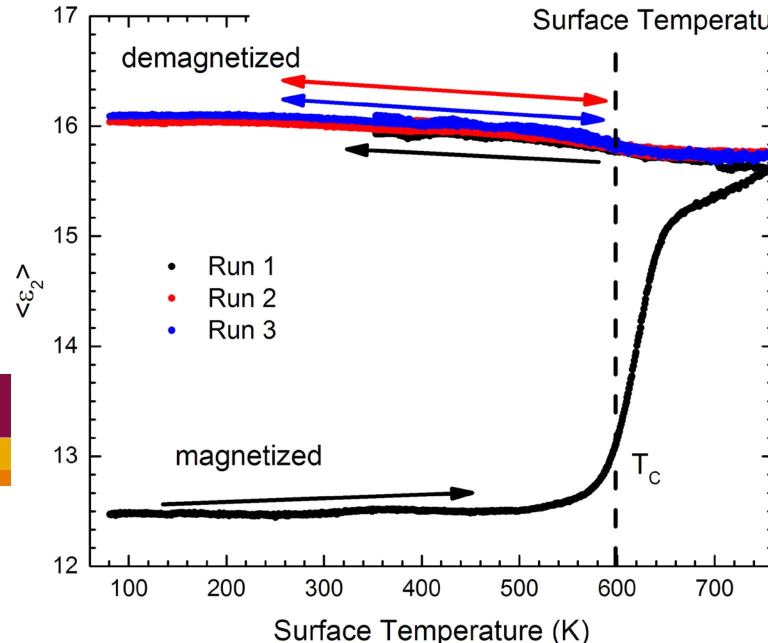


Dielectric Function vs. Temperature

- A discontinuity is observed about the Curie temperature, where the film becomes paramagnetic.

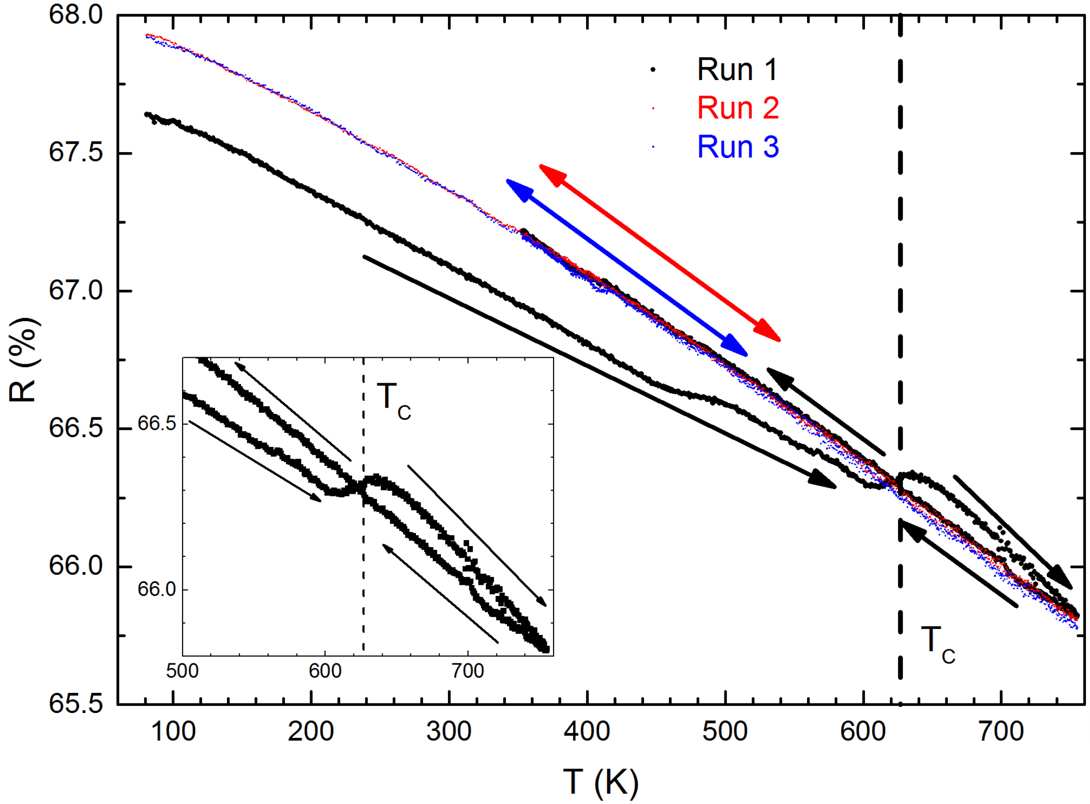
- We observe a difference in the values of epsilon which corresponds to a difference in conductivity. We believe this to have to do with scattering between orbitals based on spin preference.





New Mexico State University
All About Discovery!
nmsu.edu

Reflectivity



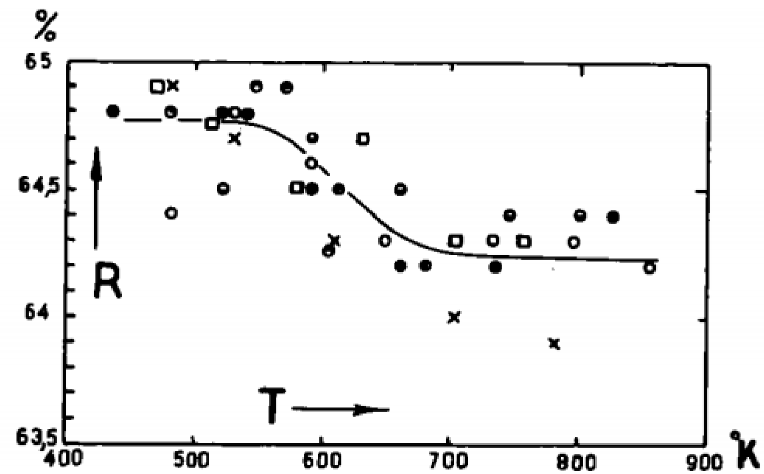


Fig. 1. Reflectivity of Nickel near the Curie-point.

Conclusions

- We have discussed the electronic and vibrational optical analysis of the substrate, LSAT.
- We have discussed the improvement to the current optical constants of Ge and $GeO_{2.}$
- We have discussed the temperature and magnetization dependence of the optical constants of Ni.

Thank you!

- My advisor, Dr. Stefan Zollner
- My committee: Dr. Urquidi, Dr. Engelhardt, and Dr. Quintana
- Our collaborators
- The physics department for being the place where I have grown for the past 5 years
- My funding agencies! AFOSR (FA9550-13-1-0022), ARO (W911NF-14-1-0072), NSF (DMR-1104934 and DMR-1505172). DOE CINT (Contract DE-AC52-06NA25396 and DE-AC04-94AL85000). The work at the University of Fribourg was supported by the Schweizerische Nationalfonds (SNF) through grant No. 200020-153660.

Zollner Ellipsometry Research Group

Lovely spring dust storm in the back

ellipsometry.nmsu.edu

New Mexico State University
All About Discovery!
nmsu.edu

Questions

???

- Experimental Methods
- LSAT
  - Near IR to Near UV Analysis
  - Infrared Analysis
- Thermal Ge Oxide and Ge
  - Prepartation
  - Analysis
- Temperature Dependence of Ni Optical Constants
- Conclusions