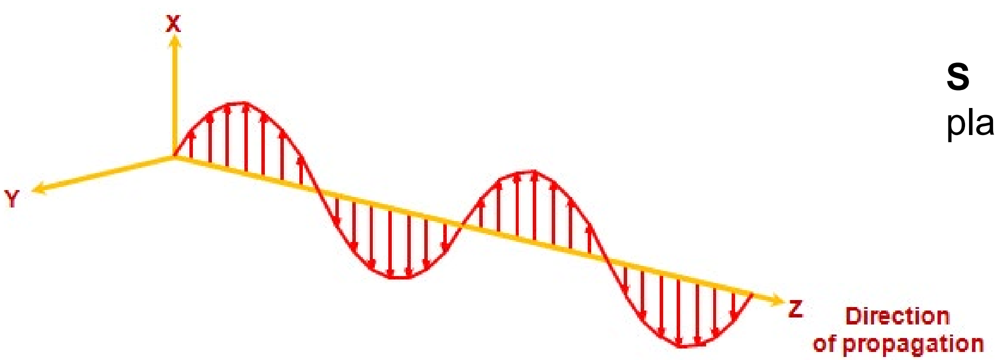
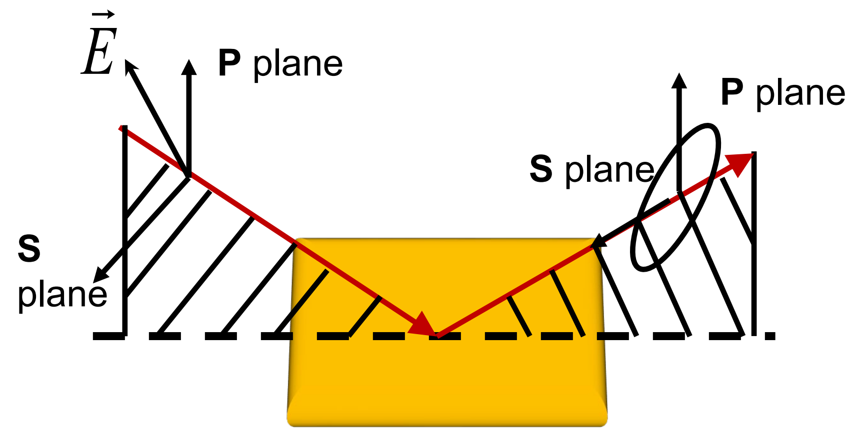
Ellipsometry of $Ni_{1-x}Pt_x$ and Related Silicides

Lina Abdallah





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Ahmet Ozcan, Christian Lavoie (IBM); Mark Raymond (Globalfoundries)
R.J. Davis (Ohio State) - samples

CV

- BS: University of Jordan, Amman, Jordan (2002-2006)
- MS: University of Jordan, Amman, Jordan (2006-2009)
- MS: New Mexico State University, Las Cruces, NM, fall 2012
- Ph.D. candidate, New Mexico State University (spring 2010-present)

Ellipsometry Publications

- C.V. Weiss, J. Zhang, M. Spies, **L.S. Abdallah**, S. Zollner, M.W. Cole, and S.P. Alpay, *Bulk-like dielectric properties from metallo-organic solution-deposited $SrTiO_3$ films on Pt-coated Si substrates*, J. Appl. Phys. **111**, 054108-1-9 (2012).
- C. M. Nelson, M. Spies, **L.S. Abdallah**, S. Zollner, Y. Xu, and H. Luo, *Dielectric function of $LaAlO_3$ from 0.8 to 6.6 eV between 77 and 700 K*, J. Vac. Sci. Technol. A **30**, 061404-1 (2012).
- S. G. Choi, J. Hu, **L.S. Abdallah**, M. Limpinsel, Y. N. Zhang, S. Zollner, R. Q. Wu, and M. Law, *Pseudodielectric function and critical-point energies of iron pyrite*, Phys. Rev. B **86**, 115207 (2012).
- **L.S. Abdallah** et al., *Compositional dependence of $Ni_{1-x}Pt_x$ alloys ($0< x <0.25$) determined by spectroscopic ellipsometry*, Thin Solid Films (in print).
- **L.S. Abdallah** et al., *Optical conductivity of $Ni_{1-x}Pt_x$ alloys ($0< x <0.25$) from 0.76 to 6.6 eV*, AIP Advances 4, 017101 (2014).
- **L.S. Abdallah** et al., *Optical Conductivity of $Ni_{1-x}Pt_xSi$ Monosilicides ($0<x<0.3$) from Spectroscopic Ellipsometry*, submitted to J. Vac. Sci. Technol.
- **L.S. Abdallah** et al., *Infrared Optical Conductivity of $Ni_{1-x}Pt_x$ Alloys and $Ni_{1-x}Pt_xSi$ Monosilicides from Spectroscopic Ellipsometry,* (in preparation).

Ellipsometry Presentations

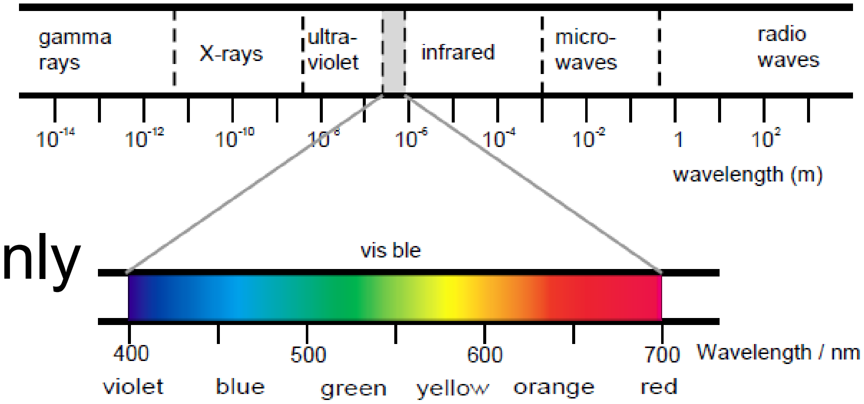
- A.A. Medina**, L.S. Abdallah**, and S. Zollner, *Temperature dependence of the dielectric function of Germanium by spectroscopic ellipsometry*, Four Corners Section Meeting of the APS, Tucson, AZ, Oct. 20-21 (2011).
- **L.S. Abdallah** et al., *Dielectric function of Ni-Pt alloys from 0.6 to 6.6 eV by spectroscopic ellipsometry*, Four Corners Section Meeting of the APS, Tucson, AZ, Oct. 2011.
- **L.S. Abdallah** et al., *Dielectric function of Ni-Pt alloys from 0.6 to 6.6 eV by spectroscopic ellipsometry*, APS March meeting, Boston, MA, 29 February 2012.
- M. Spies, **L.S. Abdallah**, S. Zollner, C.V. Weiss, J. Zhang, S.P. Alpay, and M.W. Cole, *Dielectric and optical properties of* $SrTiO_3$ *films deposited from metallo-organic solution*, APS March meeting, Boston, MA, 1 March 2012.
- C.M. Nelson, M. Spies, **L.S. Abdallah**, and S. Zollner, Y. Xu and H. Luo, *Preparation of Abrupt* $LaAlO_3$ *Surfaces Monitored by Spectroscopic Ellipsometry*, AVS Symposium, Albuquerque, NM (May 2012).
- C.M. Nelson, M. Spies**, L.S. Abdallah**, and S. Zollner, Y. Xu and H. Luo, *Preparation of Abrupt LaAlO3 Surfaces Monitored by Spectroscopic Ellipsometry*, The Seventh Multifunctional Materials Workshop (MFM-7), Gamboa, Panama, (August 2012).
- **L.S. Abdallah** et al., *Compositional dependence of the dielectric function and optical conductivity of NiPt alloy thin films*, APS Four Corners Section, Socorro, NM (2012).
- Cesar A. Rodriguez, C.M. Nelson, **L.S. Abdallah**, and S. Zollner, *Determination of RGB color coordinates from spectroscopic reflectance measurements*, Four Corners Section Meeting of the APS, Socorro, NM (2012).
- **L.S. Abdallah** et al., *Composition dependence of the optical constants of NiPt alloys determined by spectroscopic ellipsometry*, Conference for Undergraduate Women in Physical Sciences, Lincoln, NE (October 2012).
- A.A. Medina, **L.S. Abdallah**, and S. Zollner, *Temperature Dependence of the Dielectric Function of Germanium by Spectroscopic Ellipsometry*, AVS Symposium, Tampa, FL (2012).
- C.M. Nelson, M. Spies, **L.S. Abdallah**, S. Zollner, Y. Xu, and H. Luo, *Preparation of Abrupt LaAlO3 Surfaces Monitored by Spectroscopic Ellipsometry*, AVS Symposium, Tampa, FL (2012).
- **L.S. Abdallah** et al., *Compositional dependence of the dielectric function and optical conductivity of NiPt alloy thin films*, AVS Symposium, Tampa, FL (2012).
- **L.S. Abdallah** et al., *Optical Constants of Ni-Pt and Ni-Pt-Si Thin Films*, AVS Chapter Symposium, Albuquerque, NM (2013).
- C.A. Rodriguez, K. Mitchell, S. Zollner, T. Willett-Gies, and **L.S. Abdallah**, *Optical Constants of Thin Film Metal Oxides*, AVS Chapter Symposium, Albuquerque, NM (2013).
- L.G. Pineda, **L.S. Abdallah**, and S. Zollner, *Optical Properties of Bulk Nickel as a Function of Temperature*, Rio Grande Symposium, Albuquerque, NM, 07 October 2013.
- L.G. Pineda, **L.S. Abdallah**, and S. Zollner, *Optical Properties of Bulk Nickel as a Function of Temperature*, APS Four Corners Section Meeting, 10/18-19/2013, Denver, CO.
- **L.S. Abdallah** et al., *Optical Constants of Ni1-xPtx Monosilicides From Spectroscopic Ellipsometry*, APS Four Corners Section Meeting, 10/18-19/2013, Denver, CO.
- C.M. Nelson, T. Willett-Gies, A. Ghosh, **L.S. Abdallah**, S. Zollner, *Electronic and Vibrational Properties of Nickel Oxide (NiO) using Spectroscopic Ellipsometry*, AVS Symposium, Long Beach, CA (2013).
- **L.S. Abdallah** et al., *Optical Constants of Ni1-xPtx Monosilicides From Spectroscopic Ellipsometry*, AVS Symposium, Long Beach, CA (2013).
- S. Zollner, C.M. Nelson, T. Willett-Gies, **L.S. Abdallah**, and A. Ghosh, *Dielectric function of NiO and Si from 25 meV to 6 eV: What's the difference?,* APS March meeting, Denver, CO, 3-7 March 2014.
- **L.S. Abdallah** et al., *Infrared optical conductivity for Ni1-xPtx alloys and Ni1-xPtxSi monosilicides*, APS March meeting, Denver, CO, 3-7 March 2014.
- **L.S. Abdallah** et al., *Infrared optical conductivity for Ni1-xPtx alloys and Ni1-xPtxSi monosilicides*, AVS Surface Analysis conference, Albuquerque, NM, 2-6 June 2014.

Outline

- Electromagnetic Radiation as a Probe for Materials Properties
- Ellipsometry: Experimental setup
- Ellipsometry Data Analysis
- Motivation: Ohmic contacts for CMOS devices
- First Result:
  Optical Constants of $Ni_{1-x}Pt_x$ Alloys
- Second Result:
  Optical Constants of $Ni_{1-x}Pt_xSi$ Monosilicides
- Third Result:
  Infrared Optical Properties of $Ni_{1-x}Pt_x$ Alloys and $Ni_{1-x}Pt_xSi$ Monosilicides.

Electromagnetic Radiation

- Each material has electronic states at unique energy levels.



- When you expose a material to radiation from all wavelengths, only the λ that matches that level can interact with the electronic state.
- VIS/UV radiation alters the electron energies of loosely bound electrons of atoms or molecules
- IR radiation causes changes in the vibrational energy of molecules.

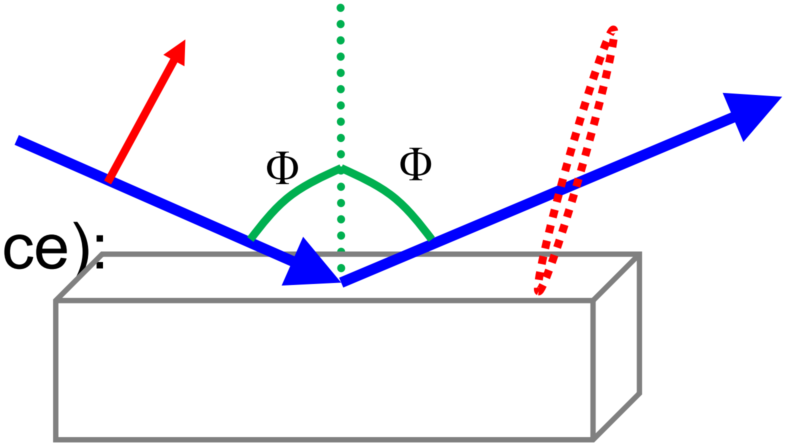
Why Ellipsometry?

- How thick is my film?

Interference condition (normal incidence):

$$2nd = N\lambda$$

n: refractive index
d: thickness
N: integer
λ: wavelength



- Learn about **materials properties**

Infrared light:	Lattice vibrations
Visible and UV light:	Electronic properties and band structure

- Optical constants for optical applications.

- Microstructure (surface roughness, crystallinity).

- Composition.

Ellipsometry:

- Light wave can be described as superposition of two electric field components
- <u>s and p polarization</u>

Plane of incidence.

s and p waves: oscillatory directions of the electric field

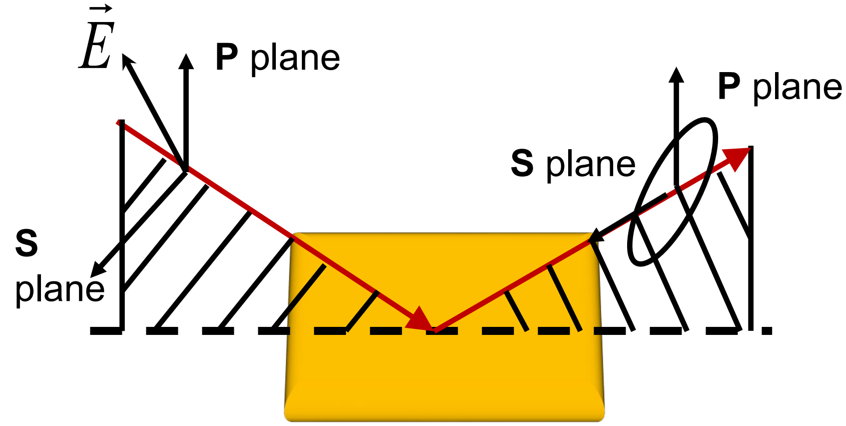
p: parallel

s: perpendicular

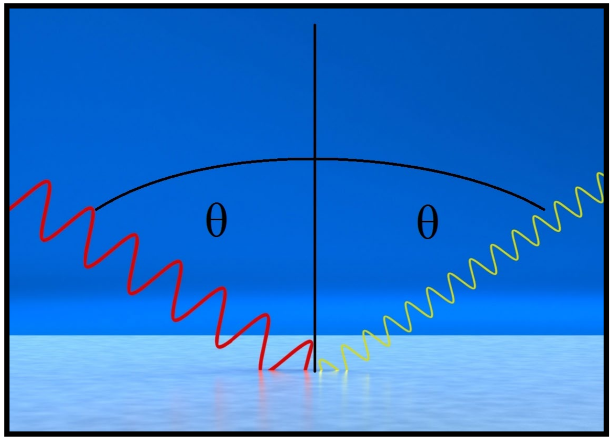
- Ellipsometry measures

<u>change in the polarization state</u>: Δ

<u>amplitude ratio</u>: ψ



change in the polarization state



Amplitude ratio

Fundamental Equations Of Ellipsometry:

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

Angle of incidence

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

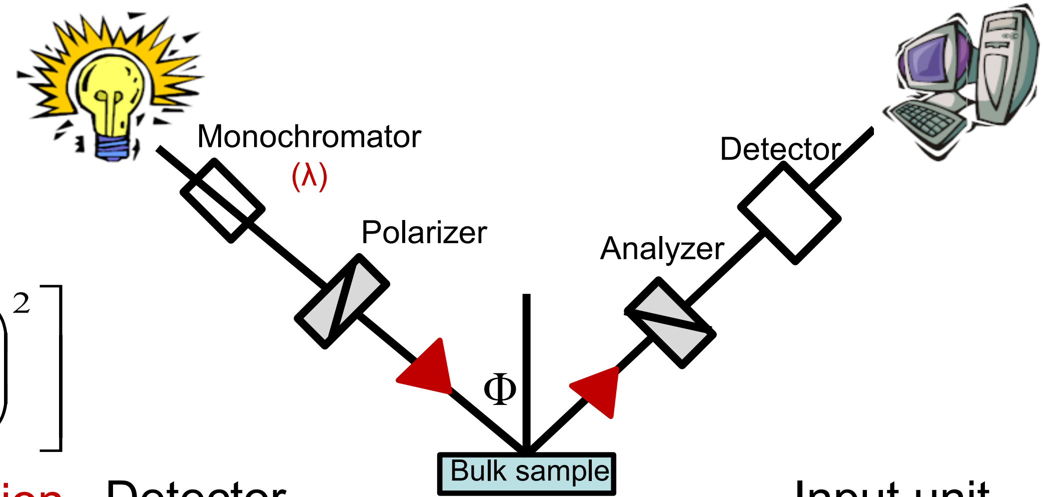
$\tilde{n} = n + ik$ Complex index of refraction

n, k : Optical constants

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

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

$$\varepsilon_2 = 2nk$$



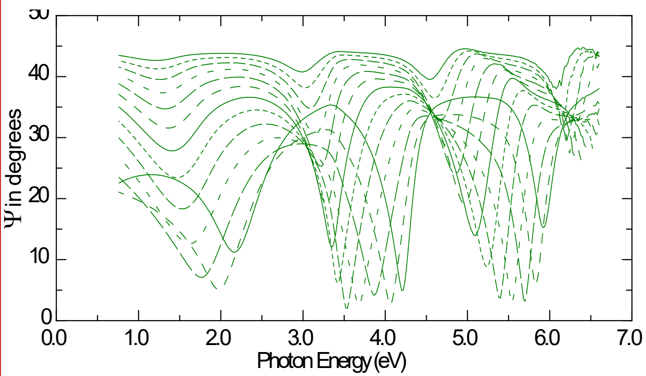
Detector

Input unit

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

Data analysis

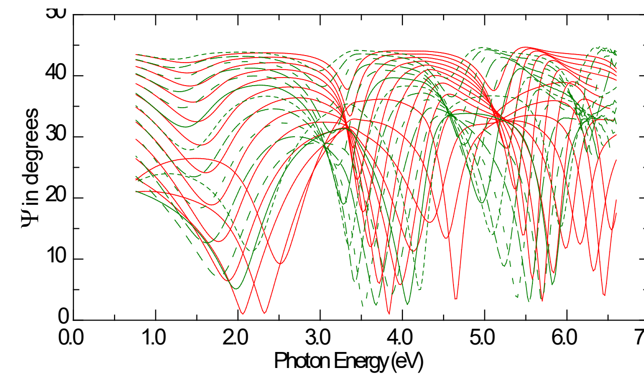
Experimental Data



Build a model

2	Layer 2	t_2
1	Layer 1	t_1
0	substrate	∞

Generated Data



Compare Exp.
And Gen. data

Match ??

NO

Change model parameters

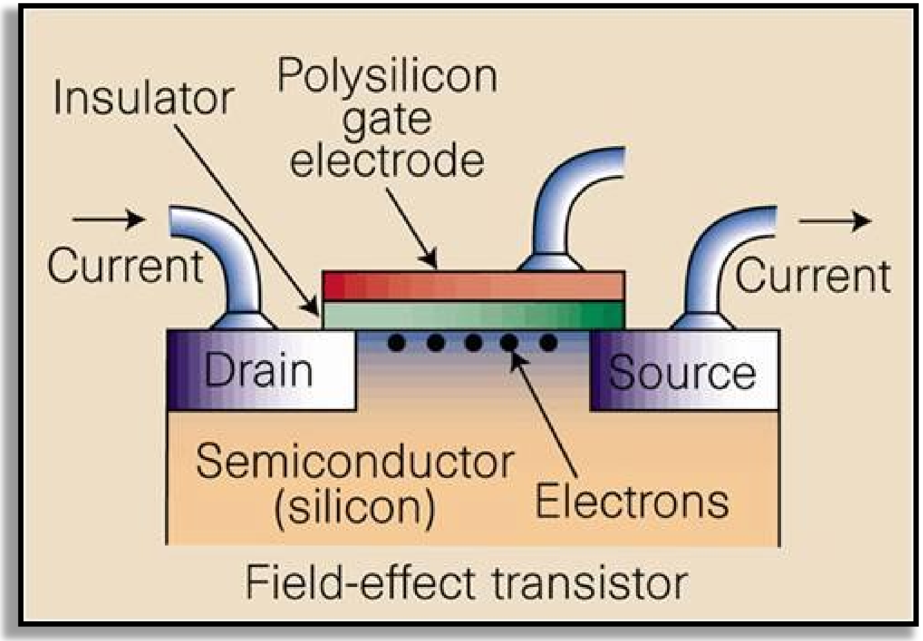
YES

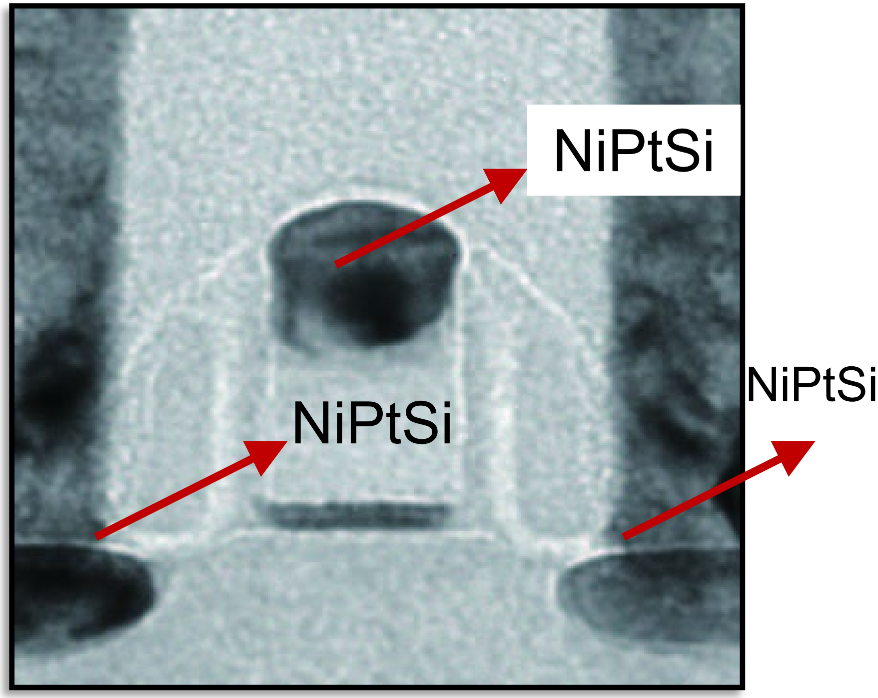
- Well known material (Si, SiO_2)
Tabulated data

- New material (NiPt, NiPtSi)
Set of oscillators
Solve numerically

Motivation: NiSi thickness metrology

MOSFET: metal–oxide–semiconductor field-effect transistor

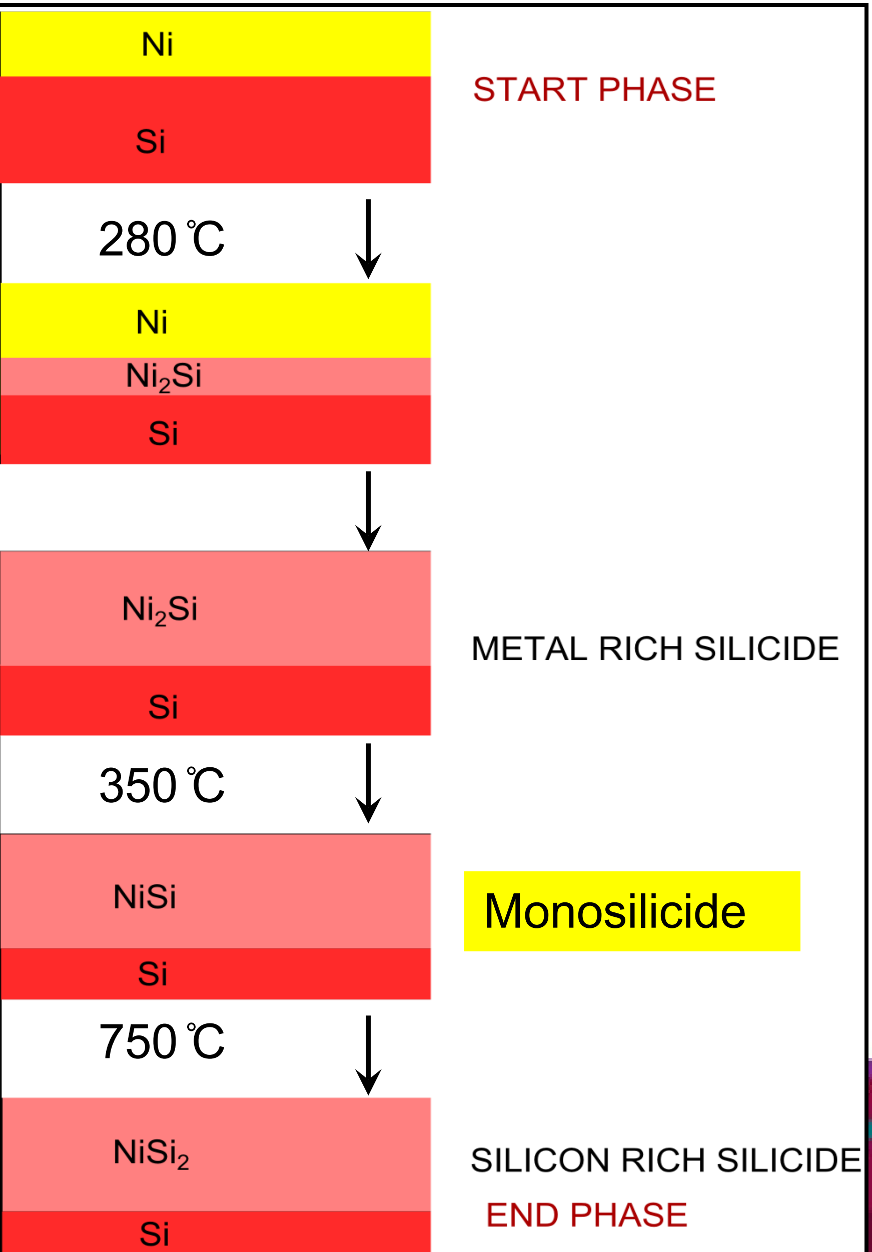




- Low resistivity
- Low formation temperature
- Low Si consumption

32 nm SOI CMOS (Greene et al.)
industrial self-aligned silicide process

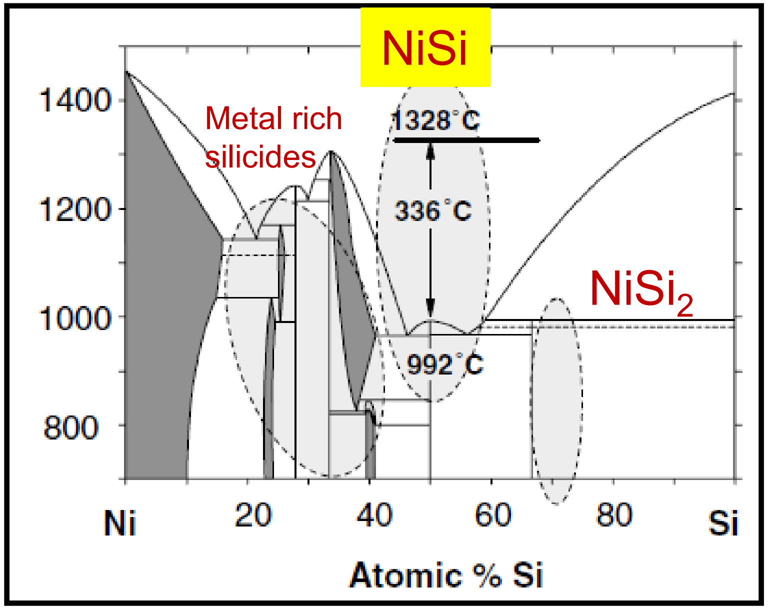
Ni Silicide Formation



NiSi: Unstable at high temperatures

$NiSi_2$ Formation

Agglomeration.



Effects of additive elements on the phase formation and morphological stability of nickel monosilicide films

C. Lavoie [a,b,*], C. Detavernier [c], C. Cabral Jr. [a], F.M. d'Heurle [a], A.J. Kellock [d], J. Jordan-Sweet [a], J.M.E. Harper [e]

Microelectronic Engineering **83,** 2042 (2006)

Ni-Pt Silicides

$$NiSi + Si \rightarrow NiSi_2 \text{ (higher resistivity)}$$

(need to push this reaction to higher temperatures.)

$$Ni_{1-x}Pt_xSi + (1-x)Si \rightarrow (1-x)NiSi_2 + xPtSi$$

Pt delays $NiSi_2$ nucleation (entropy of mixing)

$$G(\mathrm{NiSi/Pt}) \langle G(\mathrm{NiSi_2}) + G(Pt)$$

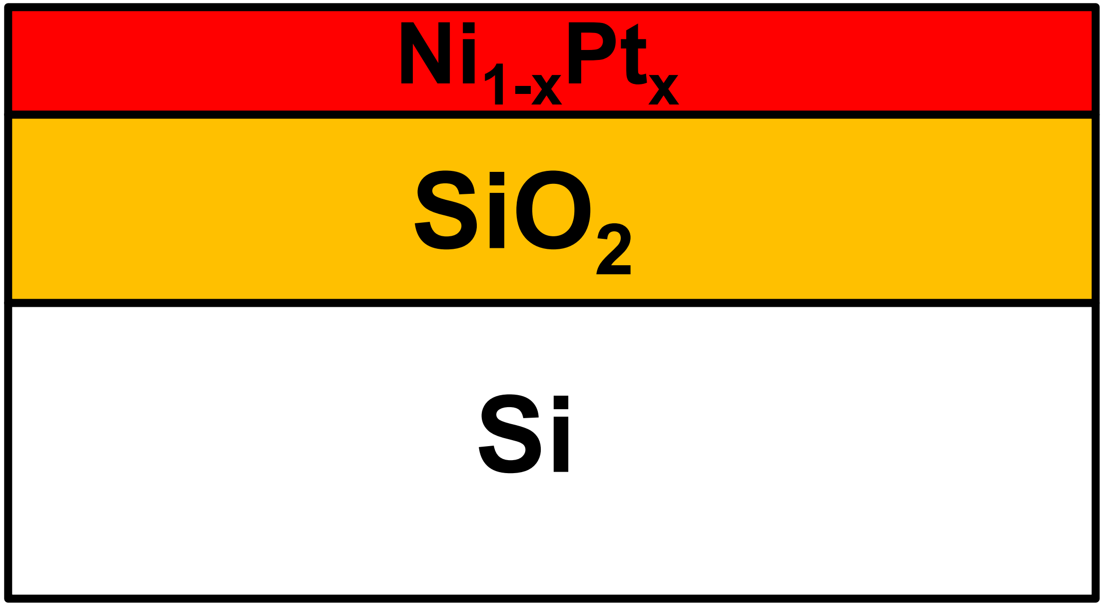
Formation of $NiSi_2$ is energetically disfavored

C. Lavoie [a,b,*], C. Detavernier [c], C. Cabral Jr. [a], F.M. d'Heurle [a], A.J. Kellock [d], J. Jordan-Sweet [a], J.M.E. Harper [e]

Microelectronic Engineering **83,** 2042 (2006)

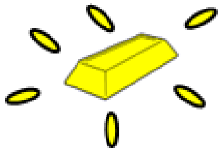
First Result

Optical constants of $Ni_{1-x}Pt_x$ alloys (0 to 25% Pt)

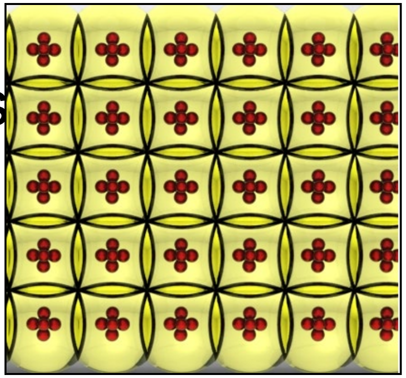


Ellipsometry of thin metal films

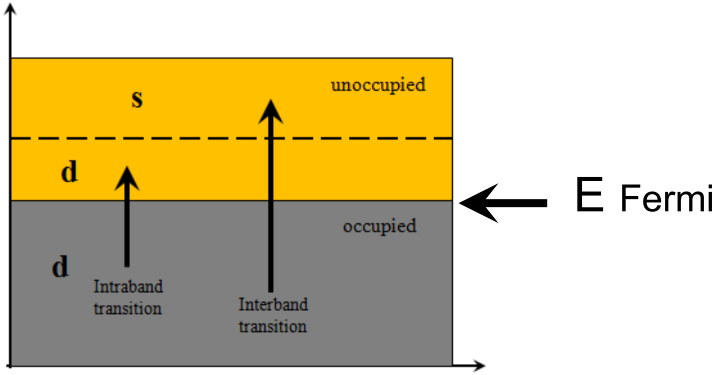
High reflection coefficient



Outermost electrons shared by all the surrounding atoms



Zero band gap: almost any frequency of light can be absorbed.

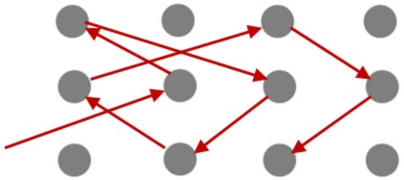


For metal films k≠0, ε is complex

ε decomposed into two components

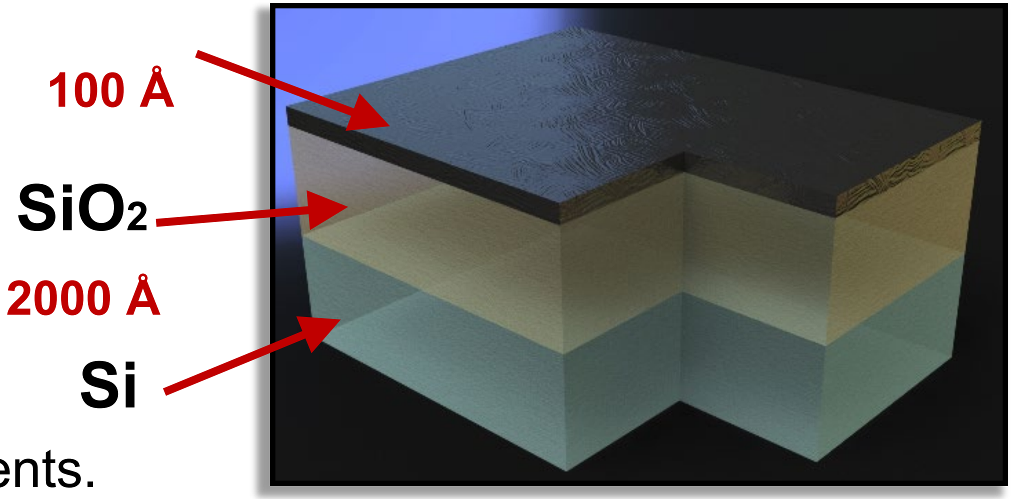
$$\varepsilon = \varepsilon_{FCA} + \varepsilon_{bound}$$

Free carriers (Drude) **Bound carriers** (Lorentz)



Samples and Experimental Details

- Films were deposited using **Physical Vapor Deposition**.
- Different Pt concentrations (0%, 10%, 15%, 20%, 25%)
- with/without annealing (500˚C for 30 s)

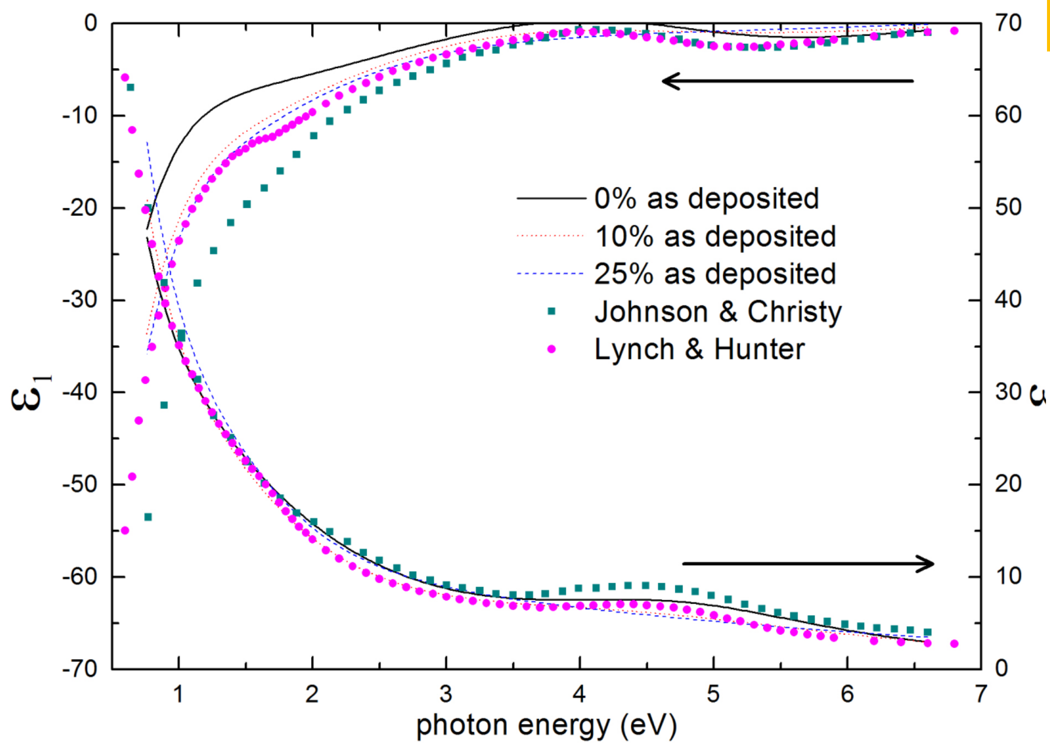


- Room temperature measurements.
- **Fourteen angles of incidence (20˚ to 80˚, steps of 5˚)**
- Broad photon energy range (0.6 to 6.6 eV), 20 meV steps, 300 data points per angle. **2 nm resolution (1 mm slits)**
- Each measurement lasts **24 hours**

Results

- Dielectric Function

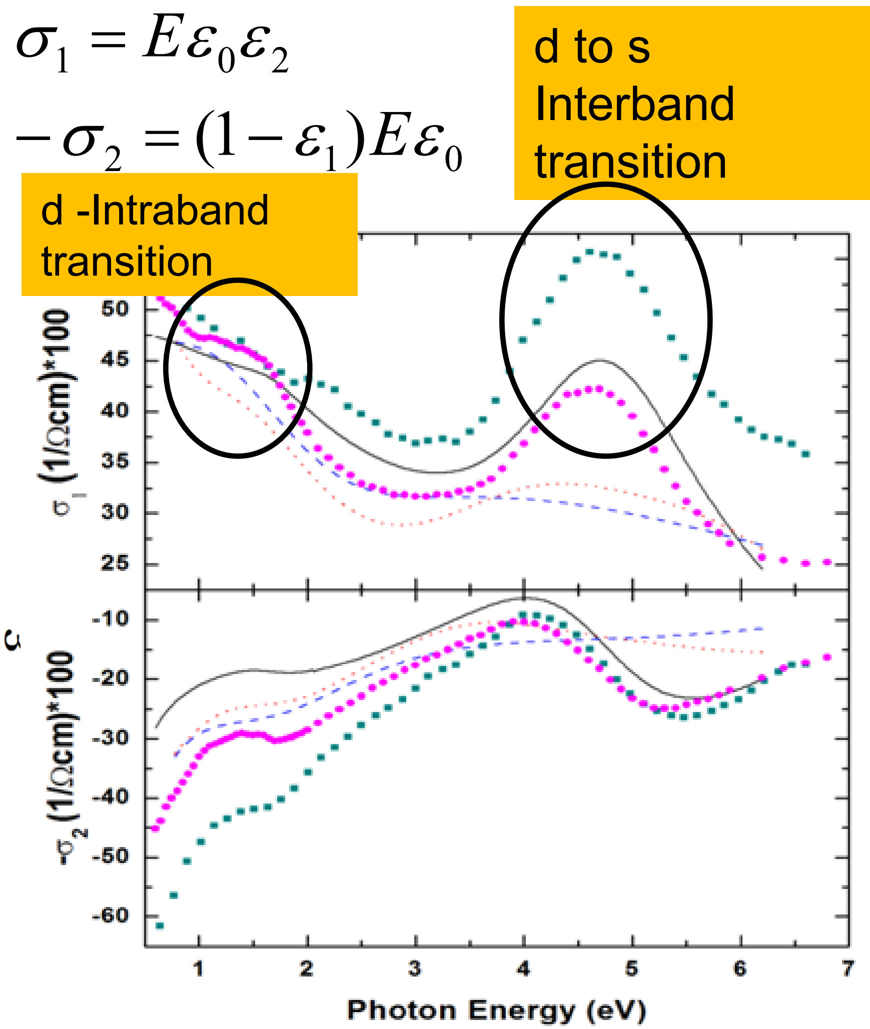
ε_2 **Describes absorption**



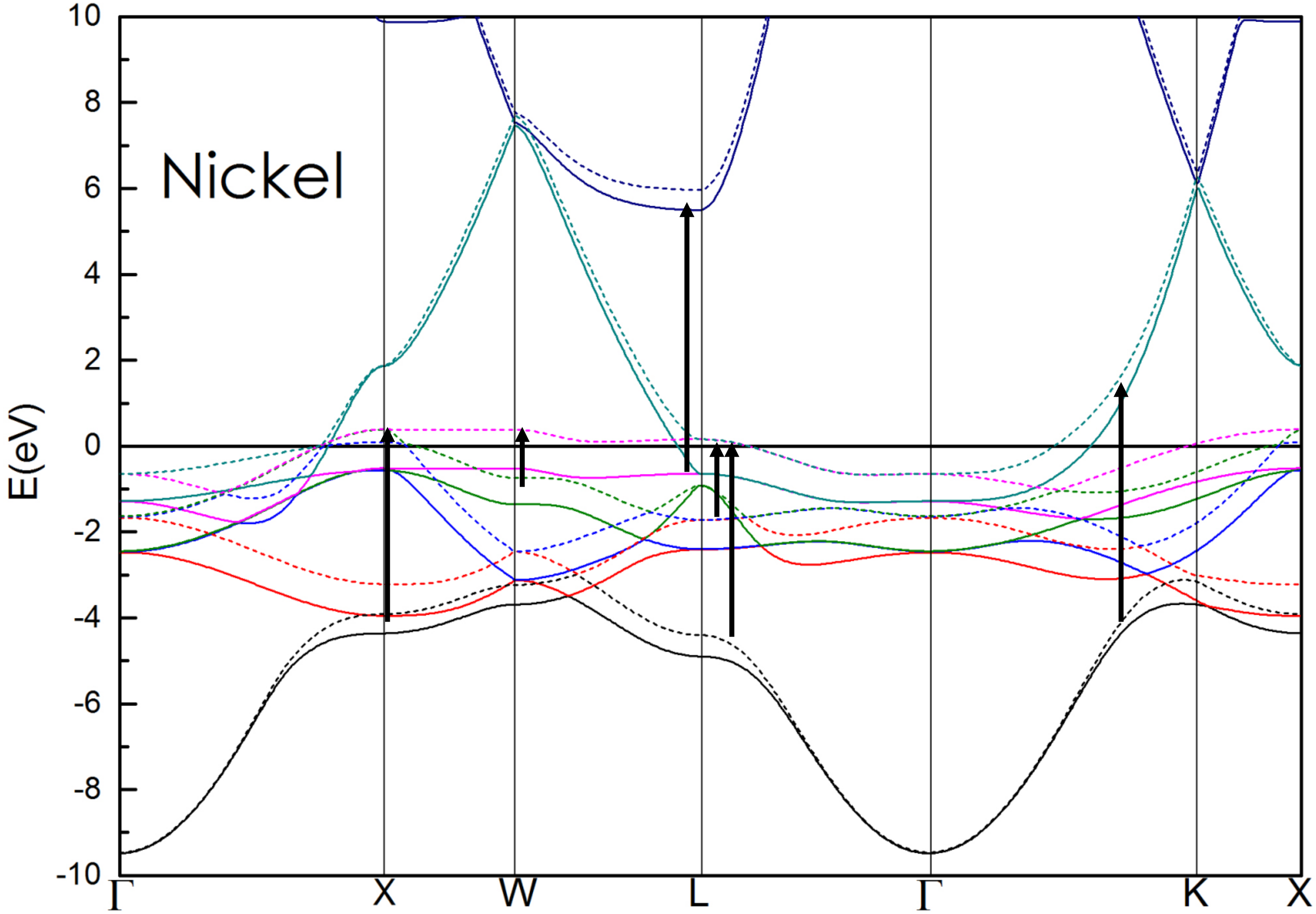
- Optical Conductivity

$$\sigma_1 = E\varepsilon_0\varepsilon_2$$

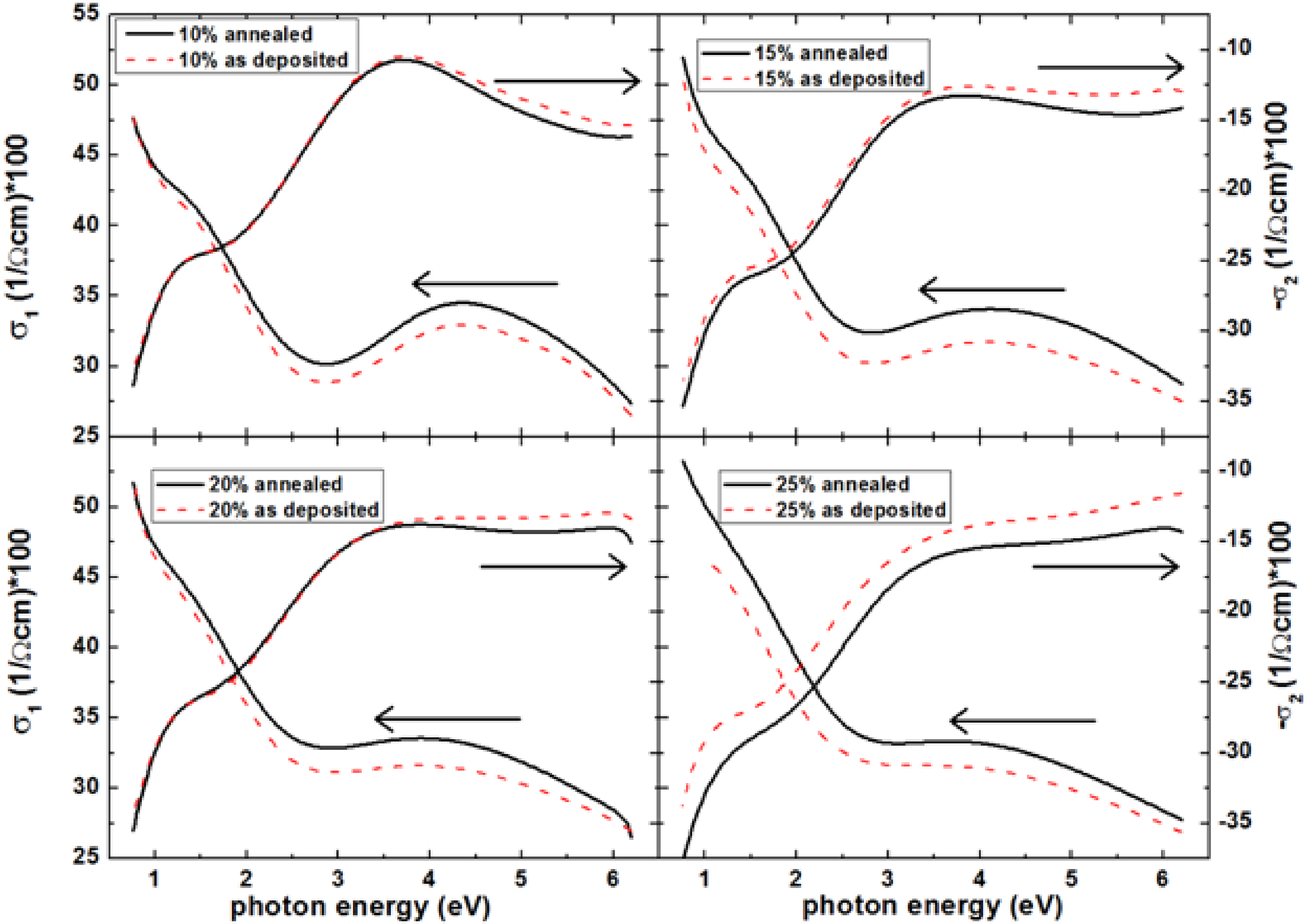
$$-\sigma_2 = (1-\varepsilon_1)E\varepsilon_0$$



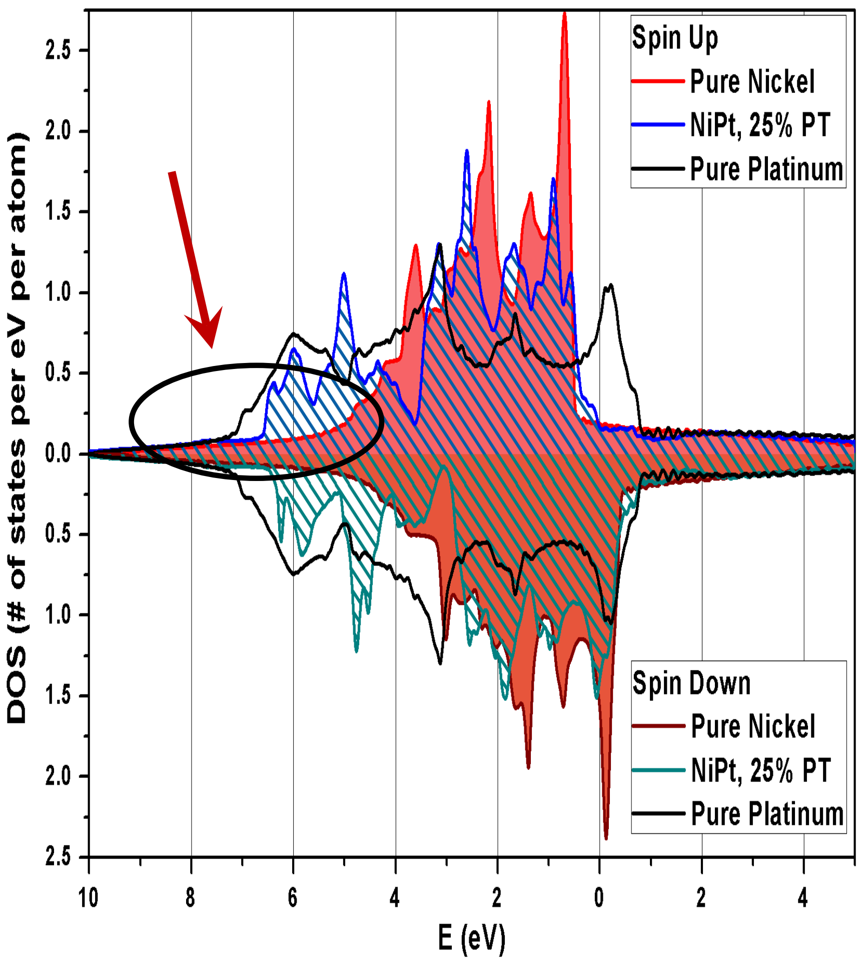
Band Structure of Nickel: Possible transitions



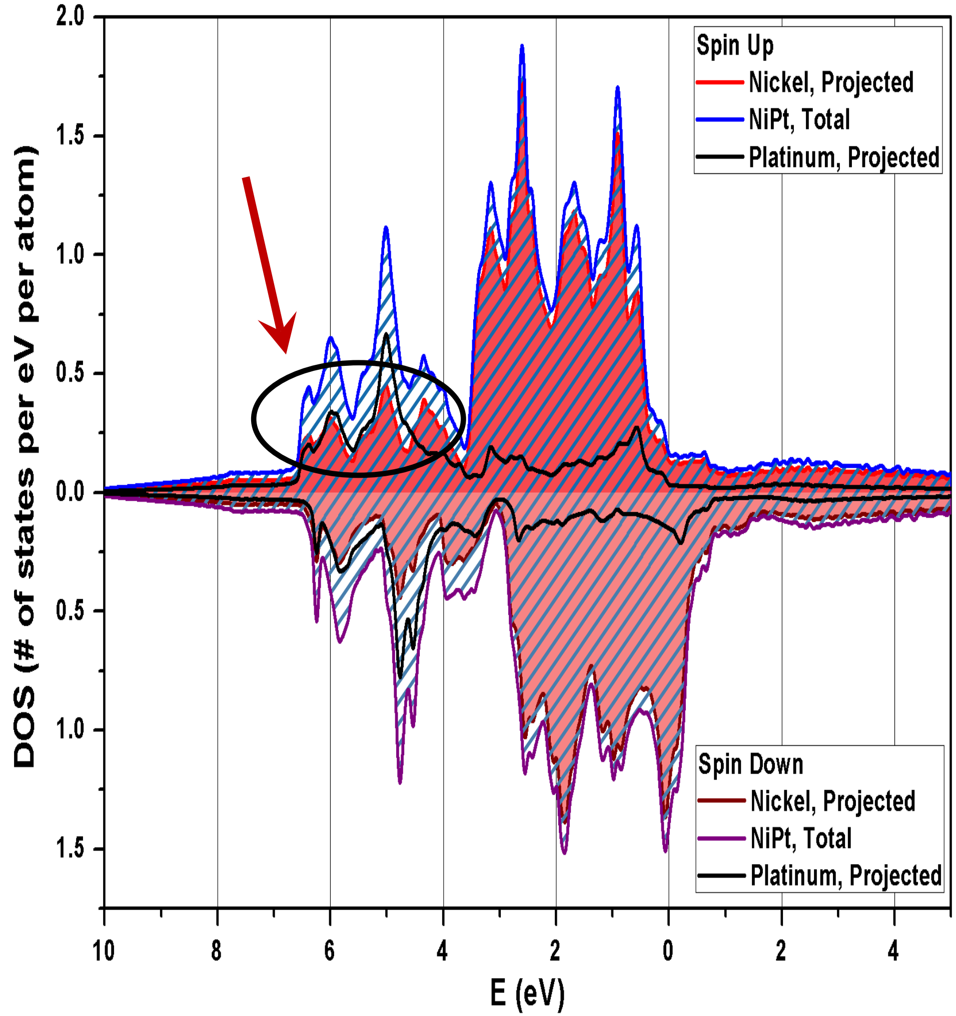
$Ni_{1-x}Pt_x$ optical conductivity for different compositions



Total DOS



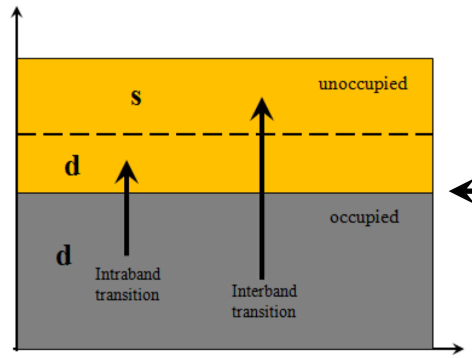
Ni_3Pt Projected DOS



Discussion:

Initial guess

3	water	
2	Oscillator model	100 Å
1	SiO_2	2000 Å
0	Si	



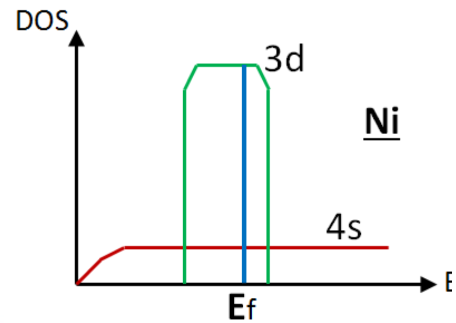
Oscillator Model:

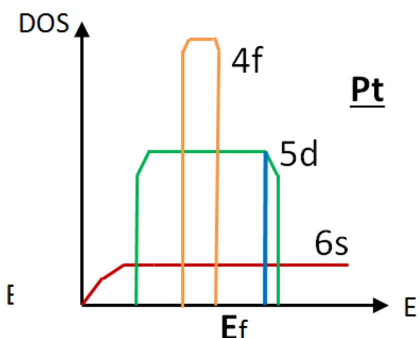
- Drude oscillator (free electrons)
- Lorentz @ 1.5 eV (d-intraband transition)
- Lorentz @ 4.7 eV (interband transition)
- IR pole @ 0 eV (???, see IR analysis later)
- UV pole @ 11 eV

- Same peaks were observed in pure nickel

- Annealed samples show higher conductivity than as deposited samples due to improved crystallinity

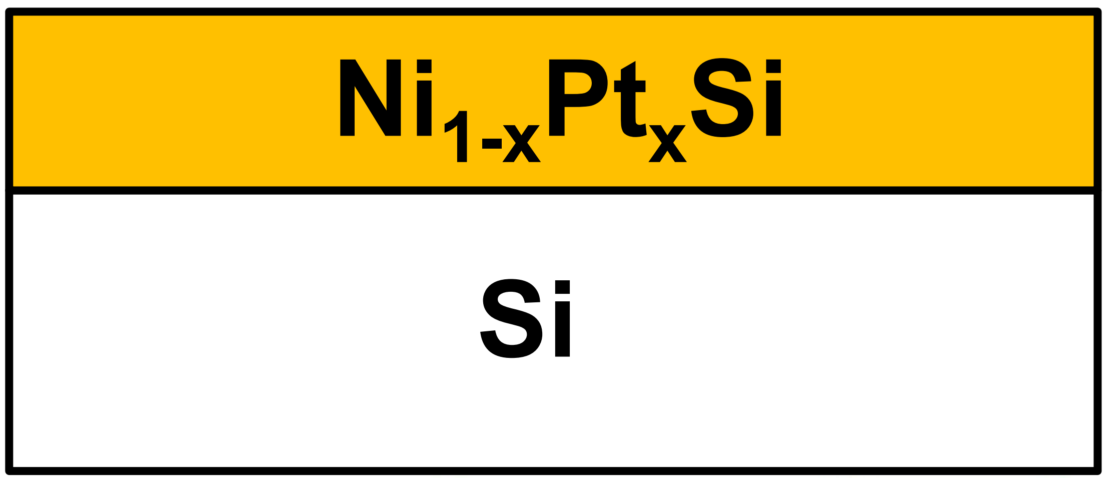
- Absorption peak gets broader with increasing Pt content





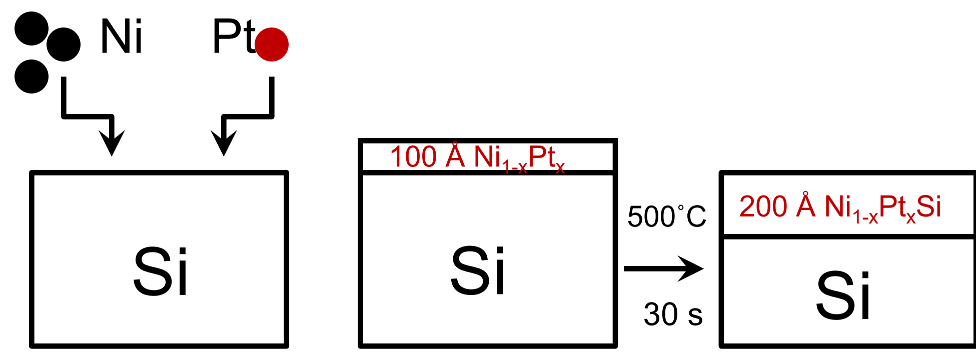
Second Result

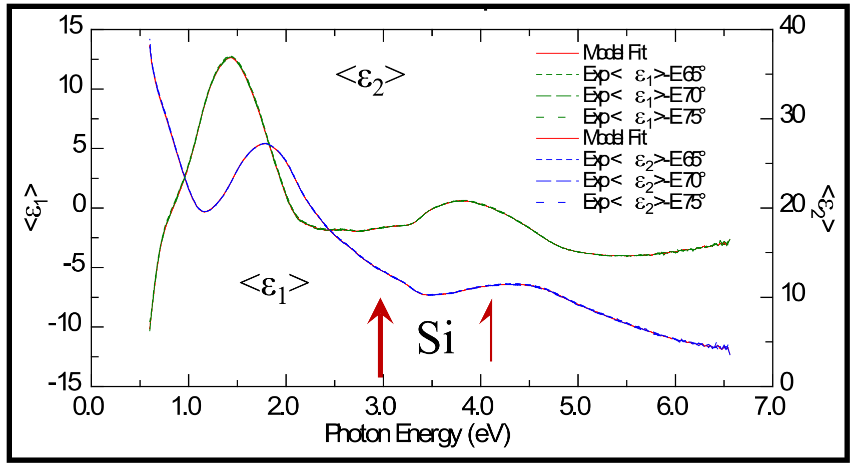
Optical constants of $Ni_{1-x}Pt_xSi$ monosilicides
(0 to 30% Pt)



Monosilicides $(Ni_{1-x}Pt_x)Si$

- $Ni_{1-x}Pt_x$
  (0%, 10%, 20%, 30% Pt)
- 500˚C for 30 s
- Thickness of resulting silicide = 2*metal thickness
- SiO_2 is native oxide on NiSi.
- Three angles of incidence: 65˚ to 75˚
- Vary thickness of silicide to minimize Si substrate artifacts

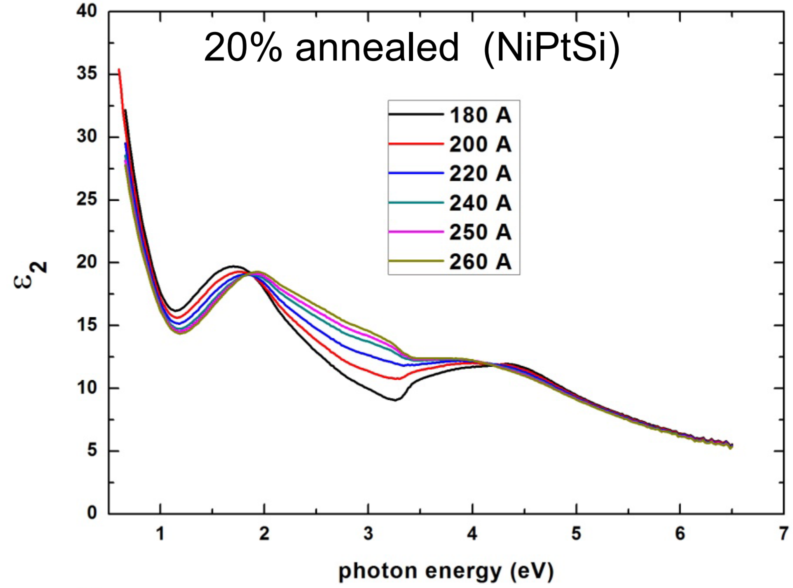


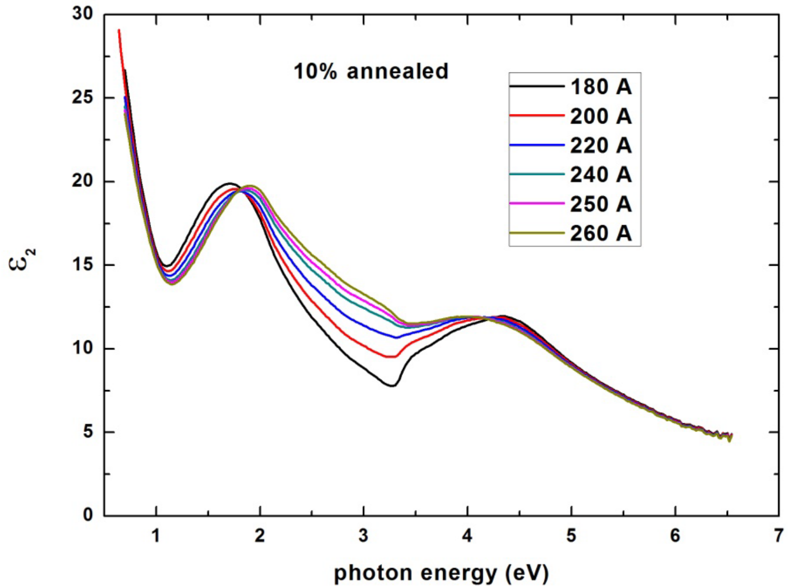


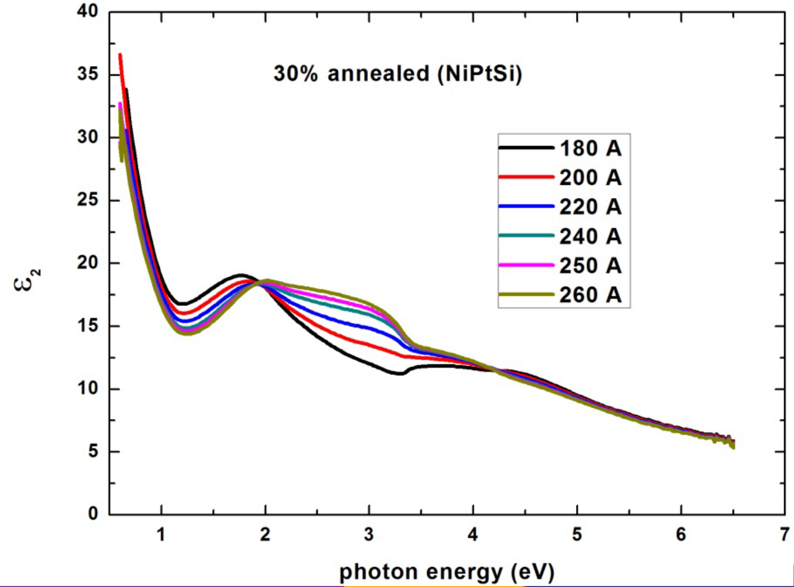
Pseudo dielectric function for mono Ni silicide (0% Pt)

Monosilicide:
Vary thickness of silicide to minimize Si substrate artifacts

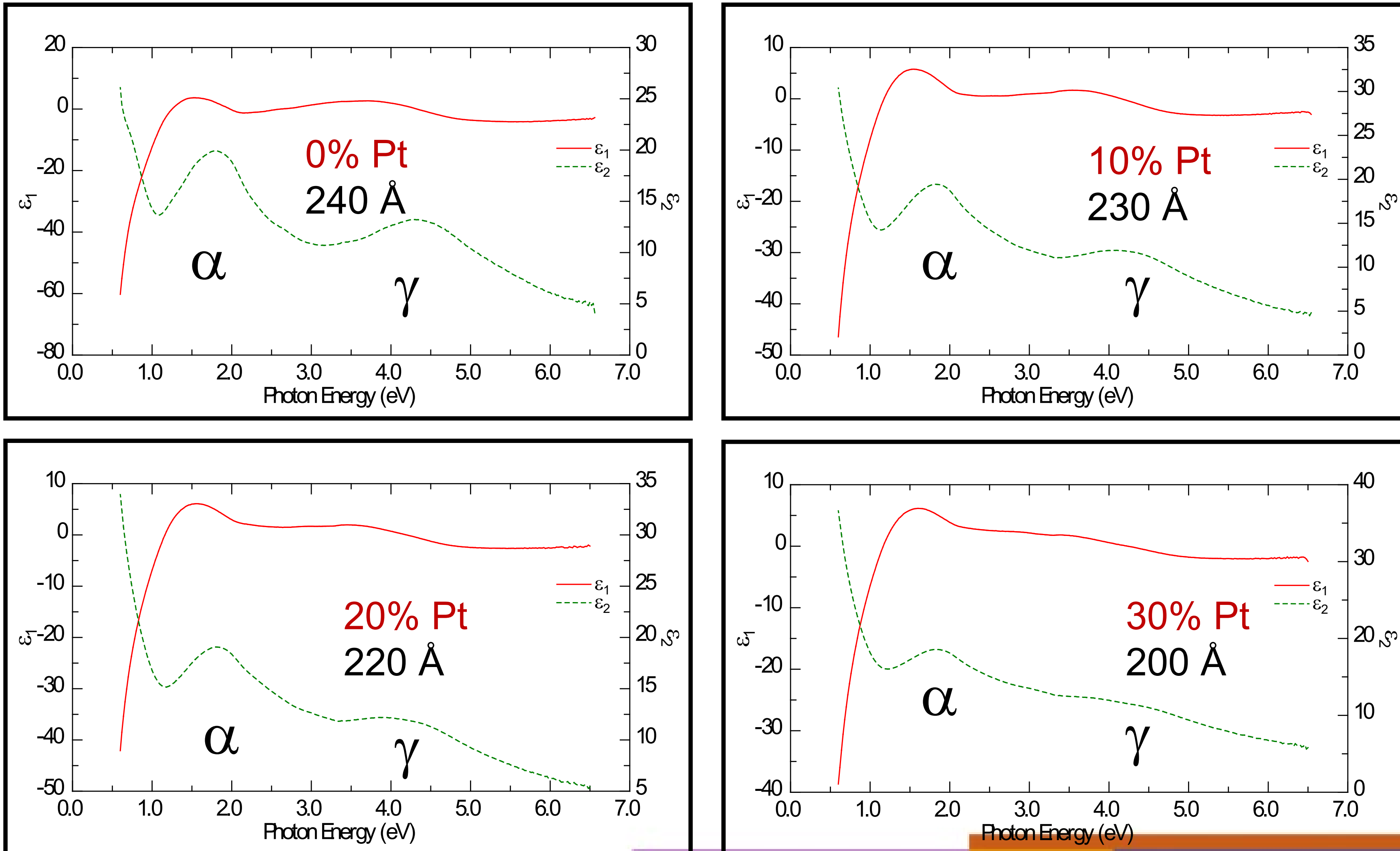
Arwin & Aspnes 1984



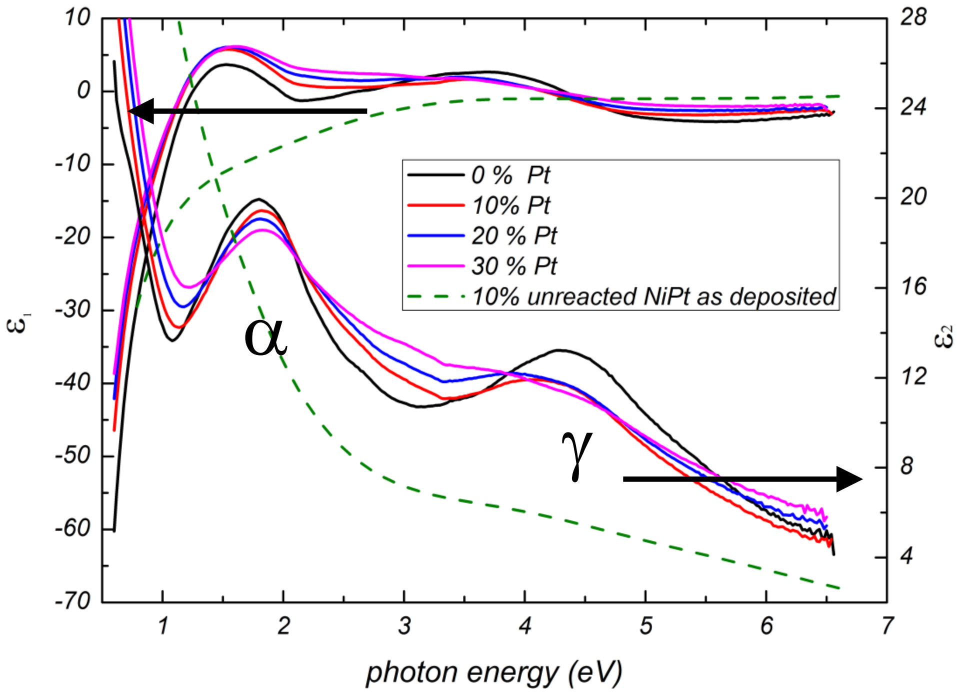


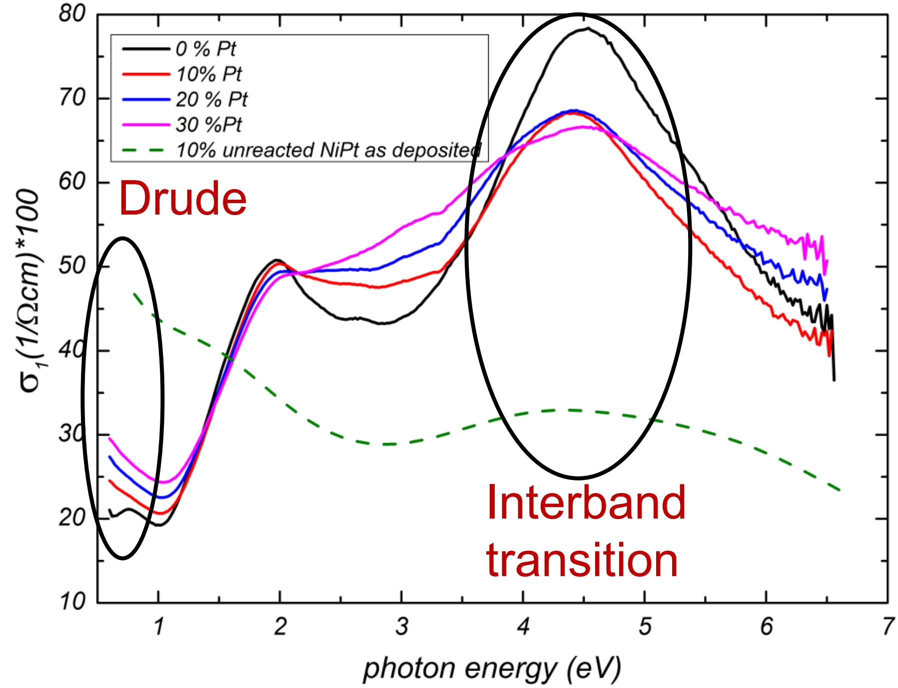


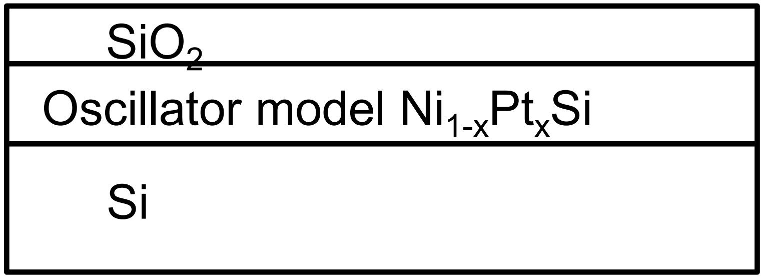
Results: Optical Constants of Monosilicide



Dielectric function and optical conductivity for monosilicide



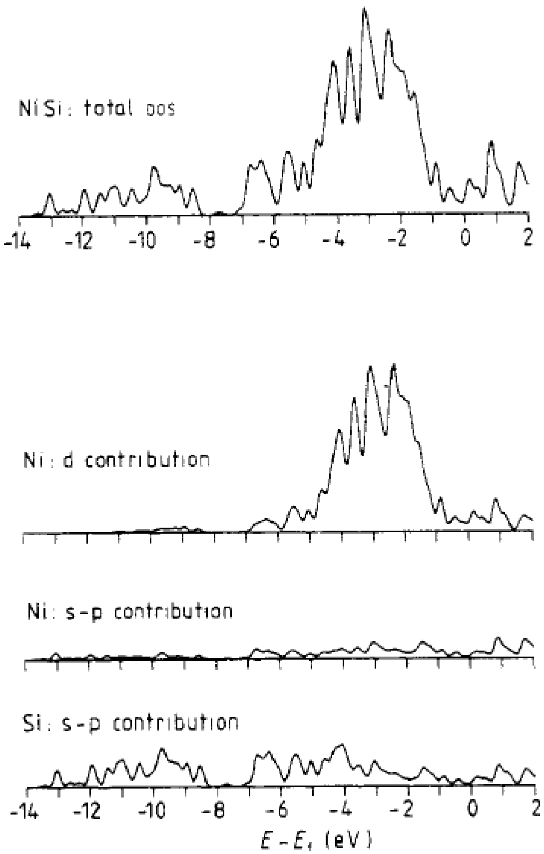




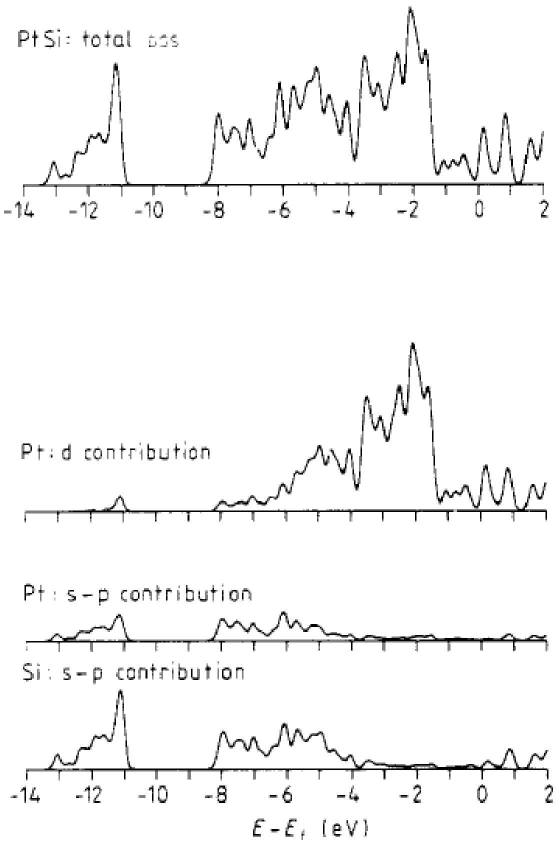
Oscillator Model:
1 Drude (Free electrons + Intraband transitions)
5 Lorentz oscillators (Interband transitions)

Literature results for NiSi and PtSi electronic structure

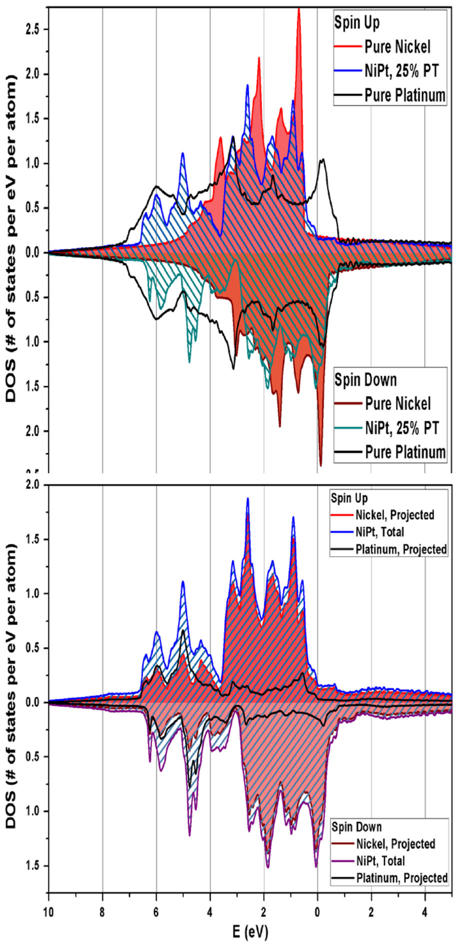
Bonding in NiSi
Ni(3d)-Si(s-p)



Bonding in PtSi
Pt(5d)-Si(s-p)



Bonding in NiPt
Ni(3d)-Pt(5d)



Bisi & Calandra (1981)

Transition metal Silicides: aspects of the chemical bond and trends in the electronic structure

Conclusion

- NiPtSi optical conductivity exhibits a metallic behavior due to the metallic content as well as interband transition due to silicon-related electronic states.
- Free carrier absorption is higher for pure metal than for the silicide. However, interband transition is higher for silicides.
- Interband transition peak gets broader with increasing Pt content in the silicide (can be explained in terms of NiPt DOS).

Third Result

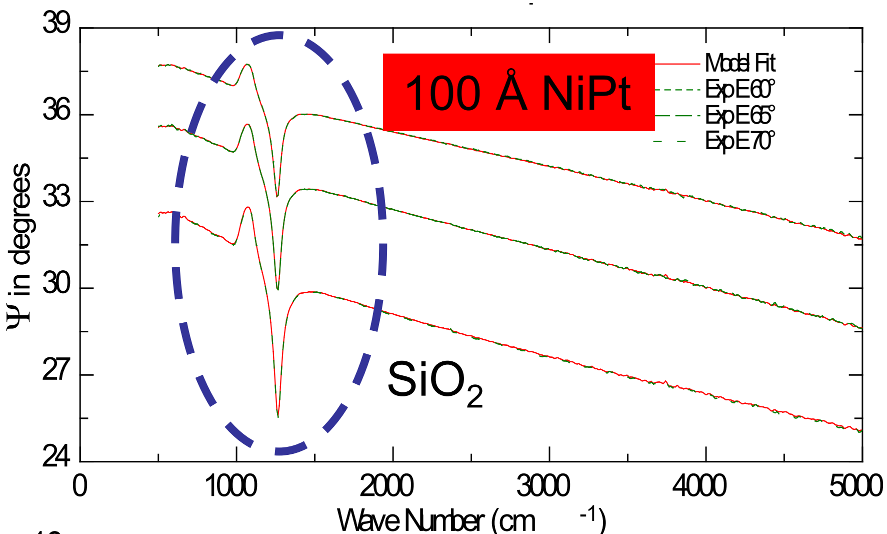
Infrared Ellipsometry

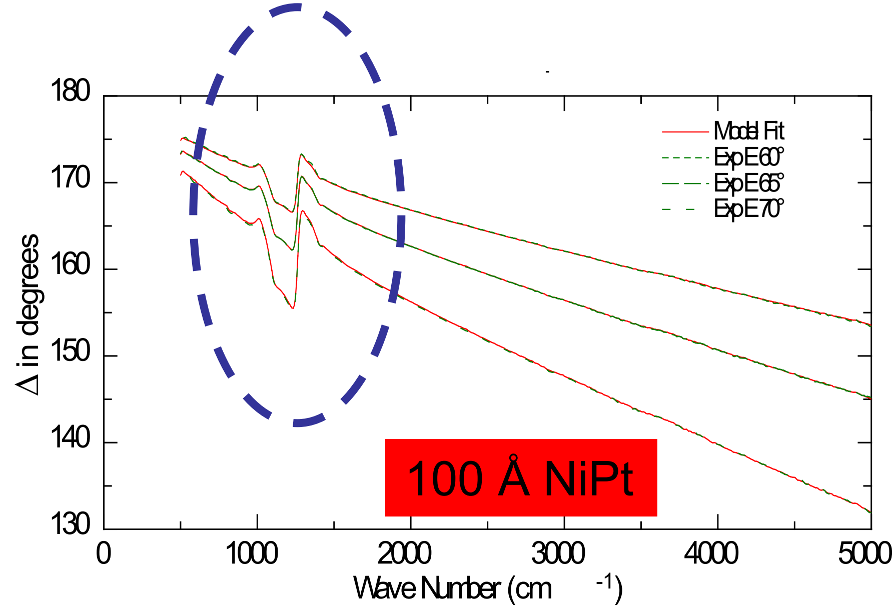
-$Ni_{1-x}Pt_x$ alloys

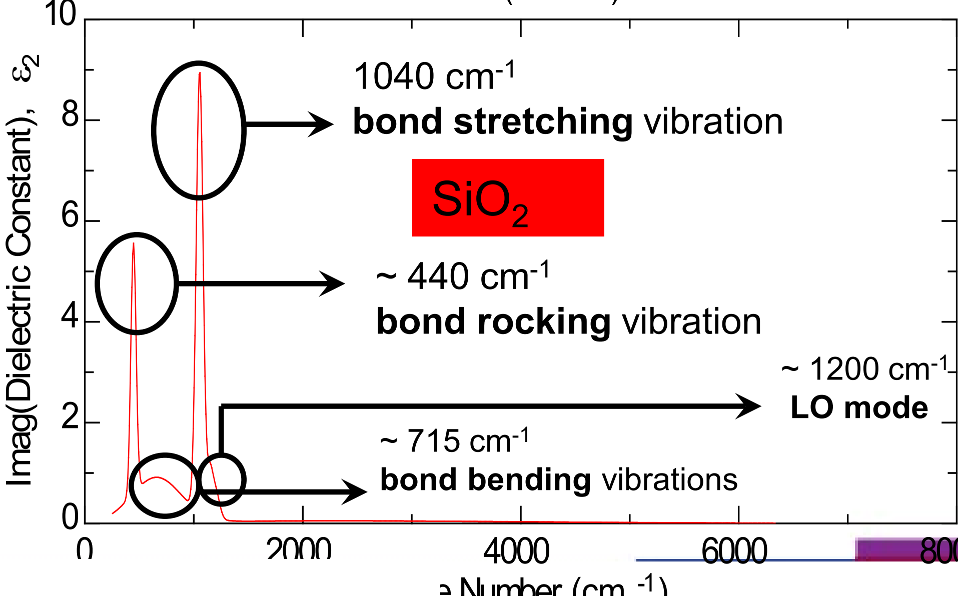
- $Ni_{1-x}Pt_x$ Si monosilicides

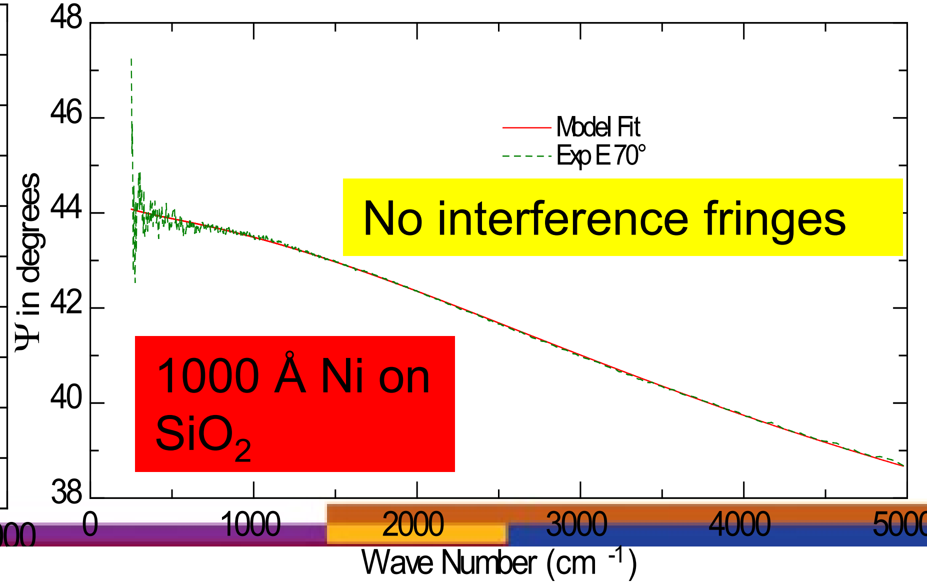
- Pure Ni films (0% Pt , different thicknesses)

$Ni_{0.9}Pt_{0.1}/SiO_2/Si$ (as-deposited)

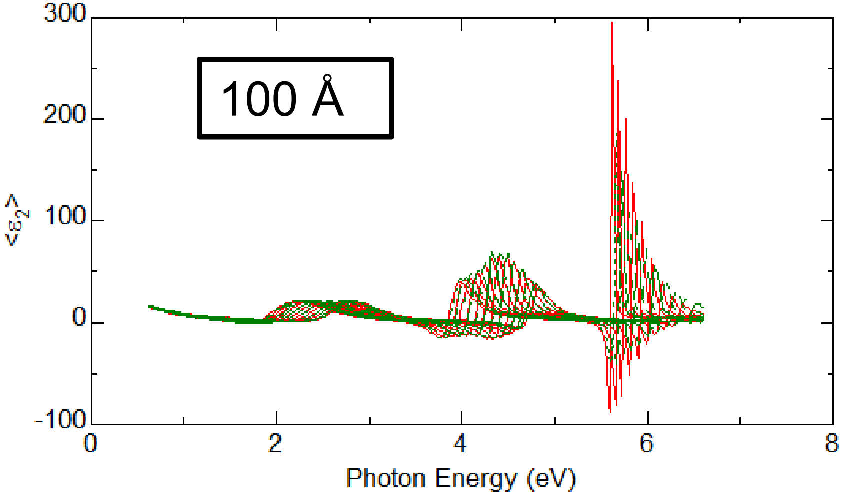


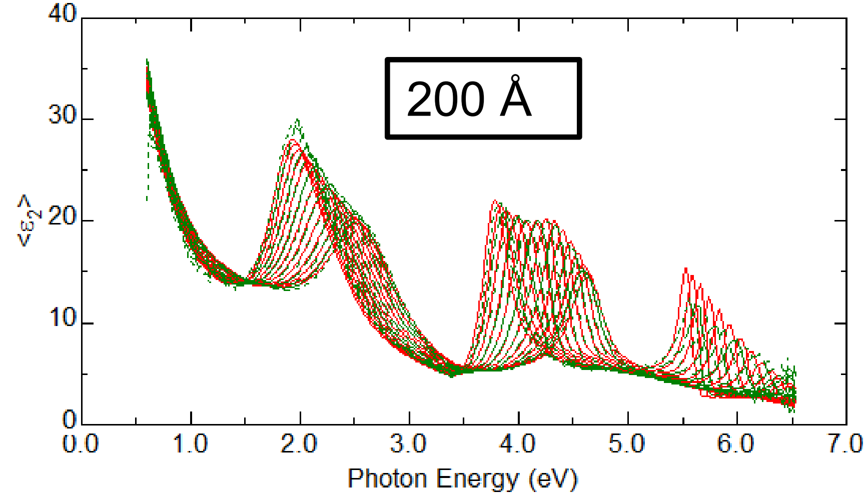


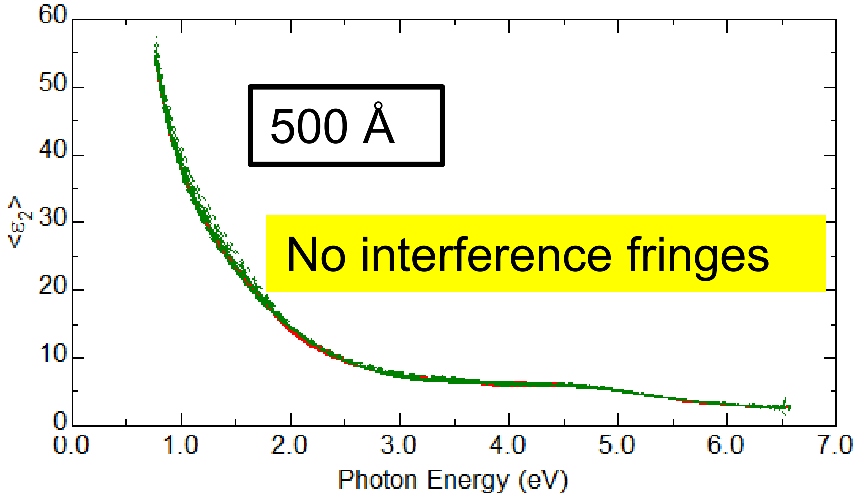


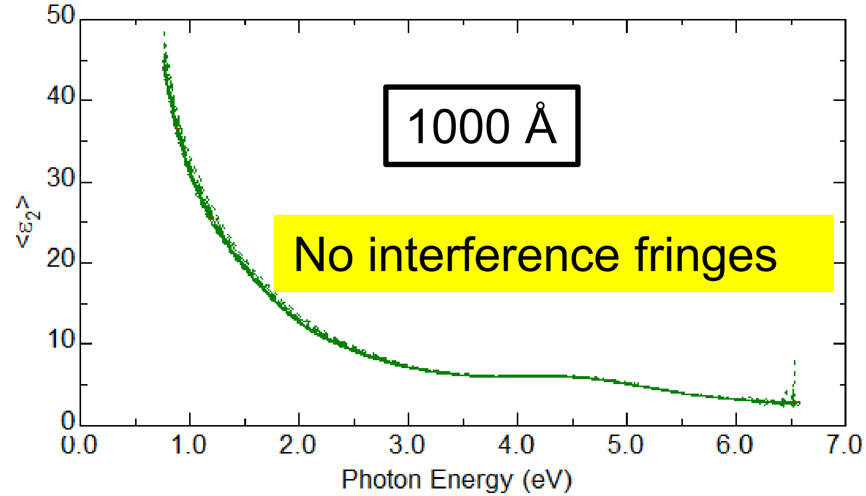


Visible Results: Pure Ni films (0%Pt/SiO_2/Si)



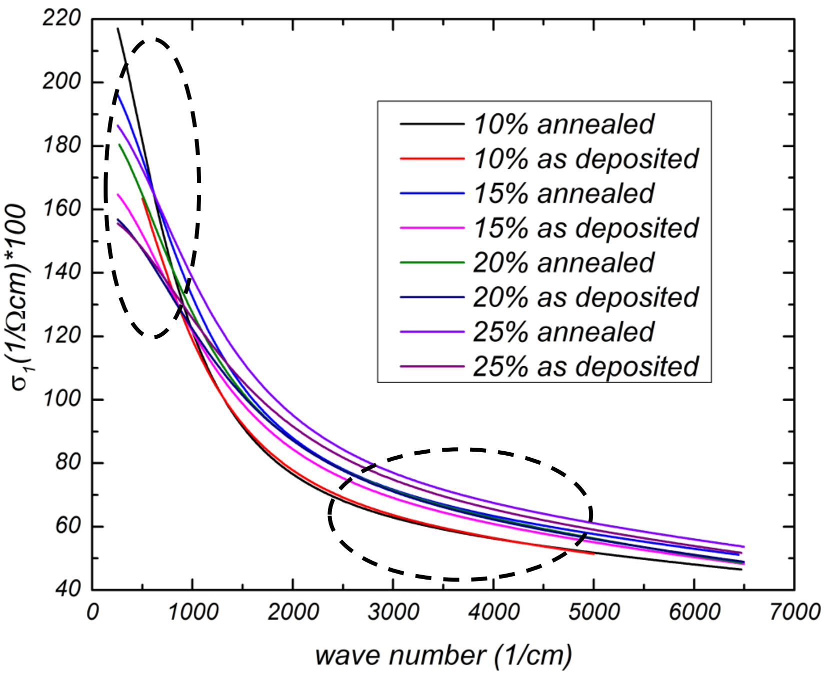


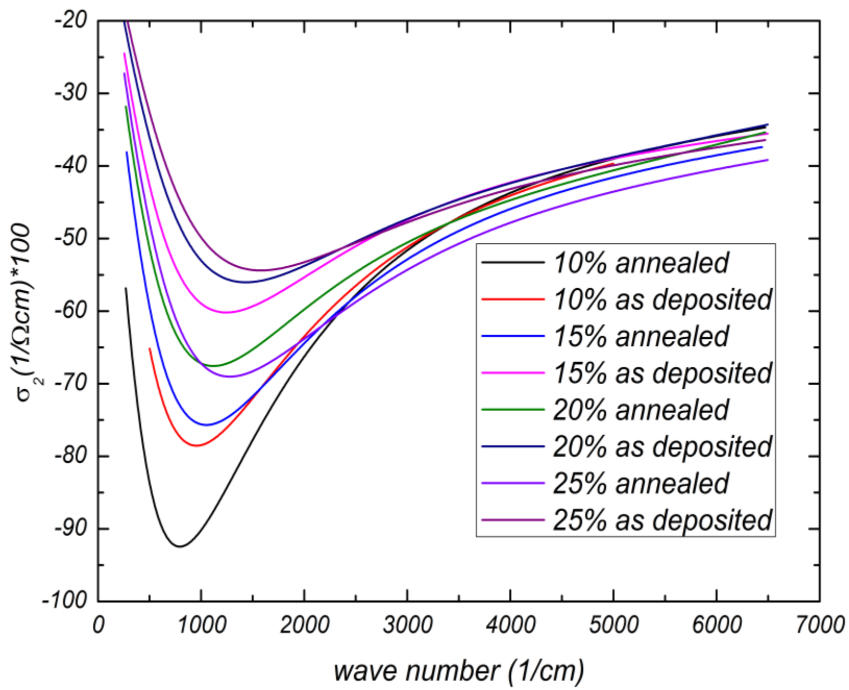




$Ni_{1-x}Pt_x$ alloys: $Ni/SiO_2/Si$

25% Pt: σ=16,000/Ωcm @ 250cm^{-1}
σ_{DC}= 30,000/Ωcm (Litschel & Pop)





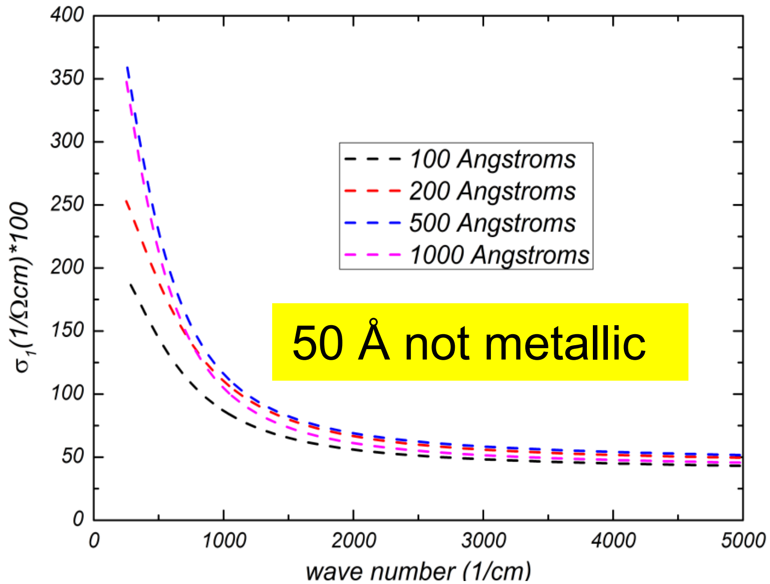
$\hbar\omega$ < 1000 cm^{-1}: σ_1↓ with Pt↑
(DC: Litschel & Pop, 1985)

$\hbar\omega$ > 1000 cm^{-1}: σ_1↑ with Pt ↑
(d-intraband transitions
Pt adds richer d-state band structure)

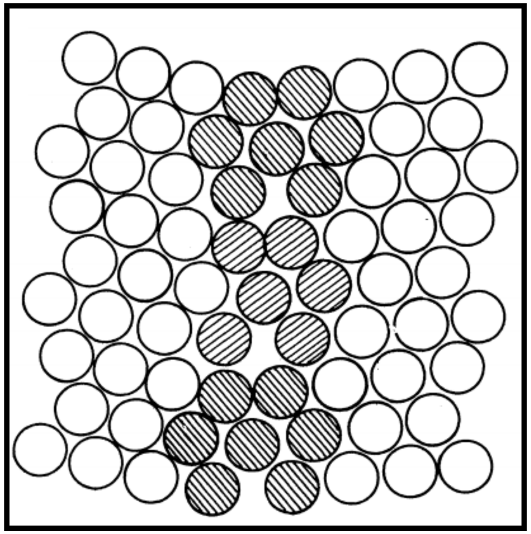
Two Drude oscillators: Two sets of electrons
1) electrons inside crystallites (grains)
2) electrons in the areas between crystallites

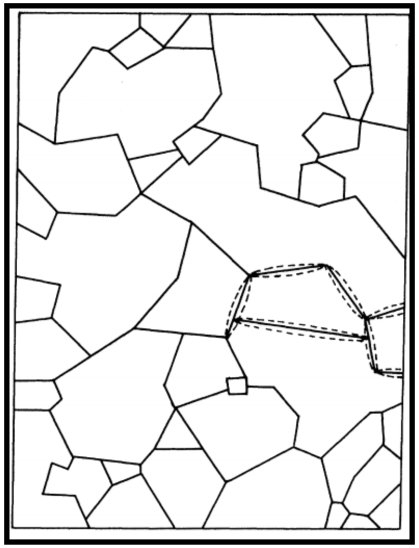
Nagel & Schnatterly, PRB, 1973; Hunderi, PRB 1973

Ni films (0% Pt): Different thicknesses

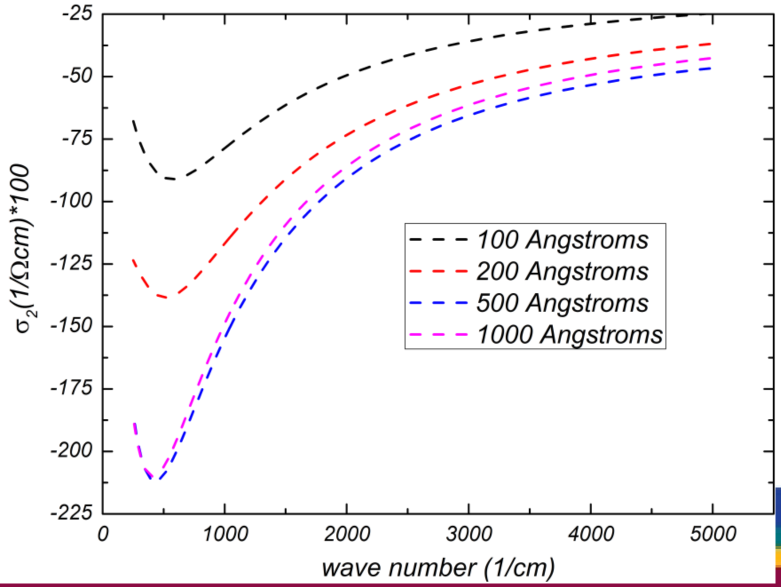


50 Å not metallic



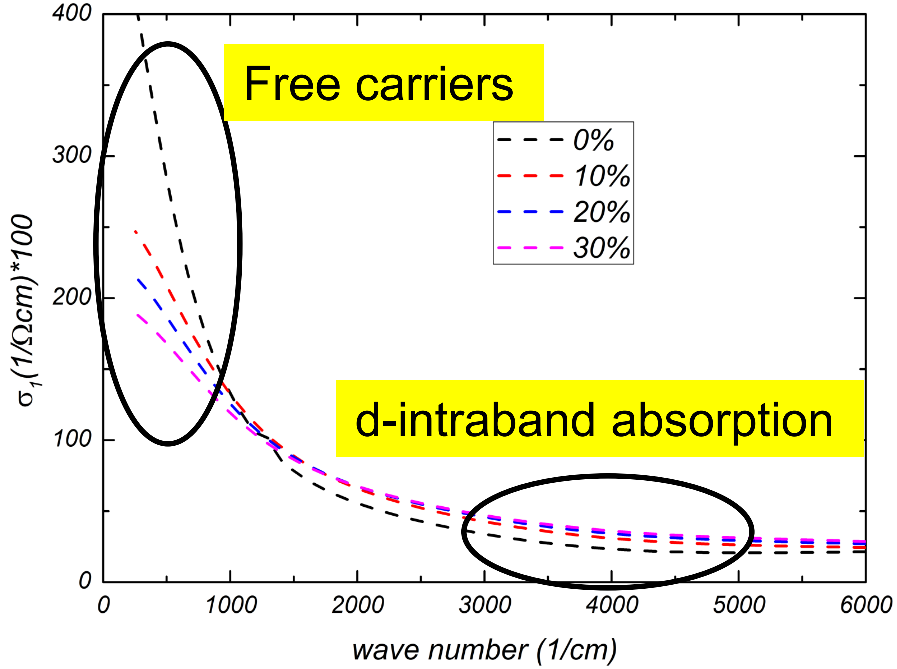


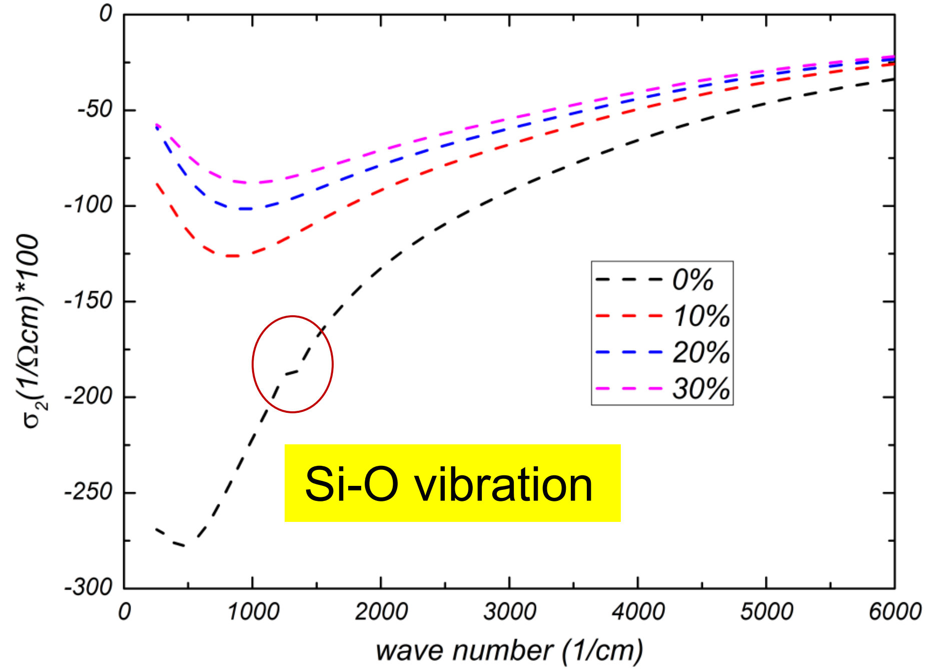
Ola Hunderi, PRB, 1973



σ_1 ↑ with t ↑
reduced grain boundary scattering in thicker films

$Ni_{1-x}Pt_xSi$ monosilicides: $Ni_{1-x}Pt_x/Si$ followed by annealing





Si-O vibration fitted using Gaussian oscillator.

$\hbar\omega < 1000\ cm^{-1}$: $\sigma_1 \downarrow$ with Pt $\uparrow$

Similar to $Ni_{1-x}Pt_x$ alloys: Ni-Pt alloy scattering

$\hbar\omega > 1000\ cm^{-1}$: $\sigma_1 \uparrow$ with Pt $\uparrow$

More d-d interband absorption as Pt content increases

DC conductivity: $\omega \longrightarrow 0$

Pure $Ni/SiO_2/Si$

t (Å)	E_{P1}	Γ_{d1}	E_{P2}	Γ_{d2}	$\sigma_0 \times 10^5$	$\sigma_{exp} \times 10^5$
100	14.5	0.08	6.3	10	3.5	
200	14.9	0.07	5.9	4.5	4.3	
500	17.9	0.05	6.1	2.8	8.6	
1000	17.6	0.05	5.7	3.1	8.3	1.43[a]

[a] Conductivity of bulk Ni from Litschel and Pop [87].

DC conductivity increases with thickness

$Ni_{1-x}Pt_x/SiO_2/Si$

x	annealed	E_{P1}	Γ_{d1}	E_{P2}	Γ_{d2}	$\sigma_0 \times 10^5$	$\sigma_{exp} \times 10^5$
0.10	no	6.8	1.4	10.6	0.11	1.42	0.23
0.10	yes	6.7	1.6	12.2	0.09	2.26	0.29
0.15	no	6.9	1.4	9.4	0.14	0.8	0.2
0.15	yes	7	1.5	10.7	0.12	1.33	0.23
0.20	no	7	1.4	9	0.16	0.7	0.19
0.20	yes	7	1.5	10.1	0.14	1.02	0.21
0.25	no	7	1.6	8.9	0.17	0.6	0.18
0.25	yes	7.1	1.6	10.2	0.15	0.9	0.22

DC conductivity decreases with Pt content

$Ni_{1-x}Pt_xSi$ monosilicides/Si

x	E_{P1}	Γ_{d1}	E_{P2}	Γ_{d2}	A_1	E_1	Γ_1	A_2	E_2	Γ_2	E_3	A_3	$\sigma_0 \times 10^5$
0	20.6	0.55	5.4	0.37	56	0.16	0.006	3.4	0.75	0.28	1.8	57.7	10.5
0.10	13.4	0.09	5.9	0.4	19.4	0.16	0.01	4.2	0.77	0.4	1.8	54.7	2.7
0.20	12	0.1	5.4	0.47	14.5	0.16	0.006	7.5	0.76	0.4	1.8	57	2.04
0.30	11	0.1	6.3	0.44	14.6	0.16	0.006	7.5	0.76	0.4	1.8	57	1.72

σ_{exp}*10^5
0.6
0.3
0.25
0.22

-Optical conductivity decreases with increasing Pt content.

- Electrical conductivity > optical conductivity

Conclusion

- **Two carrier species** in unreacted metal alloys (described by two Drude oscillators):
  - Separation in real space (interior or boundary of grains)
  - Separation in k-space (s- and d-electrons, different Fermi surface pockets)
  - d-intraband transitions with low energies
- Unreacted metals: **Conductivity depends on Pt concentration** in different ways
  - Low frequency: Increased alloy scattering (DC-like)
  - High frequency: Increased d-intraband transitions: Ni(3d) and Pt(5d) mixing
- Same results for $Ni_{1-x}Pt_xSi$ monosilicides.
- **Optical absorption (conductivity) increases with increasing metal thickness** due to the reduced scattering from grain boundaries.
- Low-frequency conductivity is higher for (unreacted) metals than for silicides.

Open Questions

- Build a single model to fit MIR and NIR/VIS/UV data
  (250 cm^{-1} to 6.6 eV)
- **Interpretation of the Drude parameters (plasma frequency and scattering rate) for Ni-Pt alloys or silicides and comparison with DC electrical measurements.**
- Comparison of Ni films with bulk Ni (mid-IR and UV)
- Temperature dependence of optical constants
  (especially near the Curie temperature)
- Optical constants of NiO
  Understand surface of metallic Ni (water layer or NiO native oxide)
- Far-infrared (100 cm^{-1}) and Terahertz measurements of optical constants
  Measurements in a magnetic field
  (University of Nebraska-Lincoln)
- FTIR ellipsometry of NiO as a function of temperature
  (near Neel temperature)

Special Thanks

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