# Time-Resolved Ellipsometry: A Historical Perspective

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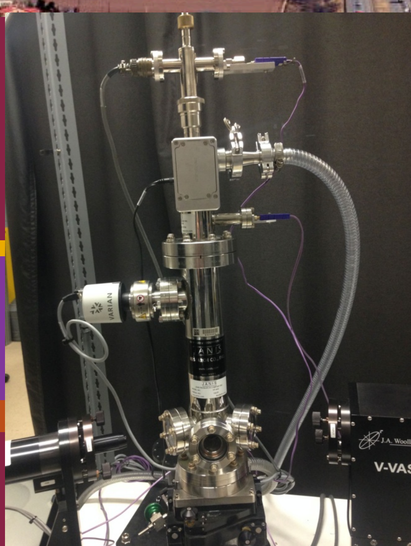
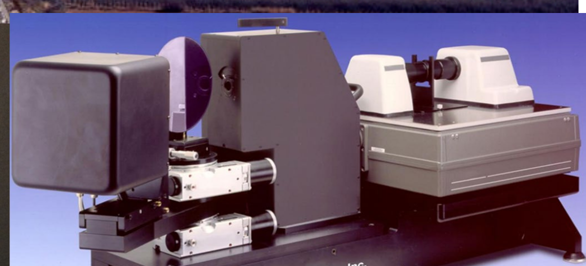
http://ellipsometry.nmsu.edu

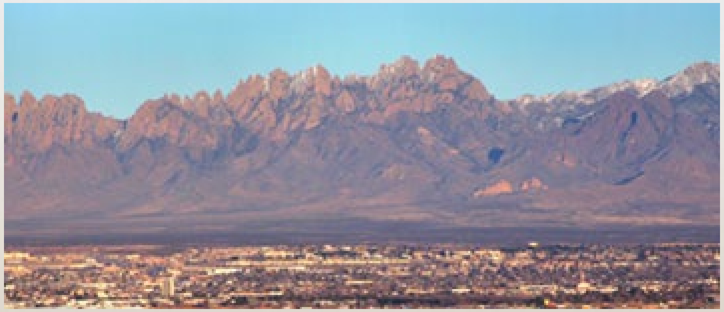





J.A. Woollam IR-VASE


NSF: DMR-
and DMR-1505172

# Dust storm in Las Cruces



**http://ellipsometry.nmsu.edu**

# Dielectric response to a time-varying field

Generalized plane wave E field, ignore spatial dispersion

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon \varepsilon_0 \vec{E}$$

$$\vec{D}(\vec{r},t) = \int \iiint \varepsilon(\vec{r}-\vec{r}', t-t')\varepsilon_0 \vec{E}(\vec{r}',t')dt'\, d^3\vec{r}'$$

Carrier diffusion makes ε nonlocal
Also: P.Y. Yu, SSC 1971

$$\vec{D}(\vec{k},\omega) = \varepsilon(\omega)\varepsilon_0 \vec{E}(\vec{k},\omega)$$

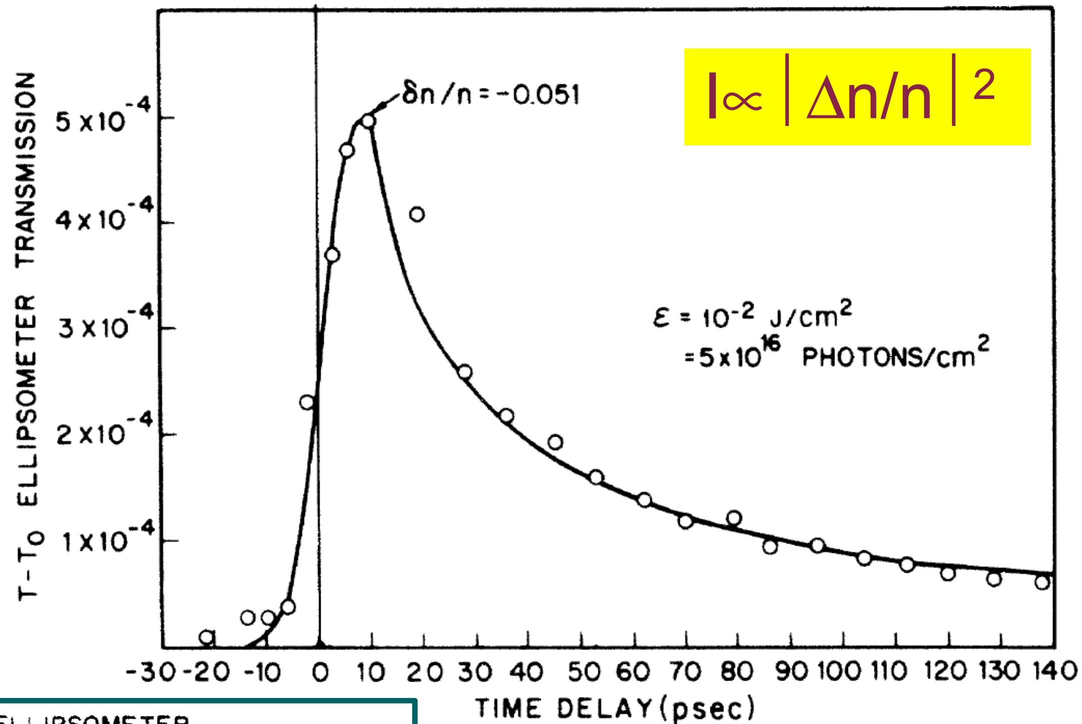
Femtosecond Ellipsometry:

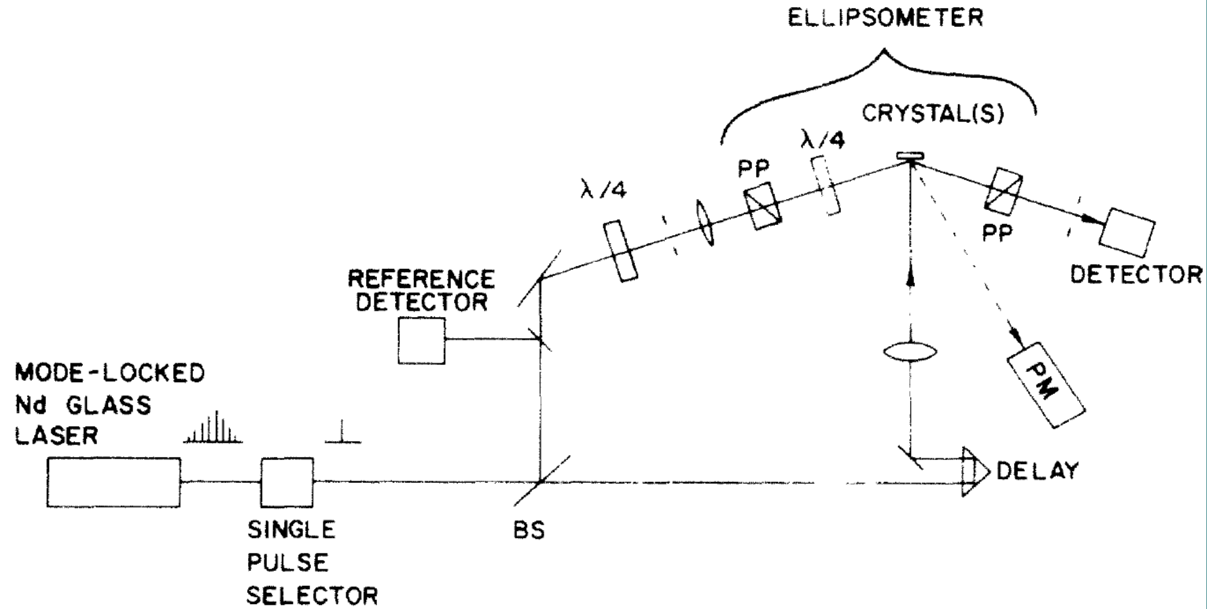
$$\vec{E}(\vec{r},t) = \vec{E}_1(t)e^{i(\vec{k}_1\cdot\vec{r}-\omega_1 t)} + \vec{E}_2(t)e^{i(\vec{k}_2\cdot\vec{r}-\omega_2 t)}$$

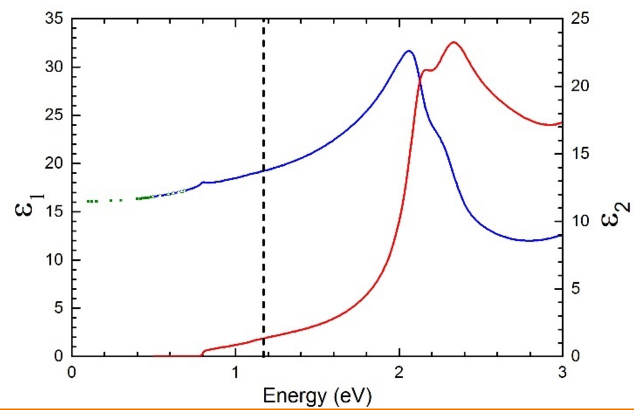
Pump beam changes ε(ω); measurable by the probe beam.
Complication: Δε(z, ω) is a function of z (through $E_1(z)$).
I have never seen a theory for this (perhaps second order).
What if there is no pump beam, but the probe beam is shorter than the lifetime of the excited state (e.g., an exciton)?

# D.H. Auston and C.V. Shank, Phys. Rev. Lett. 32, 1120 (1974)

- **Null ellipsometer**
- 10 mJ/cm², 10 ps, 1.06 μm, 1.17 eV
- $N=1.7\times10^{20}$ cm$^{-3}$, $\Delta n/n=-0.051$
- Drude response of e-h plasma
- **Ambipolar diffusion in Ge**
- Damage above 50 mJ/cm²
- No information about κ

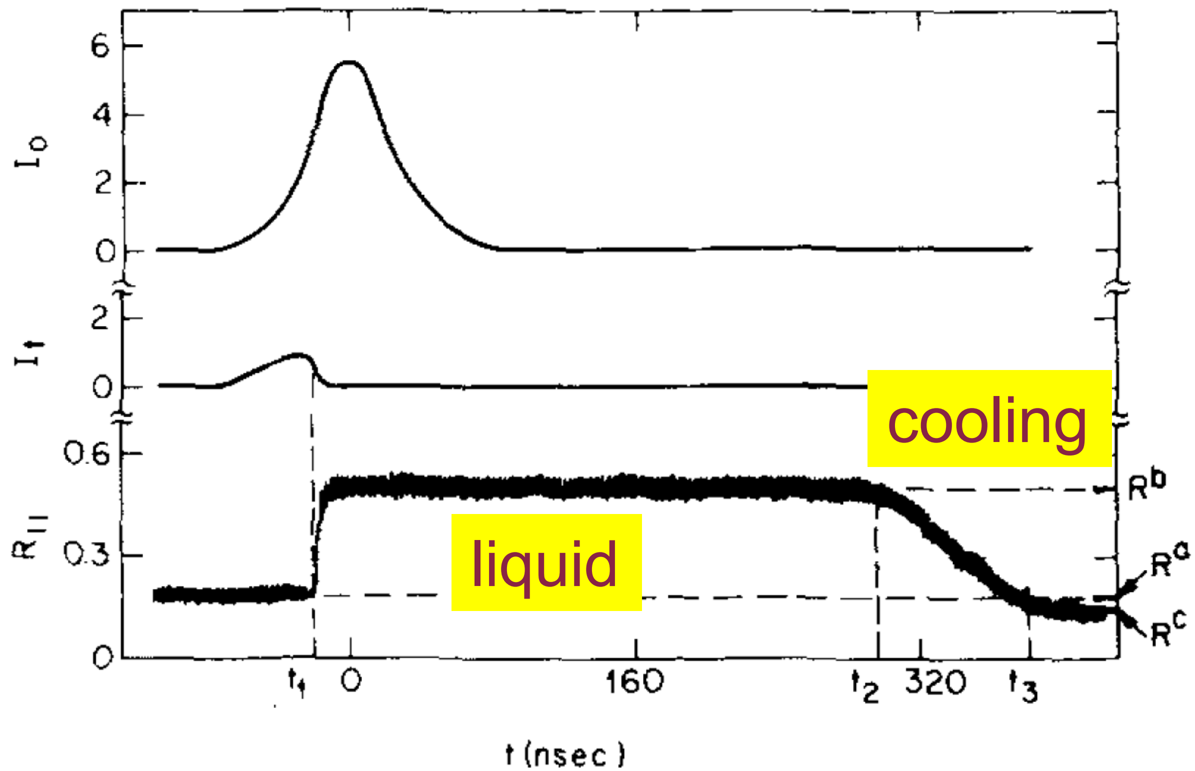


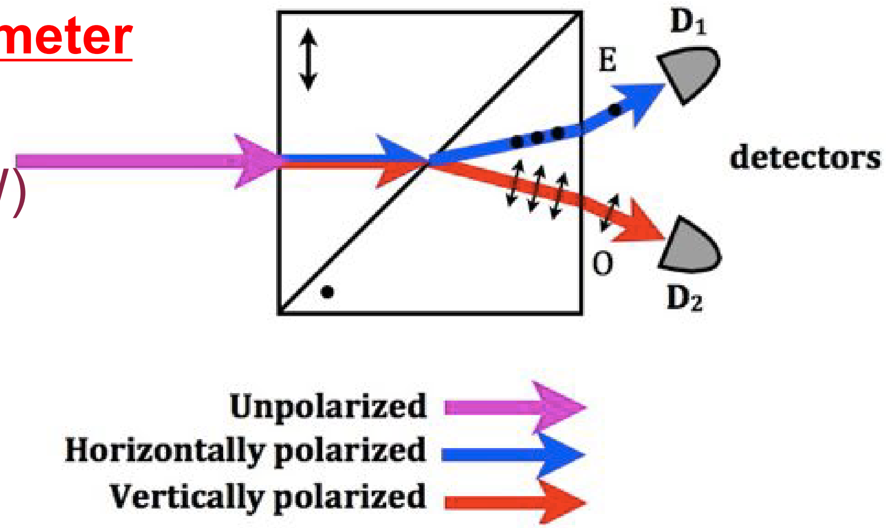
# D.H. Auston et al., Appl. Phys. Lett. 33, 437 (1978)

- Polarized reflectance ($R_p$, $R_s$)
- Measures $\tan^2\psi$
- Pump: 1.06 μm, 50 ns, single shot, 3 mm spot, 0.65 to 16 mJ/cm²
- Probe: 633 nm HeNe CW
- Fast photodiodes for detection
- Sample: As-implanted Si (111)
- Si melts above 2 J/cm² (metallic response), freezes within ns time scale

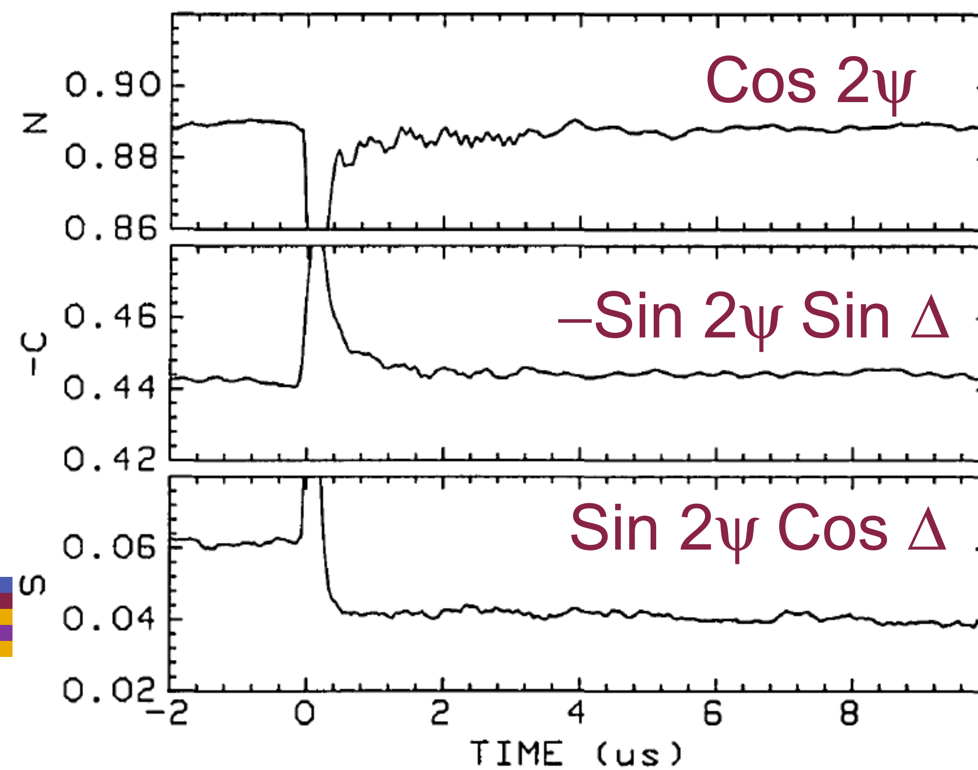


# G.E. Jellison, Jr., and D.H. Lowndes, Appl. Opt. **24**, 2948 (1985)

- Wollaston prism analyzer **PCSA ellipsometer**
- Pump: KrF, 248 nm, 35 ns, 1 J/cm$^2$
- Probe: CW HeNe laser (633 nm, 0.5 mW)
- Spot size: 20 by 50 μm
- Two fast photodiodes (2 ns) or streak camera (1 ps)
- Single shot experiment
- Zone averaging reduces errors

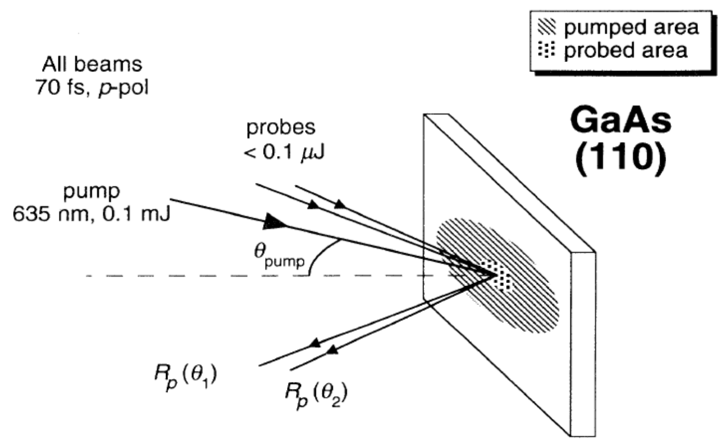



- Pump melts Si surface (50 ns)
- Pump burns off organic contamination on the surface.
- Rapid cooling after melting.
- Native oxide not affected (or regrows rapidly).



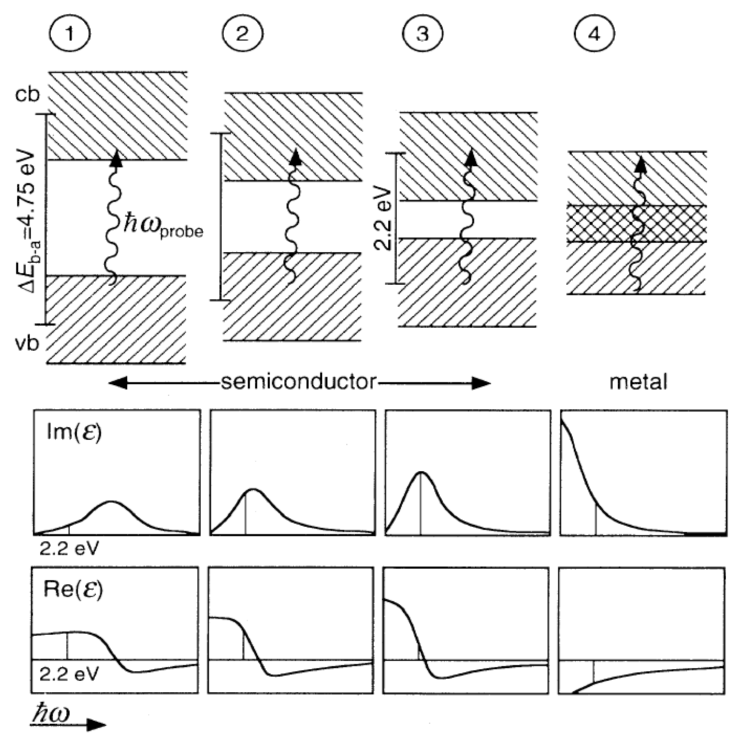
Glezer, Siegal, Huang, **E. Mazur**, Phys. Rev. B **51**, 6959 (1995)
Huang, Callan, Glezer, **E. Mazur**, Phys. Rev. Lett. **80**, 185 (1998)
Roeser, Kim, Callan, Huang, Siegal, **Mazur**, Rev. Sci. Instrum. **74**, 3413 (2003)

- Double-angle $R_p$ yields $\varepsilon$ ($\phi$=71°, 76° near $\phi_{Brewster}$)
- Pump: 1.9 eV, 70 fs, <250 mJ/cm$^2$, 10 Hz
- Two-color probe: 2.2+4.4 eV, 70 fs, 25 μm
- GaAs (110): Damage threshold 100 mJ/cm$^2$
- Oxide correction (4 nm).
- **Drude response and band gap renormalization (band gap collapses).**




| probe wavelength | $\theta_1$ | $\theta_2$ | $\theta_{pump}$ |
|---|---|---|---|
| 570 nm (2.2 eV) | 70.9° | 75.8° | 63° |
| 285nm (4.4 eV) | 58.5° | 76.0° | 68° |

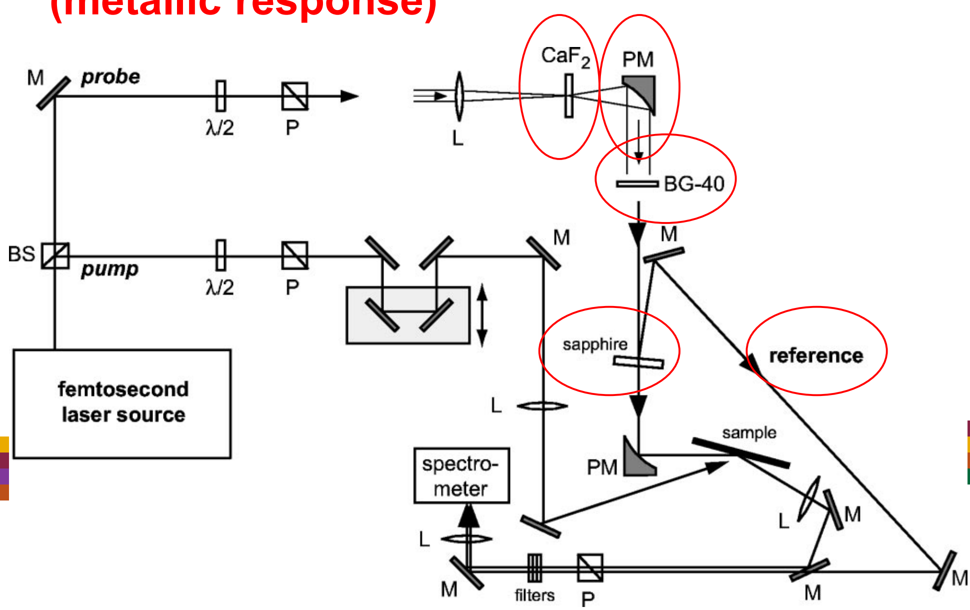
FIG. 3. Probing geometry and incident angles for the 2.2- and 4.4-eV measurements. All beams are *p* polarized.

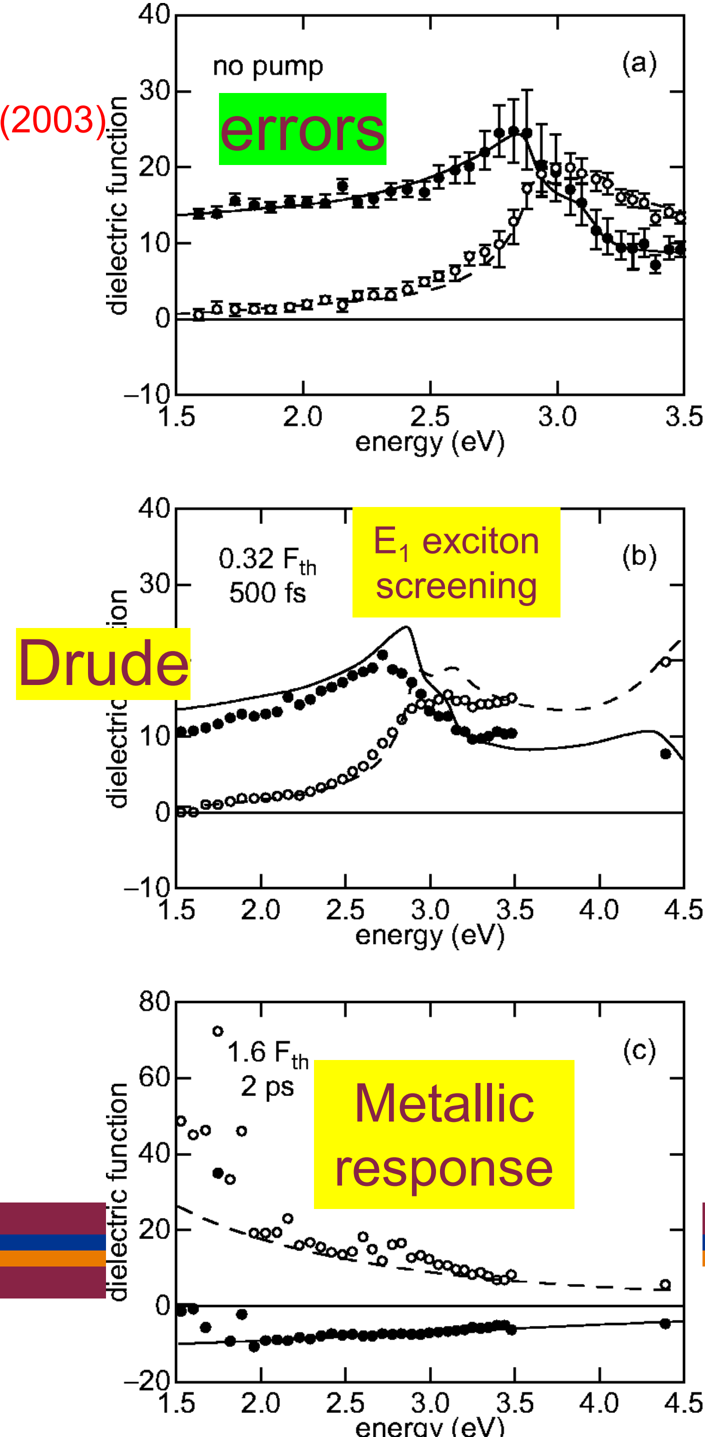



Lorentz model

Glezer, Siegal, Huang, **E. Mazur**, Phys. Rev. B **51**, 6959 (1995)
Huang, Callan, Glezer, **E. Mazur**, Phys. Rev. Lett. **80**, 185 (1998)
Roeser, Kim, Callan, Huang, Siegal, **Mazur**, Rev. Sci. Instrum. **74**, 3413 (2003)


- Double-angle $R_p$ yields ε (ϕ=58º, 75º)
- Pump: 1.9 eV, 70 fs, <250 mJ/cm², 10 Hz
- **White-light probe**: 1.5-3.5 eV, 70 fs
- GaAs (100): Damage threshold 100 mJ/cm²
- Oxide + **chirp correction**
- **Drude response (free carriers)**
- **Exciton screening (excitons lose amplitude)**
- **Lattice heating – 140 fs, 7 ps** (Lautenschlager)
- **Lattice disorder after 4 ps (high flux)**
- **Band gap renormalization (metallic response)**



Glezer, Siegal, Huang, **E. Mazur**, Phys. Rev. B **51**, 6959 (1995)
Huang, Callan, Glezer, **E. Mazur**, Phys. Rev. Lett. **80**, 185 (1998)
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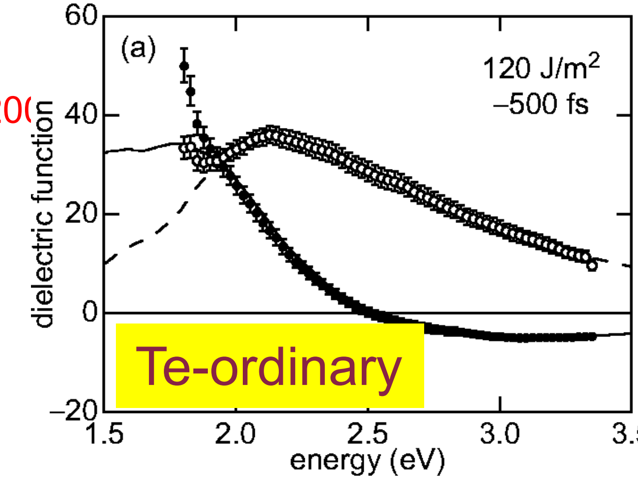
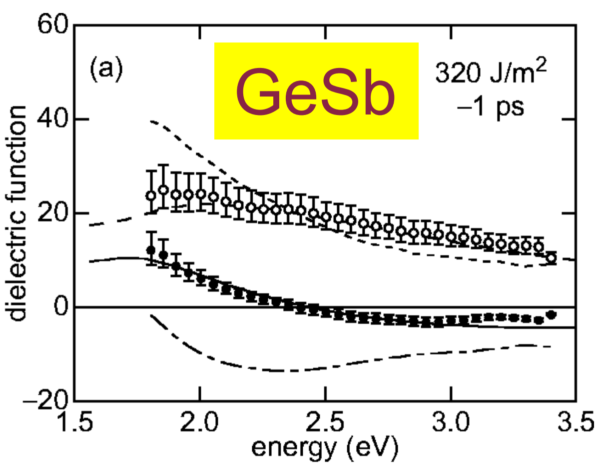
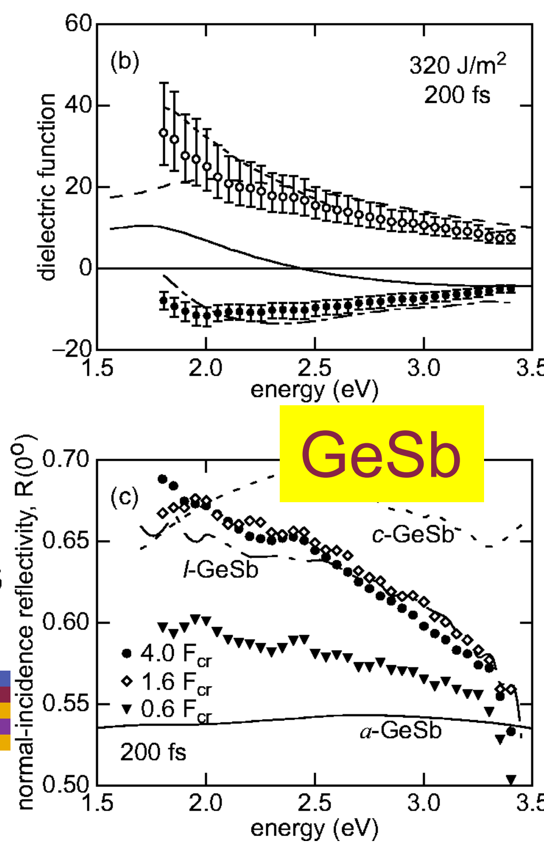
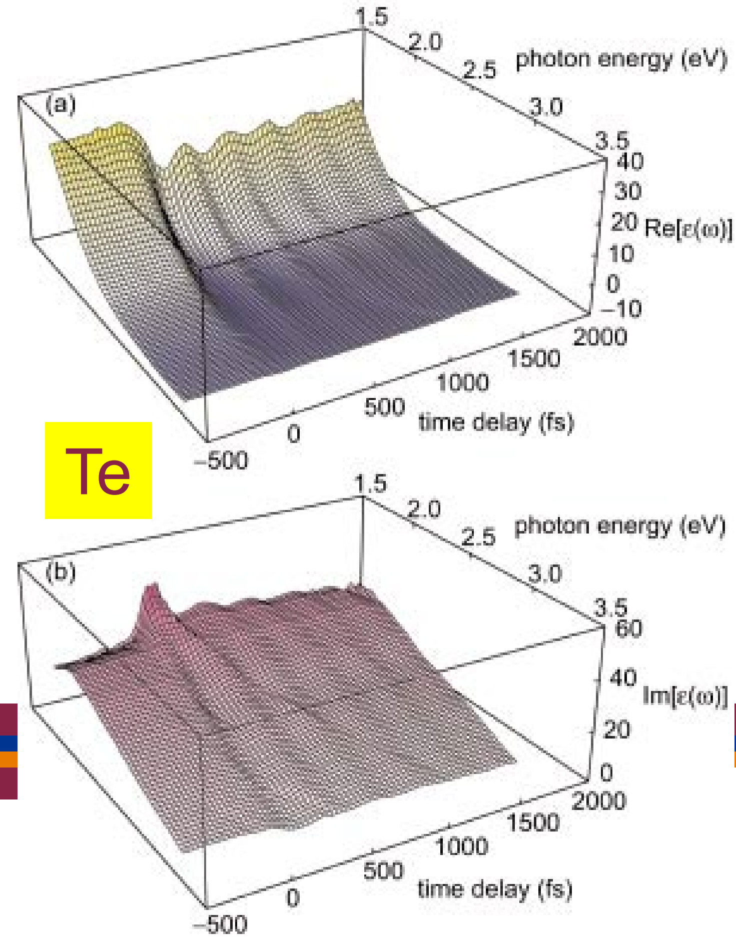
- Double-angle $R_p$ yields ε (ϕ=58º, 75º)
- White-light probe: 1.5-3.5 eV, 70 fs
- Pump: 1.9 eV, 70 fs, <250 mJ/cm$^2$, 10 Hz
- **Te: coherent phonon oscillations (3 THz)**
- **a-GeSb (phase change memories): amorphous to crystalline transition is very fast (200 fs)**



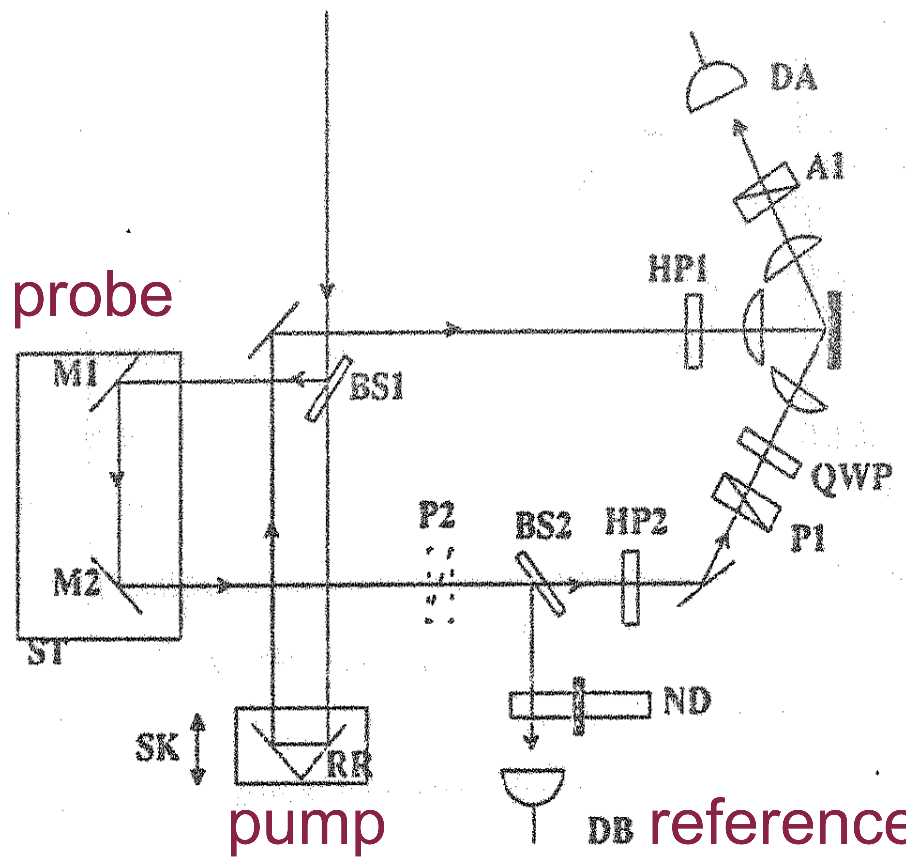



H. Choo, X. Hu, **M.C. Downer**, V. Kesan, Appl. Phys. Lett **63**, 1507 (1993)
H.R. Choo, Ph.D. thesis, Univ. of Texas at Austin (1993)

- Pump-probe: 2 eV CPM, 100 fs, 10 μm, 1-5 nJ, 1 MHz
- PCSA ellipsometer (P=0,sC,A=45º), φ=69º
- **True zero-order mica quarter-wave plate compensator with AR coating (T>90%);** rotation of P wobbles probe spot.
- A fixed (rejects scattered pump beam)
- Calcite P and A (extinction <$10^{-5}$)
- Glan-laser P (less chirp)
- Glan-Thompson A (large acceptance)
- Rapid-scan (47 Hz) time delay for pump beam avoids 1/f noise of laser.
- Amplify difference of DA and DB.
- SHG defines zero time delay.



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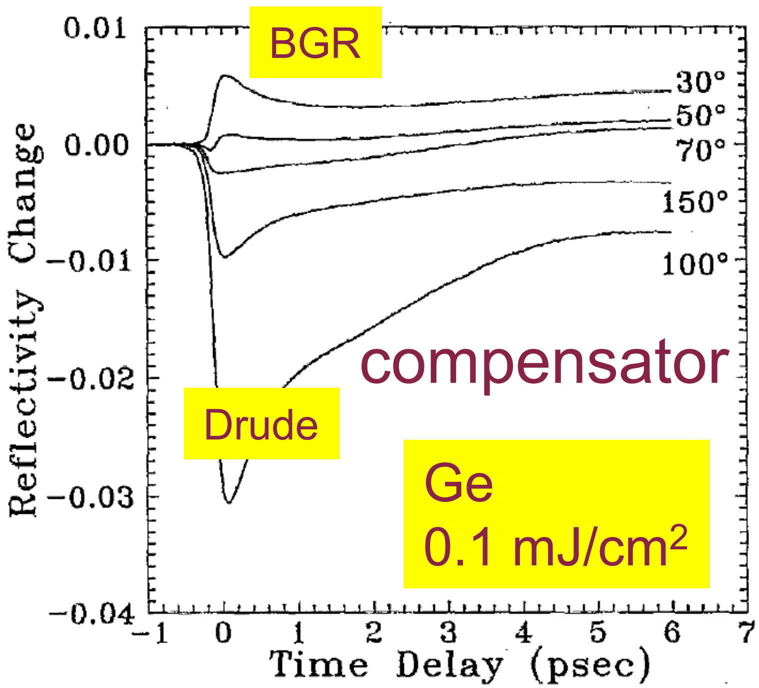
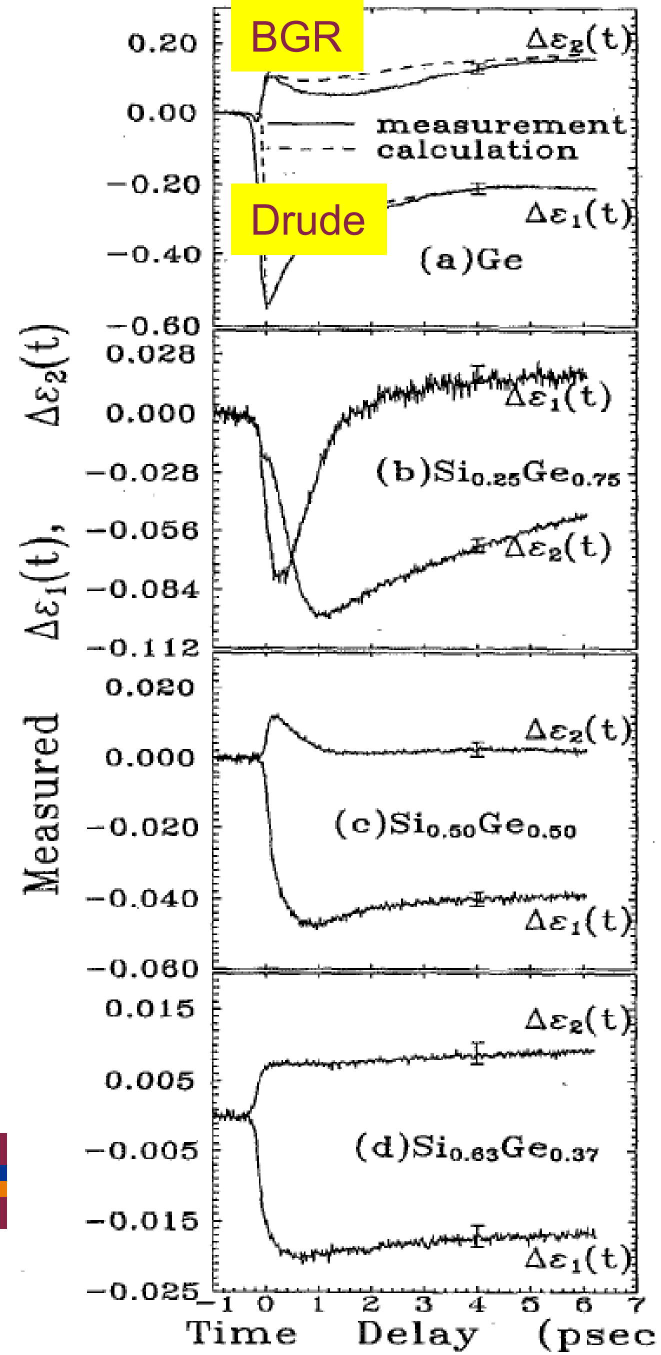
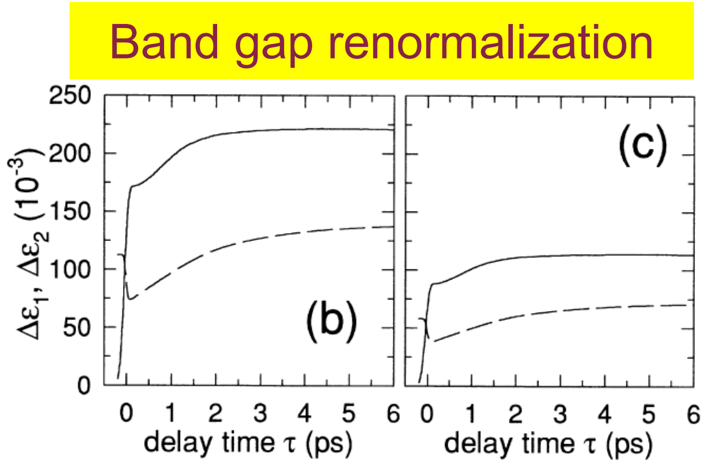
- Pump-probe: 2 eV, 100 fs, 10 μm, 1-5 nJ, 1 MHz
- PCSA ellipsometer (P=0,sC,A=45º), ϕ=69º
- **True zero-order mica quarter-wave plate compensator;** rotation of P wobbles probe spot.
- A fixed (rejects scattered pump beam)
- Rapid-scan time delay.
- Ambipolar diffusion in Ge, band gap renormalization
- Thermal band gap shrinkage (lattice heating), BGR, interband scattering (lh-hh, IVS), bleaching

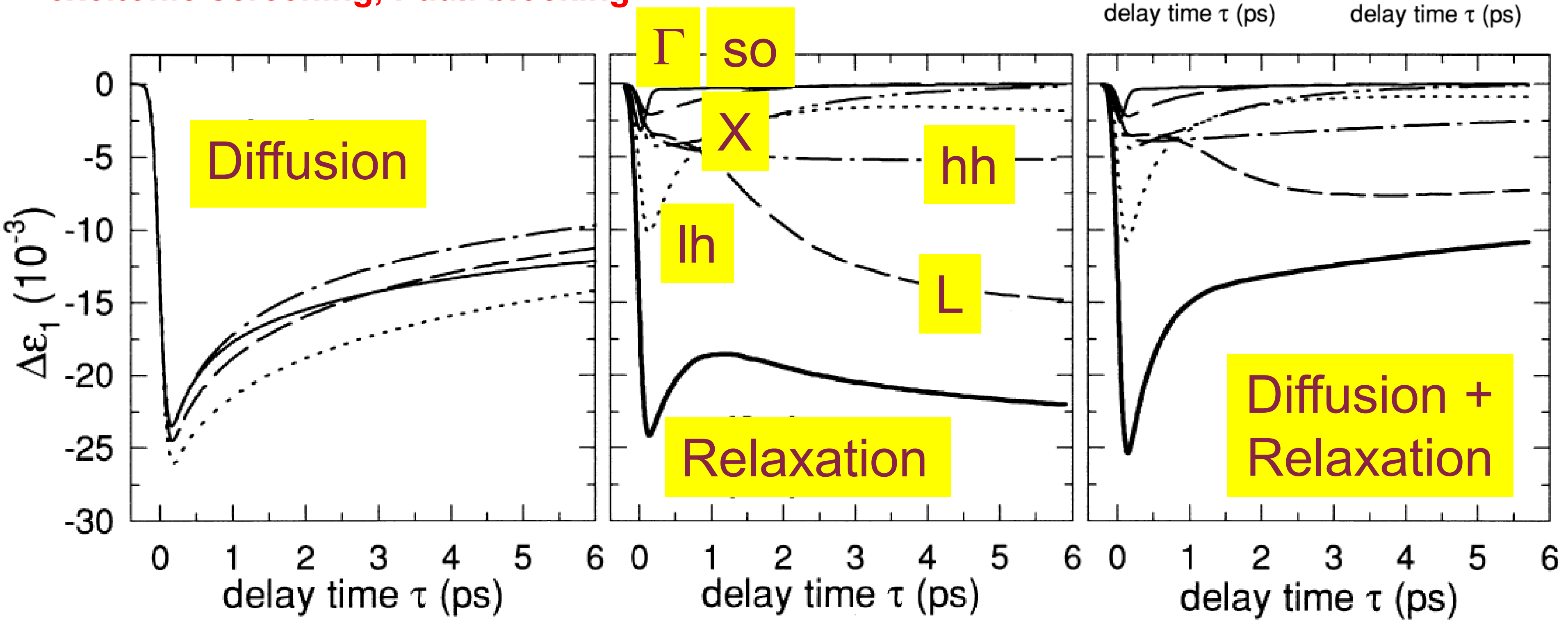


S. Zollner, K.D. Myers, J.M. Dolan, D.W. Bailey, C.J. Stanton,
**Thin Solid Films 313-314, 568 (1998);** Solid-State Commun. **104**, 55 (1997).

- Chris Stanton (U of FL, Gainesville): Monte Carlo simulation of carrier scattering in Ge.
- Ti-sapphire excitation at 1.5 eV, 100 fs, 85 MHz
- **Photon energy determines penetration depth (diffusion).**
- Pump-probe reflectance, 180 mW, 2 nJ, 40 μm, 3.6 kW/cm$^2$, $4 \times 10^{18}$ cm$^{-3}$
- **Time-dependent diffusivity, carrier relaxation (hh to lh and Γ to X to L), band gap renormalization, excitonic screening, Pauli blocking**



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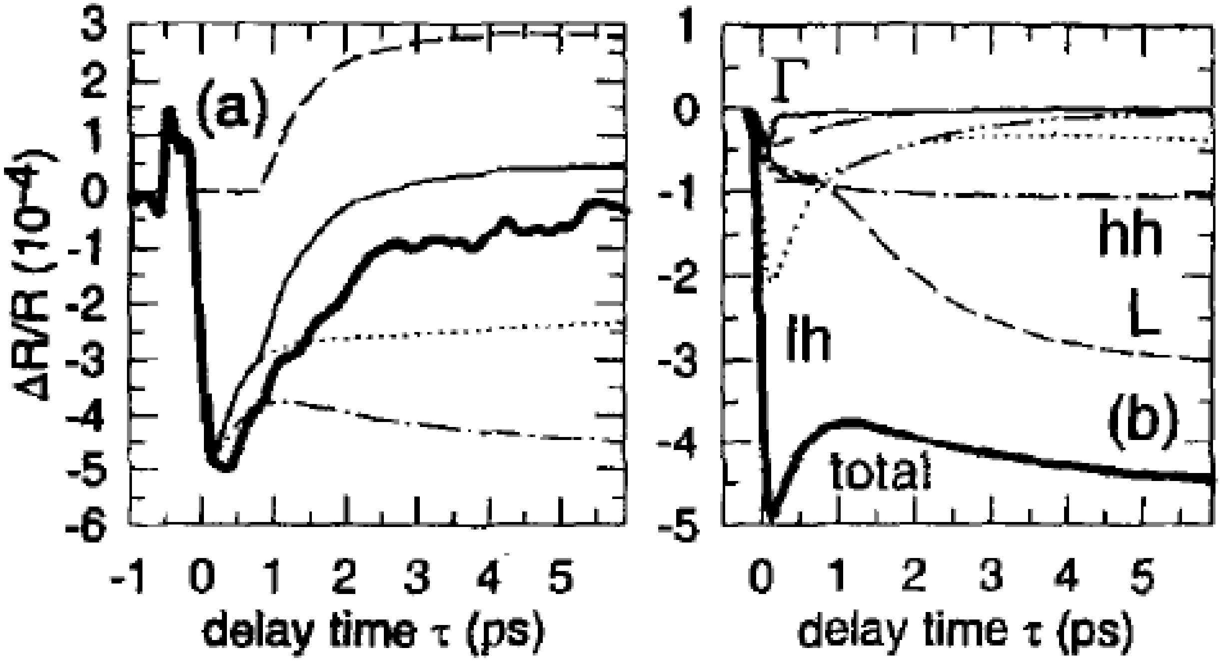
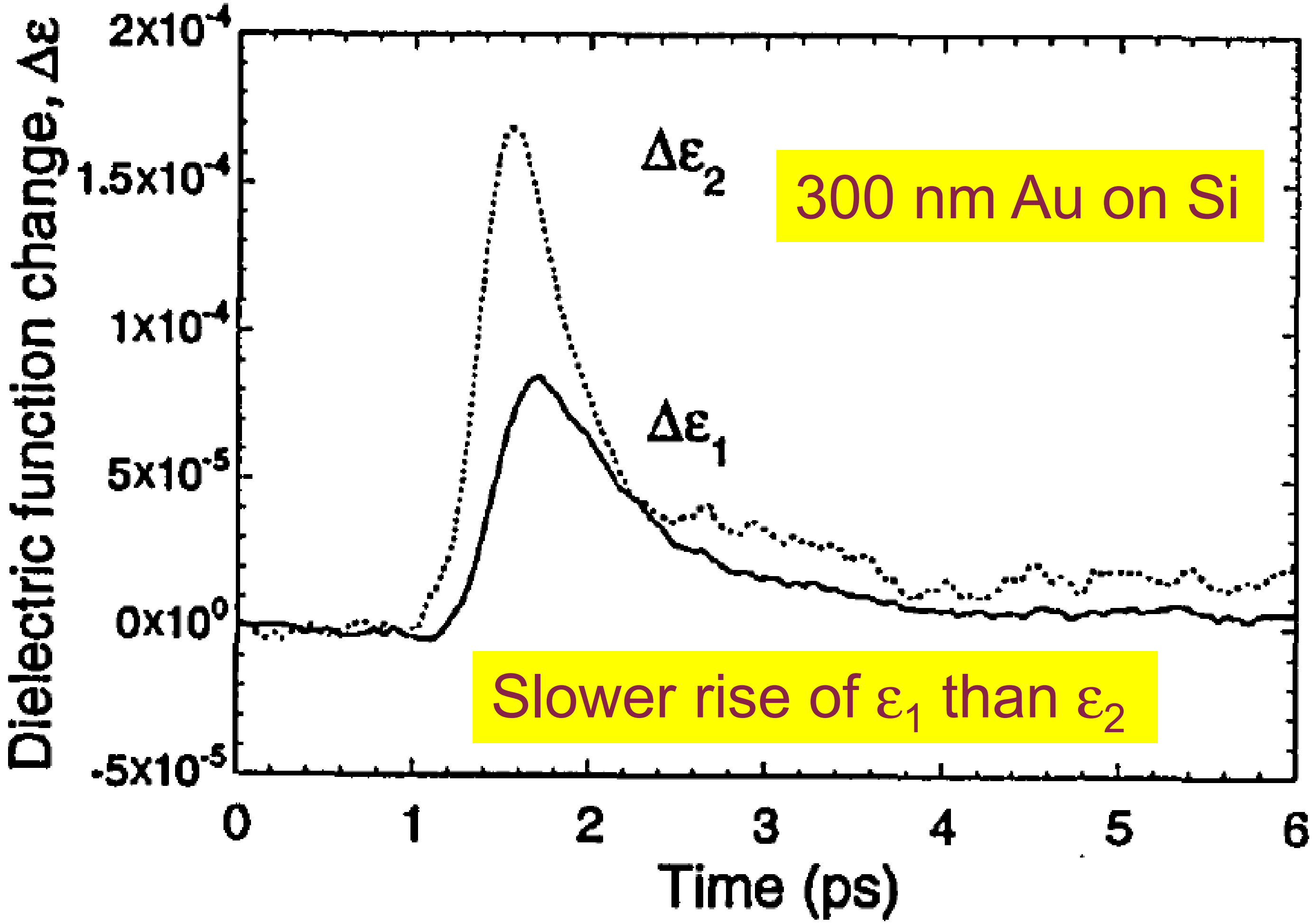
- Photon energy determines penetration depth (diffusion).
- **Pump-probe reflectance, 180 mW, 2 nJ, 40 μm, 3.6 kW/cm$^2$, $4\times10^{18}$ cm$^{-3}$**
- Time-dependent diffusivity, carrier relaxation (hh to lh and Γ to X to L), band gap renormalization, excitonic screening, Pauli blocking, coherent artifact
- Do we see phonon oscillations?



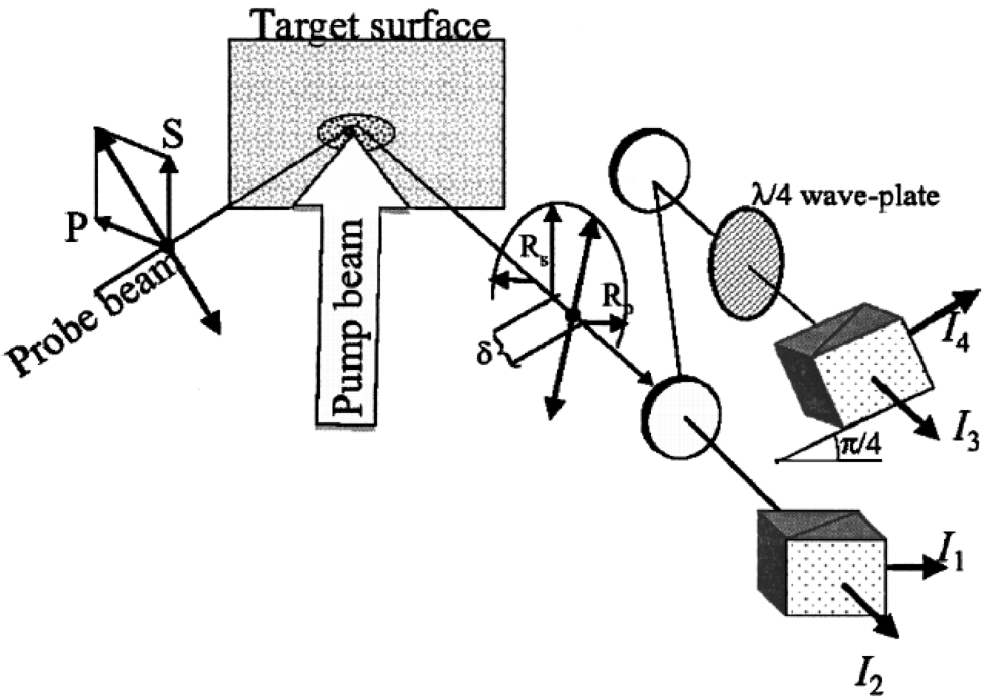
M.Y. Frankel, Optics Letters **19**, 1252 (1994)

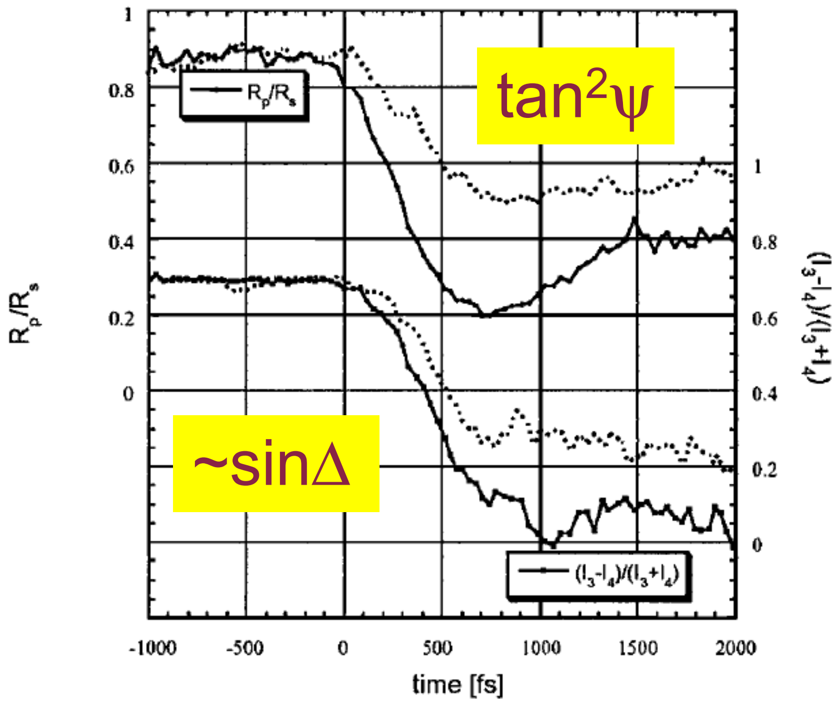
- Pump: 2 eV CPM, 150 fs, 20 μm, 7.4 mW, 100 MHz
- PCSA ellipsometer (P=90º;2C=40º,145º;A=–45º), $\phi$=70º
- **Differential lock-in detection, 3.8 MHz modulation**
- Electron heating: redistribution of electrons around Fermi edge modulates d-d interband absorption (Elsayed-Ali, PRB **47**, 13599, 1993).



H. Yoneda, H. Morikami, K. Ueda, R.M. More, Phys. Rev. Lett. **91**, 075004 (2003)

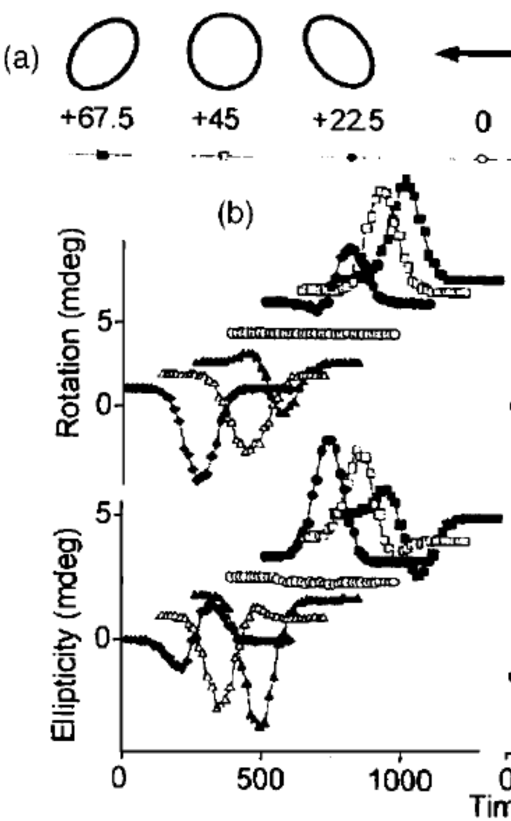
- Pump: 248 nm, 300 fs, amplified by $Kr^*F$ excimer laser, **2–50 TW/cm²**.
- Probe: 745 nm, 120 fs Ti:sapphire, 64º AOI, P=45º.
- Four-detector polarimeter. Rotating sample (single-shot).
- Laser heating of a Au target (40 eV/atom) produces liquid and **vapor/plasma**.

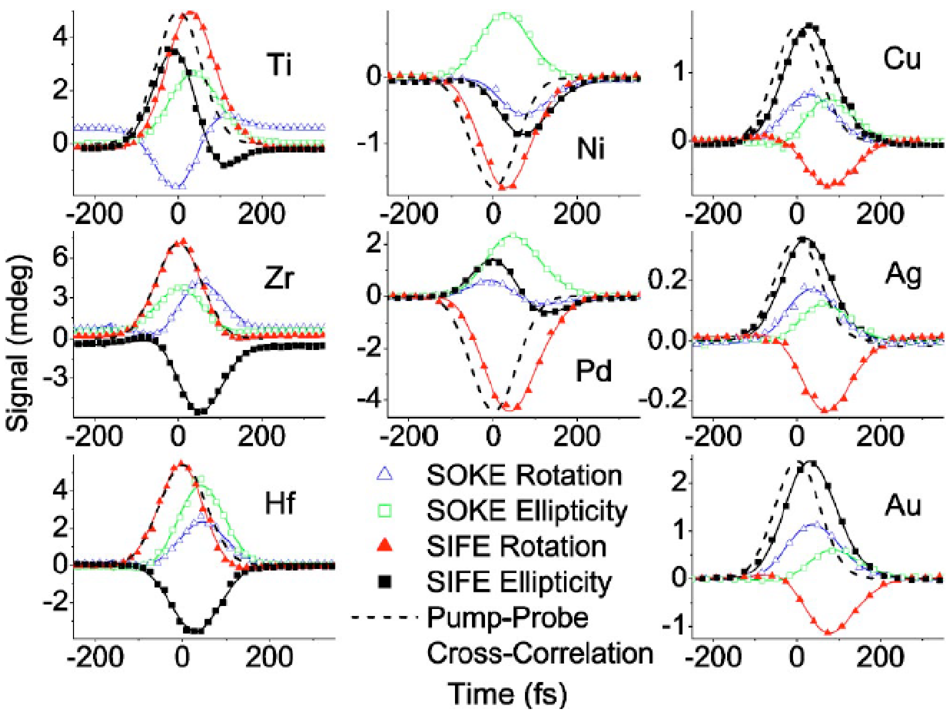


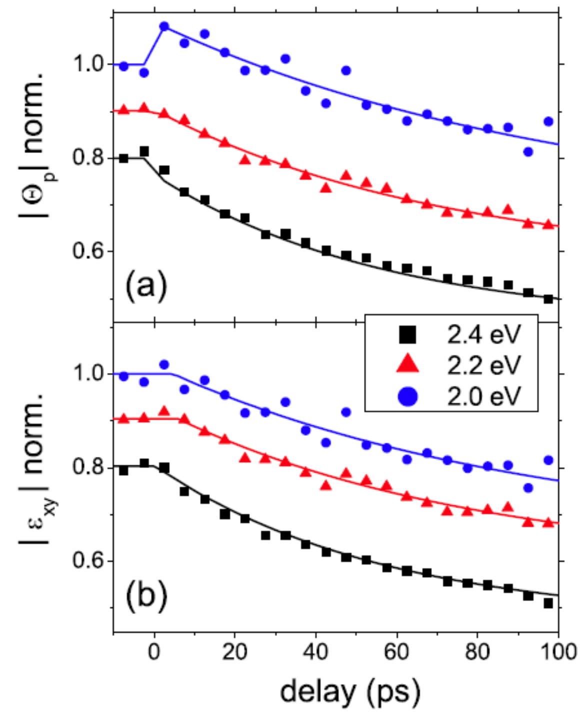
Kruglyak, Hicken, Ali, Hickey, Pym, B.K. Tanner, Phys. Rev. B **71**, 233104 (2005)

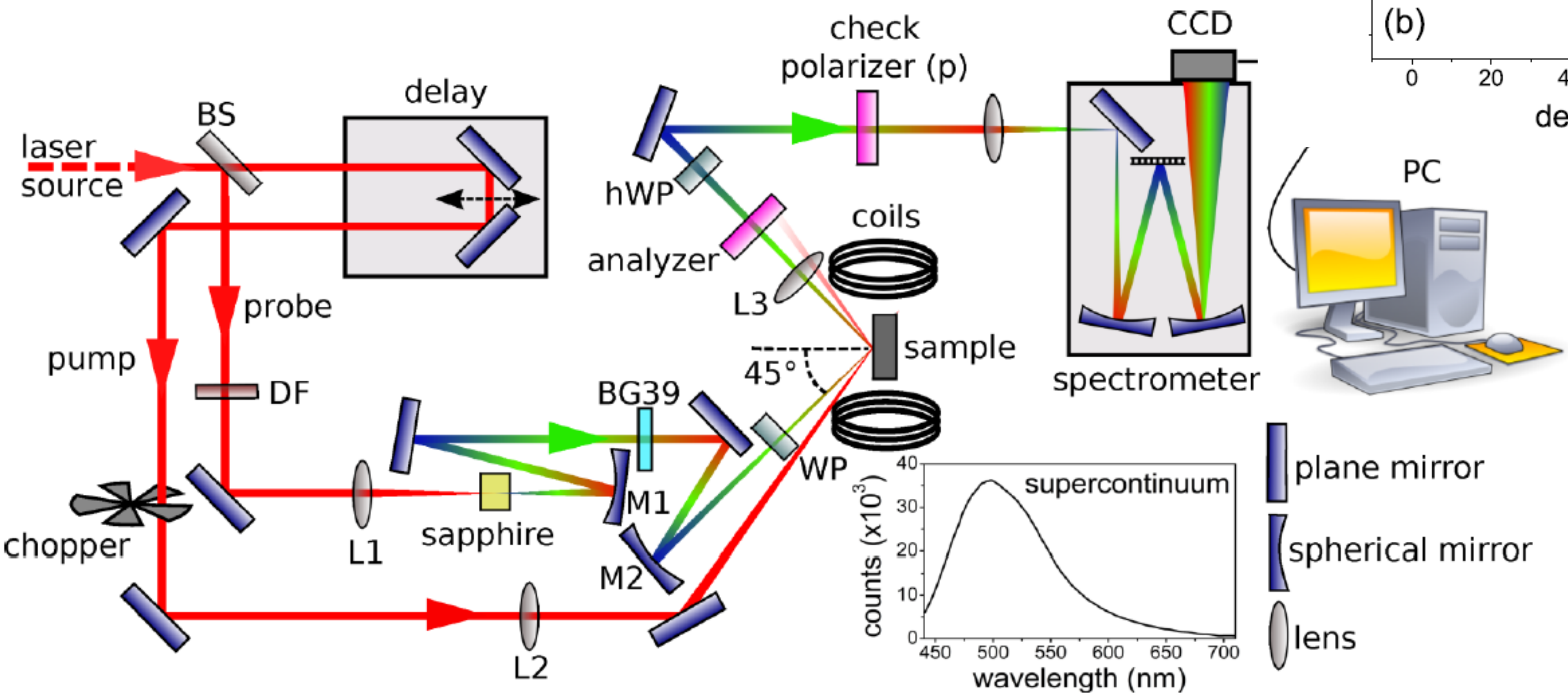
- Ti-sapphire, 1.58 eV, 80 MHz, 90 fs, 2 nJ pump
- Probe: 27° AOI, p-polarized
- fs ellipsometry of Ag, Cu, Ag, Ni, Pd, Ti, Zr, Hf on Si
- SIFE: Specular inverse Faraday effect
- SOKE: Specular optical Kerr effect
- **Nonlinear susceptibility**, Δε not calculated



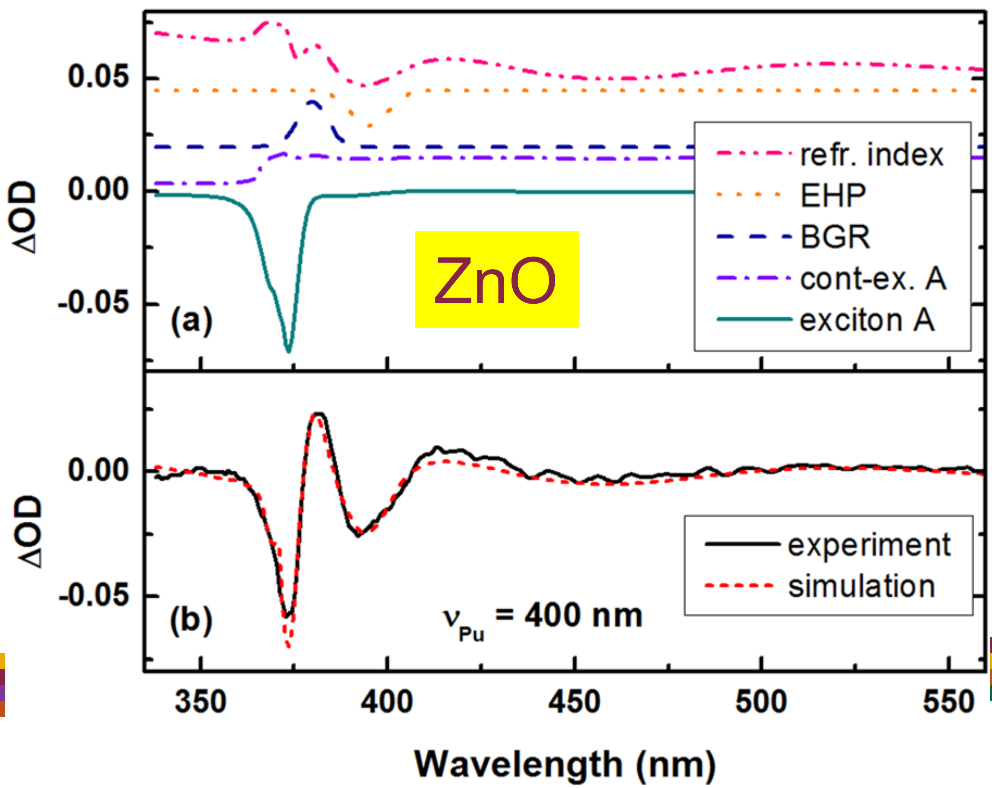
- Pump: Ti-sapphire, 1.55 eV, 1 kHz, 60 fs, 1.5 W, s-polarized. Chopped at 500 Hz.
- Probe: White light (440–720 nm), 45º AOI, s-polarized.
- Glan-Thomson prisms, $10^{-5}$ extinction.
- PCSA(HWP-P) ellipsometer (P=0, C=45º)
- **$CrO_2$ single crystals (tetragonal ferromagnet)**

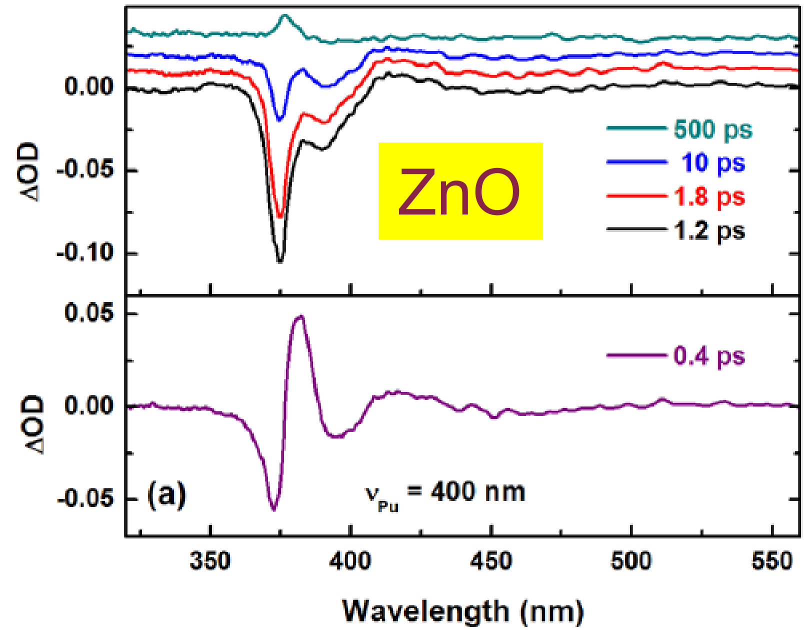


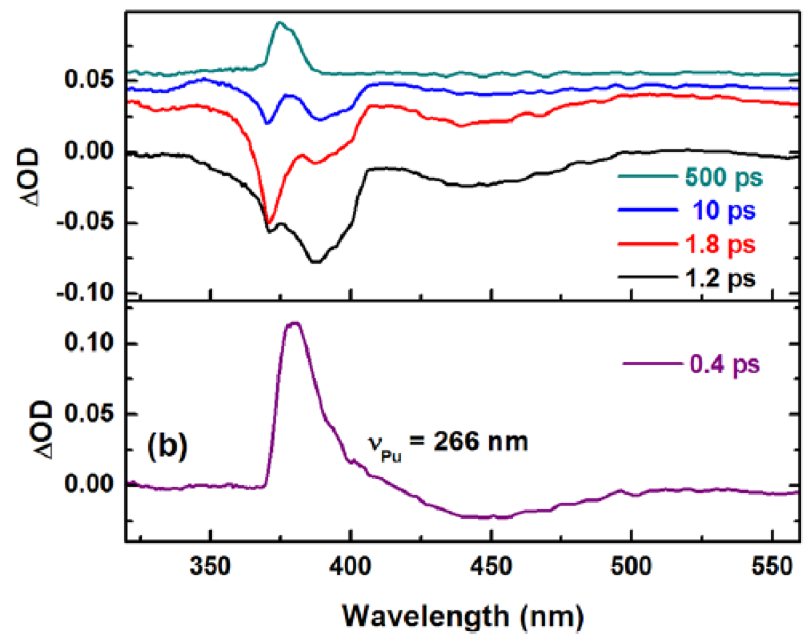



Acharya, Chouthe, Graener, Böntgen, Sturm, Schmidt-Grund, Grundmann, Seifert, J. Appl. Phys. **115** (2014)

- Femtosecond absorption spectroscopy on ZnO and $BaTiO_3$

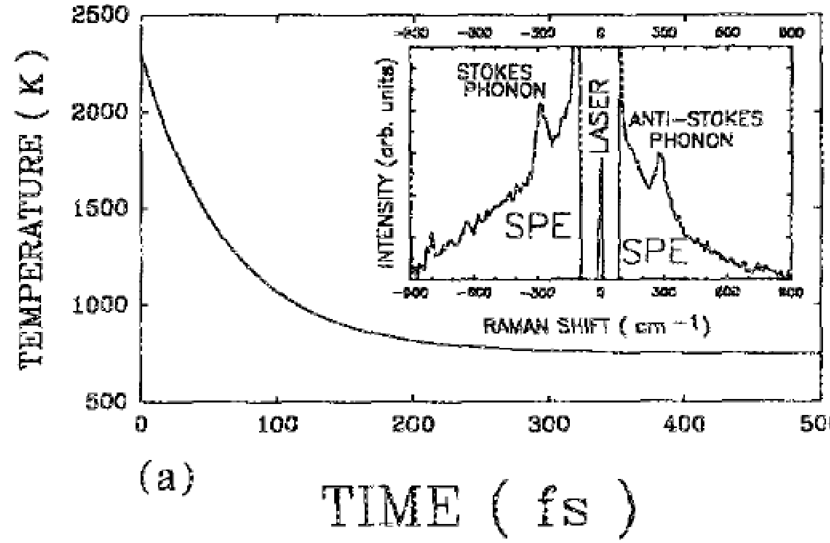


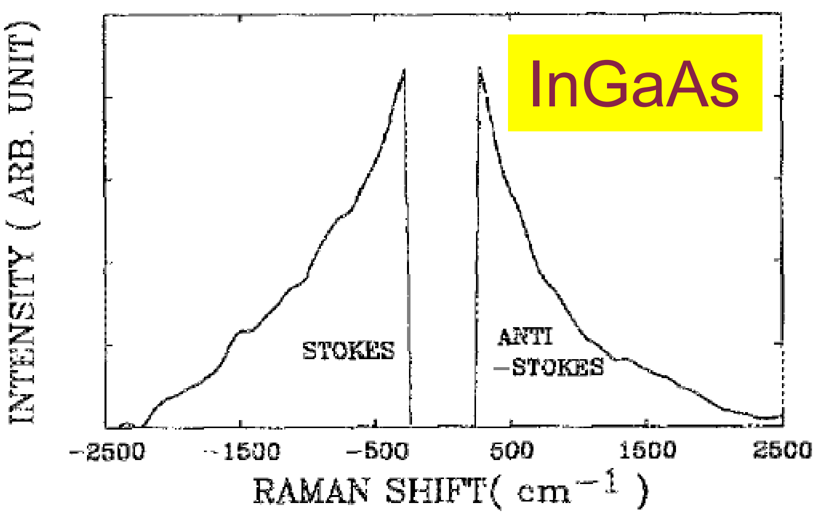



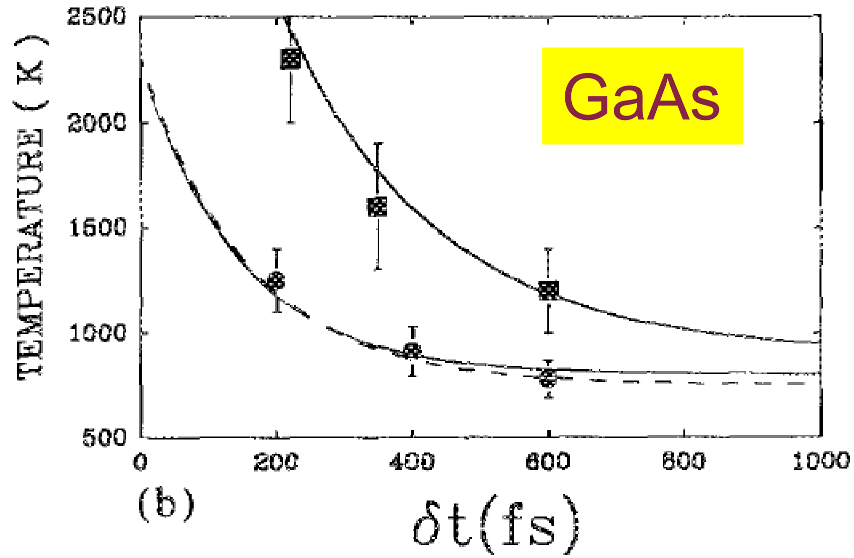



# D.S. Kim and P. Yu, Appl. Phys. Lett. **56**, 2210 (1990)

- Time-resolved Raman spectroscopy **with a single pulse**.
- The leading edge of the pulse is the pump, the trailing edge is the probe (needs convolution).
- This particular experiment did not have sufficient time resolution to measure what the authors claimed, but it is worthwhile to keep this scheme ir mind.



# Samples and Topics

- Germanium and GaAs, GaSb, InP, Si
  - Diffusion, band gap renormalization, interband scattering
  - Lattice heating (redshift and broadening of critical points)
  - Excitonic screening near $E_0$ and $E_0+\Delta_0$
- GaP: Similar to Ge. Larger band gap accessible with lasers.
- ZnO/GaP/GaN: Screening of excitons (bulk or thin films on Si). Exciton transport across interfaces.
- $SrTiO_3$: Screening excitons in bulk and type I or II QW.
- Au and other non-magnetic metals: Electron heating/cooling.
- Ni: Heat electrons above $T_c$ (tune $T_c$ with Ni:Pt and Ni:V alloys).
- Phase change materials such as GeSb
- Coherent phonon oscillations (tellurium).