OLD DOMINION UNIVERSITY

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Ultrafast Thermoreflectance Studies of Niobium Thin Films

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Thin Film, Ultra-short Pulse and Pump-probe Technique

Thin Films Different than Bulk

- One atomic layer to a micrometer
- Mechanical, optical, electrical, and thermal properties are different
- Due to low dimensionality and substrate effects
- Thermal diffusion shows anisotropic behavior

Why Ultra-short Laser Pulses

- Heat transport time through thin films: **picosecond**
- Electronic process in solid: **sub-picosecond**
- Measurement of electronic interaction: **fs laser pulse**

Process	Time scale
e-e Interaction	10^{-16} *to* 10^{-13} sec
e-Ph Interaction	10^{-13} *to* 10^{-12} sec

Pump-probe Thermo-modulation

- **Basic Principle:** change in reflectivity/transmittivity due to the change in temperature
- **Applications:** thermal conductivity, heat capacity, interface thermal conductance, thin film thickness, sound velocity, thin film damage etc.

Source: T. Susi, J. C. Meyer and J. Kotakoski, Quantifying transmission electron microscopy irradiation effects using two-dimensional materials, Nature Reviews Physics, 1, 397-405, 2019.

Energy Transport in Thin Films (Thermophysical Events)

Creation of hot electrons
(order of few hundred fs)

Application of
intense ultrafast laser pulse

Fast decay
(order of few ps)

Hot electrons
transfer energy to lattice

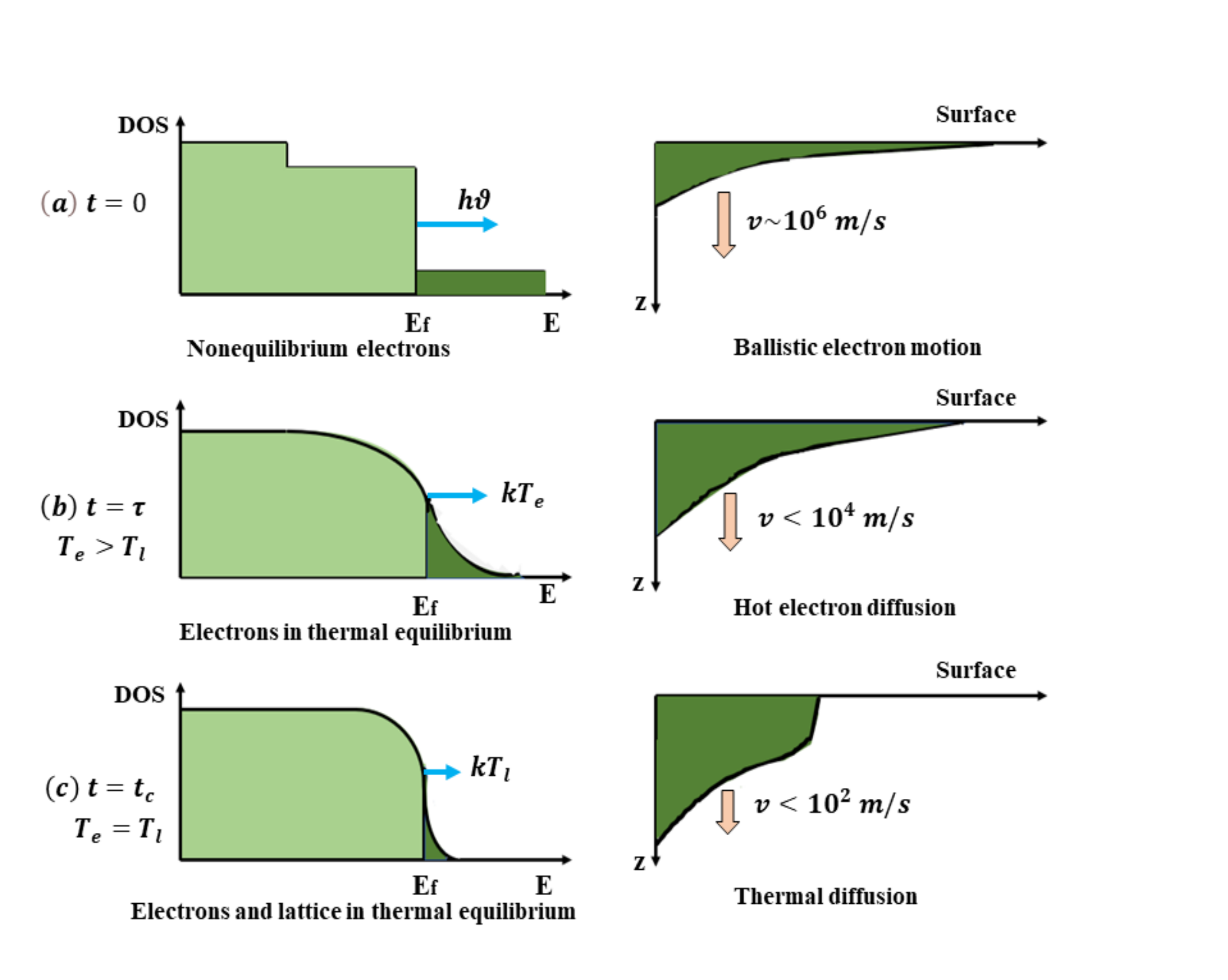
Slow decay
(order of few ns)

Change in
lattice temperature

Condition: Pulse width of the excitation laser is shorter than the electron-phonon relaxation time.

Source: K. M. Yoo, X. M. Zhao, M. Siddique, and R. R. Alfana, Femtosecond thermal modulation measurements of electron-phonon relaxation in niobium, Appl. Phys. lett., vol. 56, no. 19, pp. 1908-1910, 1990.

Energy Transport in Thin Films (Thermal Relaxation Phases)



1. **Electron temperature increases by electron-electron interaction:** drift into deeper part with ballistic motion

2. **Diffusive energy transport by electron-phonon coupling:** Strong e-ph coupling >> smaller diffusion length

3. **Energy transports due to lattice thermal diffusion:** higher heat capacity of lattice >> weak temp. gradient

Source: J. Hohlfeld, S. S. Wellershoff, J. Gudde, U. Conrad, V. Jahnke, and E. Matthias, Electron and Lattice Dynamics Following Optical Excitation of Metals, Chemical Phys., 251, 237-258, 2000.

Temperature Dependance on Reflectivity

Heated electrons and phonons alter the dielectric constant, which in turn changes the reflectivity/transmissivity:

$$\frac{\Delta R}{R} = \frac{1}{R}\left[\frac{\partial R}{\partial \varepsilon_1}\Delta\varepsilon_1 + \frac{\partial R}{\partial \varepsilon_2}\Delta\varepsilon_2\right]$$

Change in the dielectric constant is known to be proportional to the change in both electron and lattice temperature:

$$\frac{\Delta R}{R} = a\Delta T_l + b\Delta T_e$$

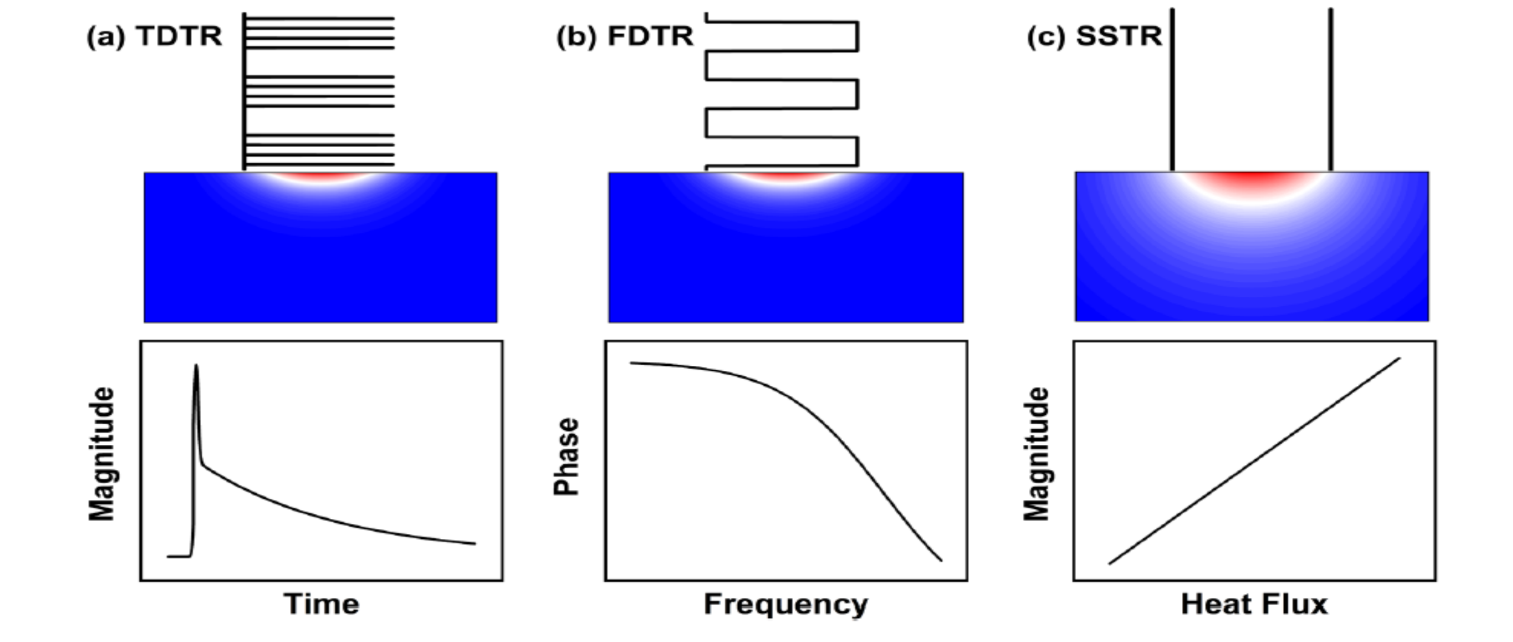
The number density of the carriers excited by the optical perturbation is crucial for e-e interaction:

$$\Delta R = \frac{\partial R}{\partial T}\Delta T + \frac{\partial R}{\partial N}\Delta N$$

Free carrier contribution to reflectivity change only lasts for about 1 ps for most metals

Source: M. Mihailidi, Q. Xing, K. M. Yoo, and R. R. Alfano, Electron-phonon relaxation dynamics of niobium metal as a function of temperature, Physical Review B, 49 (5), 3207-3212, 1994.

Thermoreflectance Based Pump-Probe Techniques



- Amplitude-modulated heat source induces both steady-state and modulated temperature rise
- TDTR and FDTR use high mod. freq. and utilize modulated temp. rise
- SSTR use low mod. Freq. and utilize steady state temp. rise

Time Domain Thermoreflectance

Measures the change in intensity of the reflected probe as a function of pump-probe delay

Frequency Domain Thermoreflectance

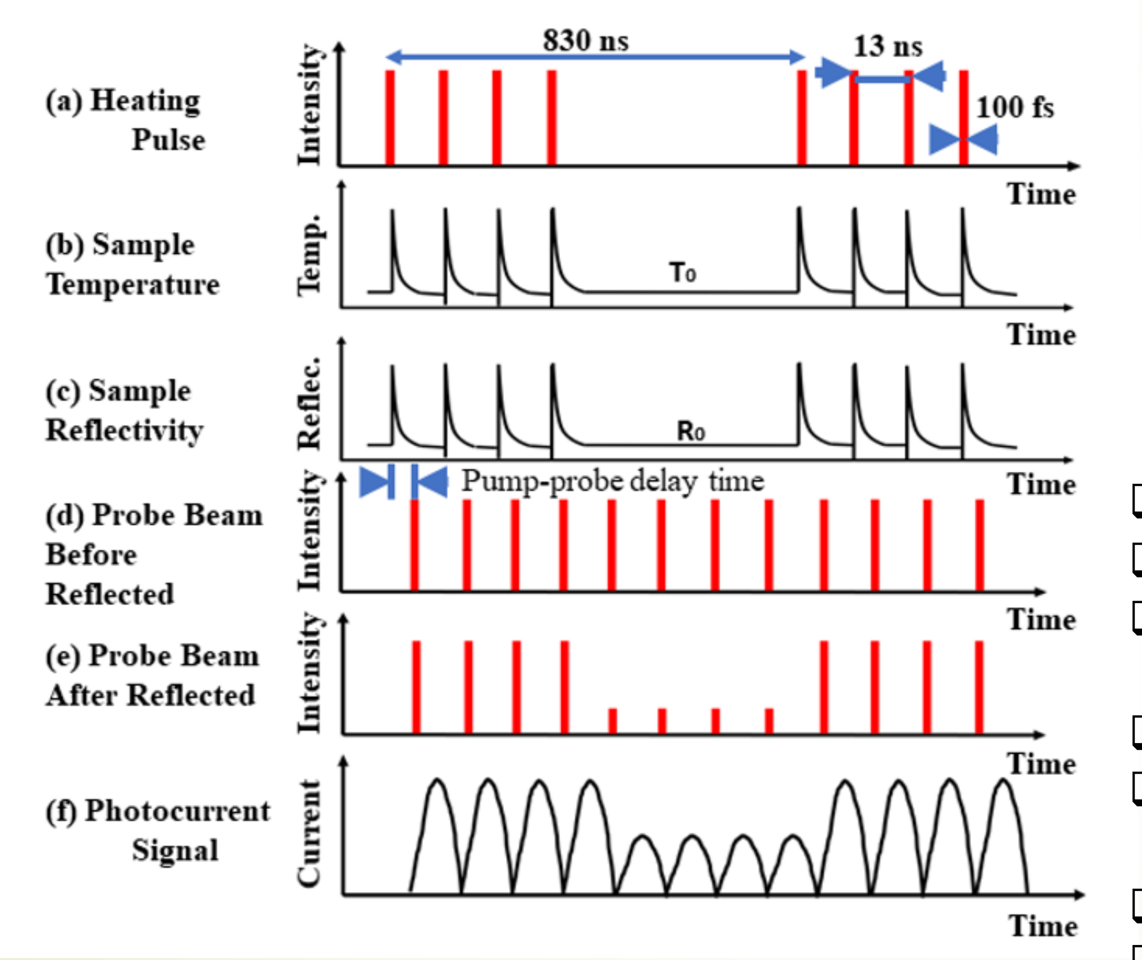
Measures , the thermally induced phase lag between the pump and probe as a function of frequency

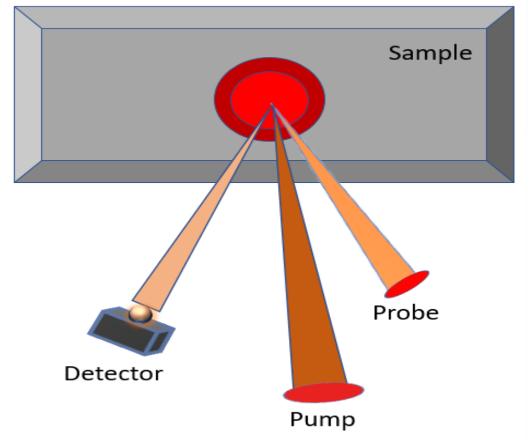
Steady State Thermoreflectance

Measures the induced magnitude of the thermoreflectance for given changes in heat flux

Source: D. H. Olson, J. L. Braun, and P. E. Hopkins, Spatially resolved thermoreflectance techniques for thermal conductivity measurements from the nanoscale to the mesoscale, J. Appl. Phys. 126, 150901, 2019.

Measurement Principle of Reflectivity Changes during Femtosecond Laser Pulse Heating

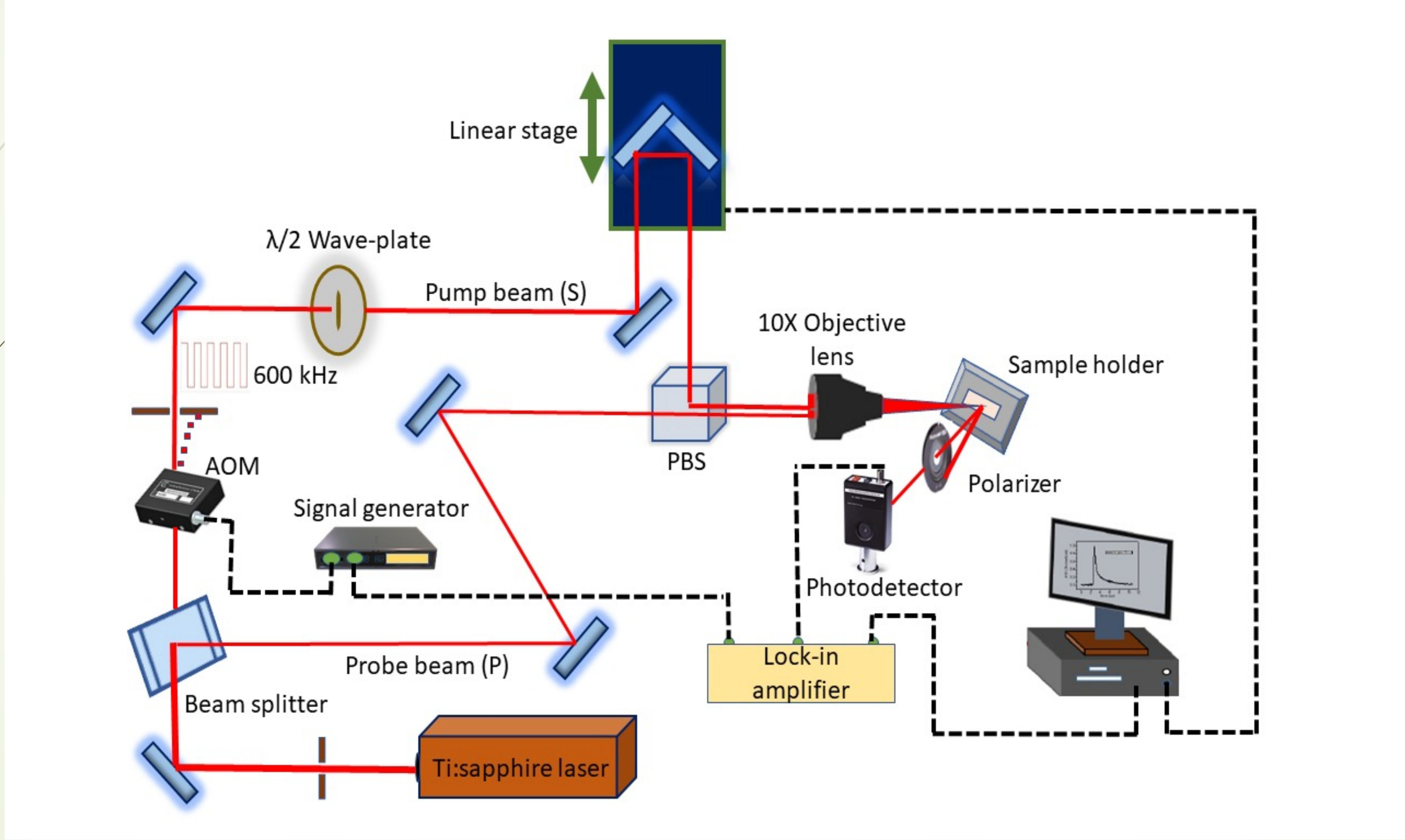




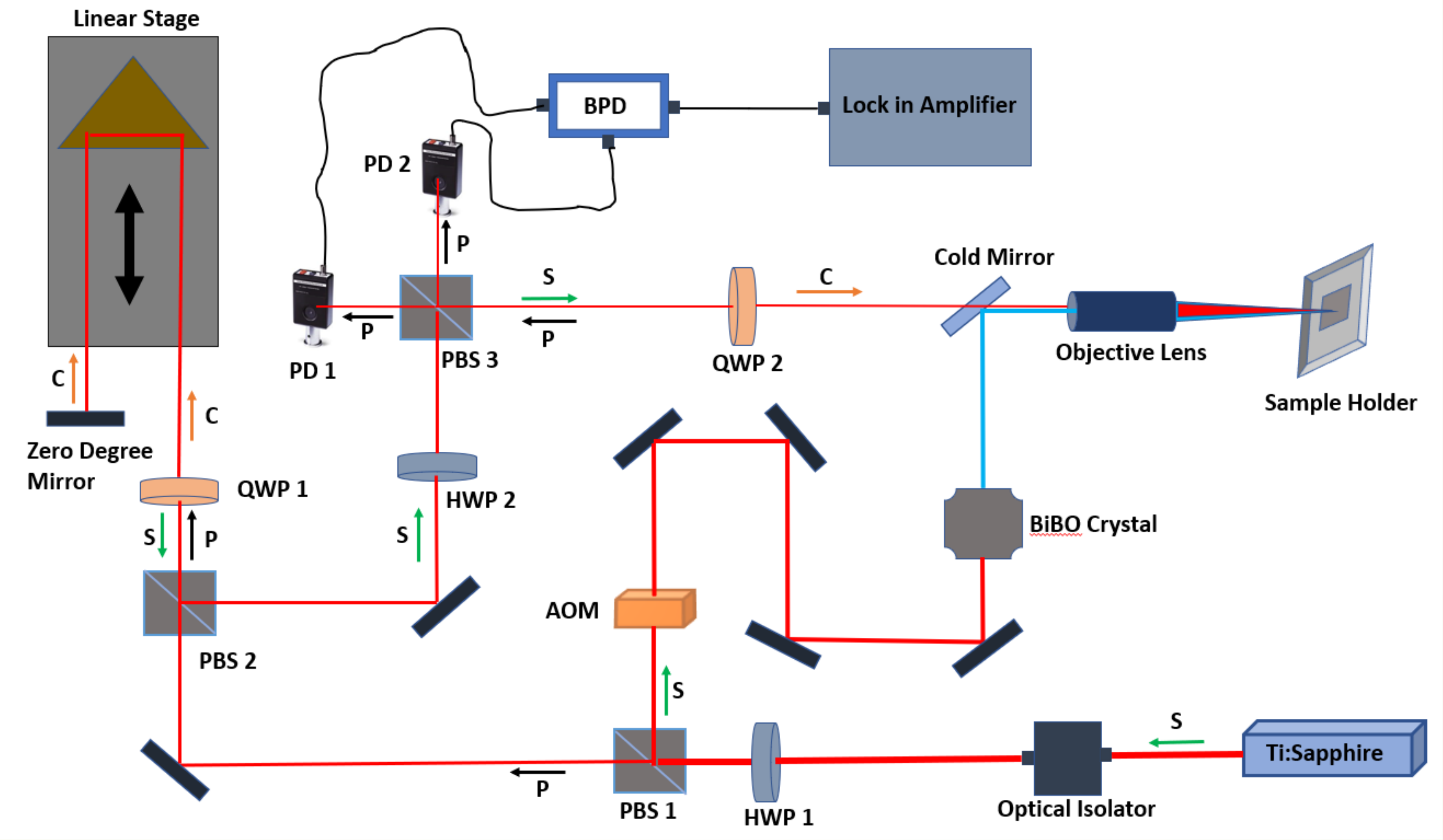
- Pump beam modulated by 1.2 MHz carrier frequency.
- Each 100-fs heating pulse separated by 13 ns.
- Interval between two individual heating event is much greater than e-ph relaxation time (few hundred fs).
- Transient variation of reflectivity from its reference value
- Probe pulses have a short time delay related to the heating pulses
- A train of probe pulse is reflected at a reflectivity R(τ)
- Periodic signal from photodetector.

Source: T. Q. QIU, T. JUHASZ, C. SUAREZ, W. E. BRONS and C. L. TIEN, Femtosecond laser heating of multi-layer metals-II. Experiments, Int. J. Heat Mars Trans, 37 (17), 2799-2808, 1994.

TDTR Experimental Setup (Lab 206 ARC ODU)

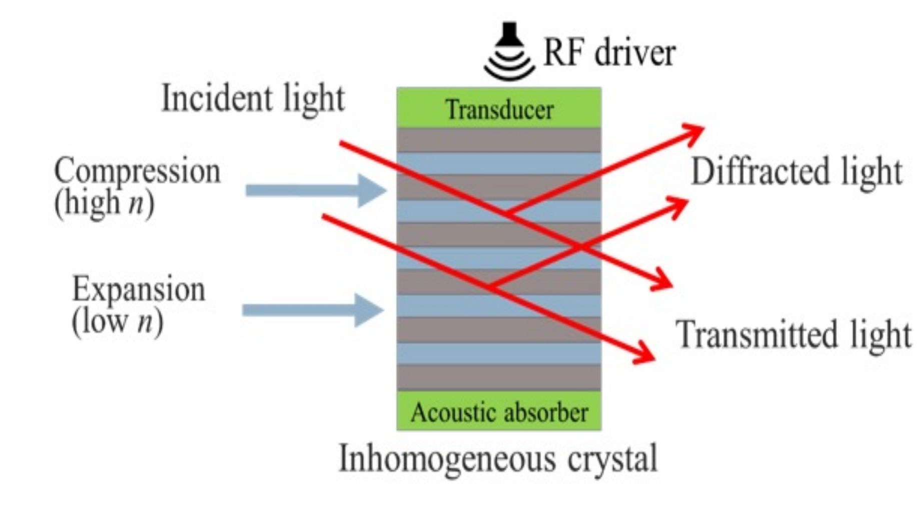


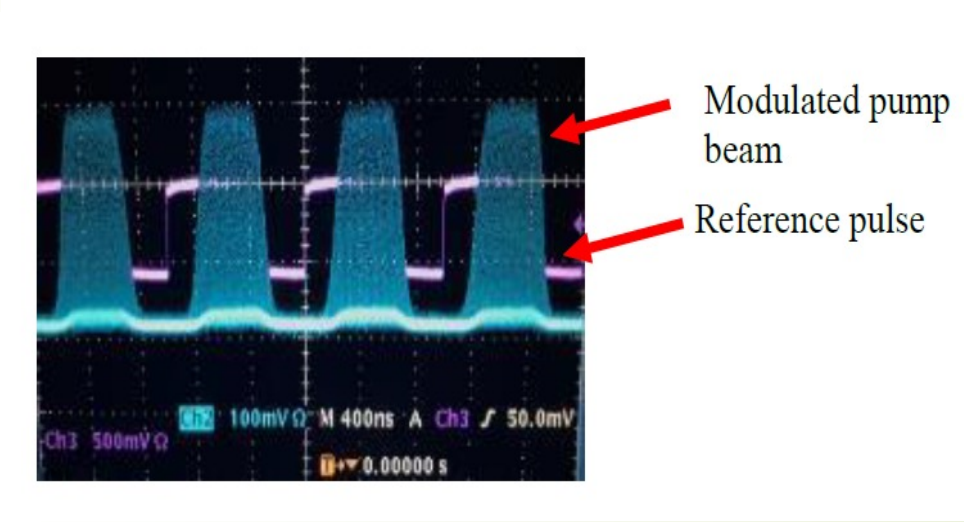
TDTR Setup Employing Colinear Detection Scheme and Path Doubling Approach



HWP: Half Wave Plate, **QWP:** Quarter Wave Plate, **PBS:** Polarized Beam Splitter, **AOM:** Acousto-Optic Modulator, **BiBO:** Bismuth Borate, **PD:** Photo Detector, **BPD:** Balanced Photo Detector

Pump Beam Passes Through AOM for Modulating Heating Event





- Propagating through a transparent crystal
- A piezoelectric transducer driven by an electrical signal produce a sound wave
- The refractive index of the crystal altered by sound vibration
- Periodic refractive index grating causes Bragg diffraction of light
- Frequency and direction of the scattered beam controlled via the frequency of the carrier.

Time Delay Between Pump and Probe by Optical Delay Line

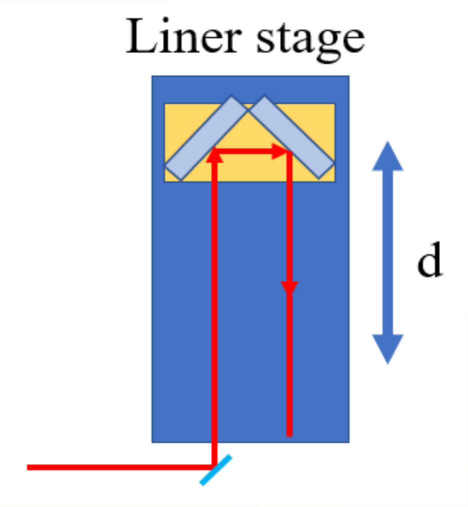
Spatial difference converts into time delay between pump and probe beam

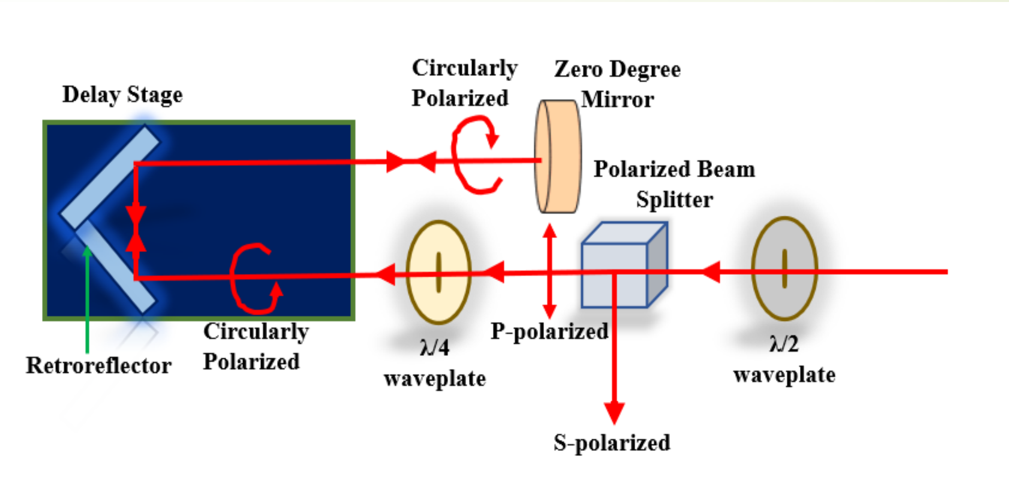
Time delay, $\tau = \frac{2d}{c}$

c = speed of light

d = distance varied

(1 mm ~ 6.66 ps)



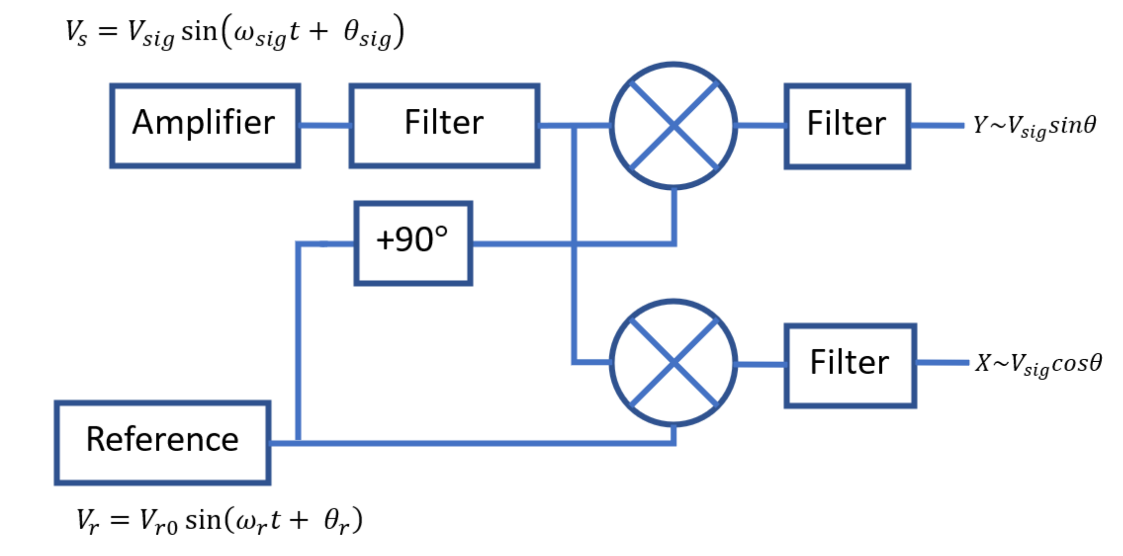


Path doubling approach to ensure enough time delay between pump and probe

Data Acquisition by Lock-in Amplifier

- Deals with very small ac signals as it combines both the time and frequency domain techniques
- Noise at frequencies other than ref. freq. canceled

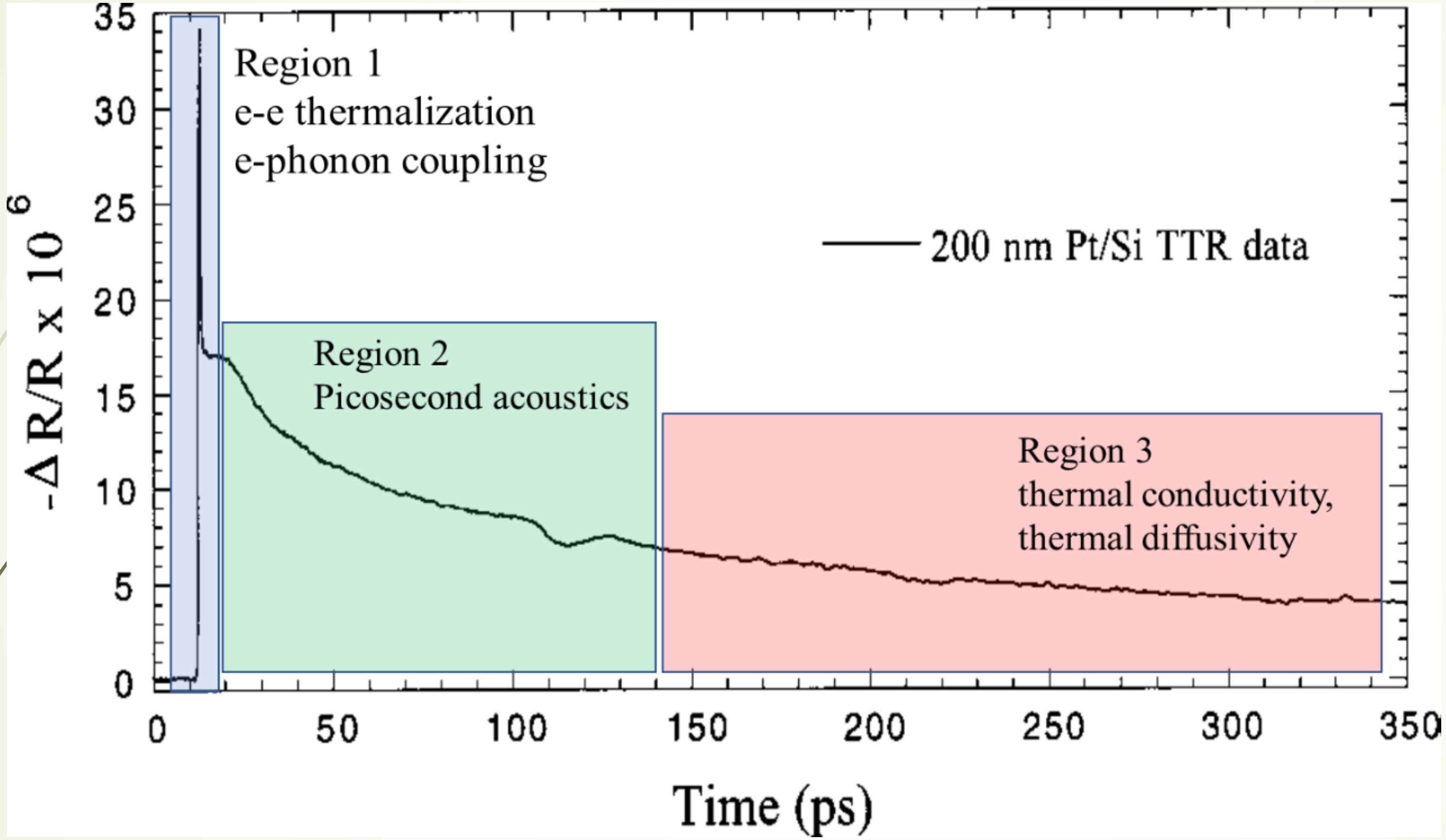
- **Basic principle:** phase sensitive detection (mixing signals and low pass filtering)
- Reference signal from AOM and input signal from photodiode
- Dual phase lock-in use two PSD: measure amplitude directly: no phase dependency



The signal amplitude and phase are calculated from in-phase and quadrature components

$$R = \sqrt{X^2 + Y^2}, \qquad \varphi = tan^{-1}\left[\frac{Y}{X}\right]$$

Applications of TDTR Measurements



Time domain thermoreflectance (TTR) data for a 200 nm Pt sample on a silicon substrate

- ❑ Measuring e-ph coupling and studying nonequilibrium electron events
- ❑ Thermal expansion induced by short pulses hit the film creates strain wave reflected back from the interface
- ❑ The shape and time interval between echoes are used for measuring film thickness and sound velocity

Source: P. M. Norris, A. P. Caffrey, R. Stevens, J. M. Klopf, J. T. McLeskey, and A. N. Smith Femtosecond Pump-Probe Nondestructive Evaluation of Materials Rev Sci. Instrum. 74, 400-406, 2003.

Two-Temperature Model

Exchange of Energy

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{\partial}{\partial x}\left(K_e(T_e,T_l)\frac{\partial T_e}{\partial x}\right) - g(T_e - T_l) + S(x,t)$$

$$C_l\frac{\partial T_l}{\partial t} = g(T_e - T_l)$$

C_e, C_l	:	Electron and lattice heat capacity
T_e, T_l	:	Electron and lattice temperature
g	:	Electron-phonon coupling factor
K_e	:	Thermal conductivity
$S(x,t)$	:	Laser source term, heat energy generated per unit volume per unit time

Using Crank-Nicolson Finite Difference Method (CN-FDM) temperature profile obtained.

Laser Source Term

$$S(x,t) = (1-R)\frac{J}{t_p d} * \exp\left[-\frac{x}{d} - 2.77\left(\frac{t}{t_p}\right)^2\right]$$

Initial Condition

$$T_e(x,-2t_p) = T_l(x,-2t_p) = T_0$$

Boundary Conditions

Heat losses from the front and back surfaces can be neglected

$$\left.\frac{\partial T_e}{\partial x}\right|_{x=0} = \left.\frac{\partial T_e}{\partial x}\right|_{x=L} = \left.\frac{\partial T_l}{\partial x}\right|_{x=0} = \left.\frac{\partial T_l}{\partial x}\right|_{x=L} = 0$$

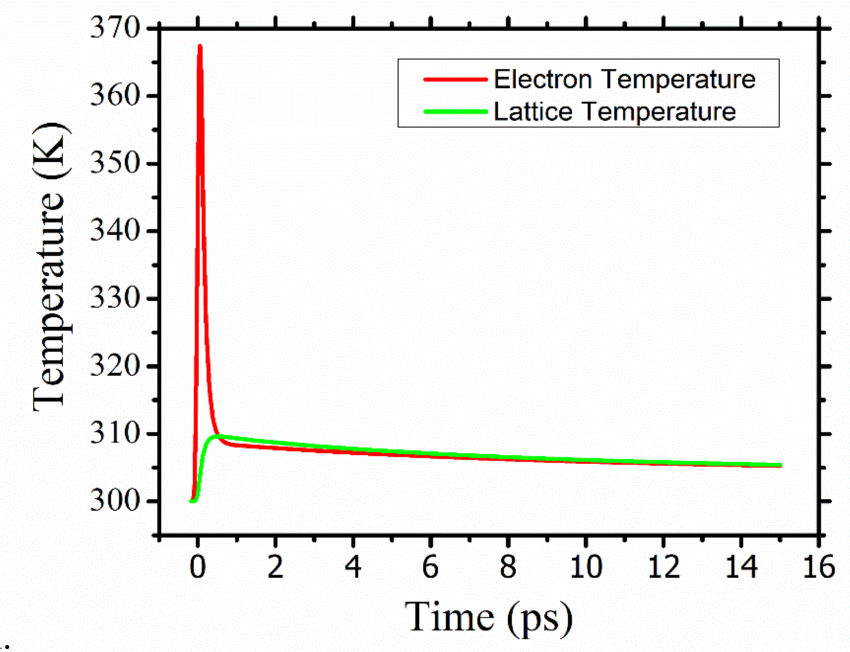
Source: S. I. Anisimov, B. L. Kapeliovich, and T. L. Perel'man, Electron Emission from Metal Surfaces Exposed to Ultrashort Laser Pulses, Sov. Phys. JETP, vol. 39, pp. 375-377, 1974.

Two-Temperature Model

Optical and thermal properties of Nb	
Electron Heat Capacity, $C_e = \rho Cp$ (J/m^3-K)	720 T_e
Lattice Heat Capacity, $C_l = \rho Cp$ (J/m^3-K)	$2.3x10^6$
Reflectivity, R	0.9
Optical Penetration Depth, δ (nm)	20

ARC Femtosecond Laser Specifications	
Center Wavelength	800 nm
Repetition Rate	80 MHz
Pulse Width	150 fs
Focal Spot Diameter (Pump)	20 μm
Focal Spot Diameter (Probe)	10 μm
Pump Energy	1.25 nJ
Pump Fluence	3.98 Jm^{-2}
Photon energy	1.553 eV

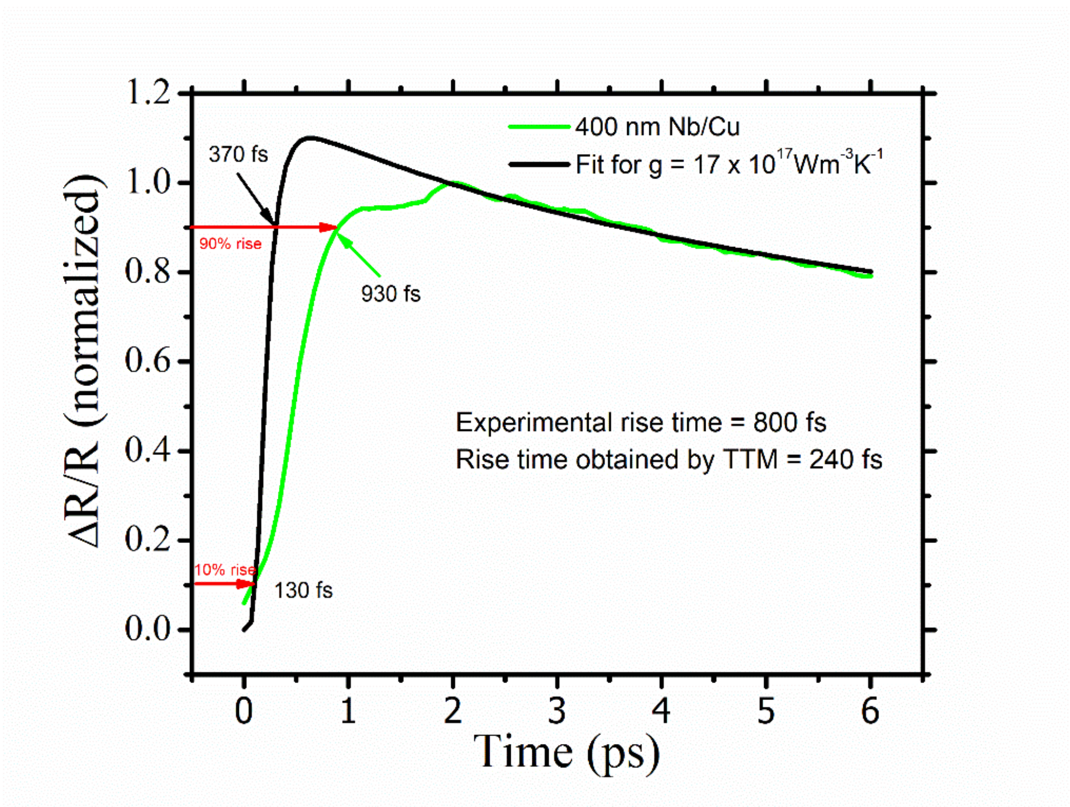
Temporal change in electron and lattice temperature for Nb by TTM



Source: K. M. Yoo, X. M. Zhao, M. Siddique, and R. R. Alfana, Femtosecond thermal modulation measurements of electron-phonon relaxation in niobium, Appl. Phys. lett., vol. 56, no. 19, pp. 1908-1910, 1990.

Source: M. Mihailidi, Q. Xing, K. M. Yoo, and R. R. Alfano, Electron-phonon relaxation dynamics of niobium metal as a function of temperature, Physical Review B, 49 (5), 3207-3212, 1994.

Measuring Electron-Phonon Coupling Factor by Fitting with TTM

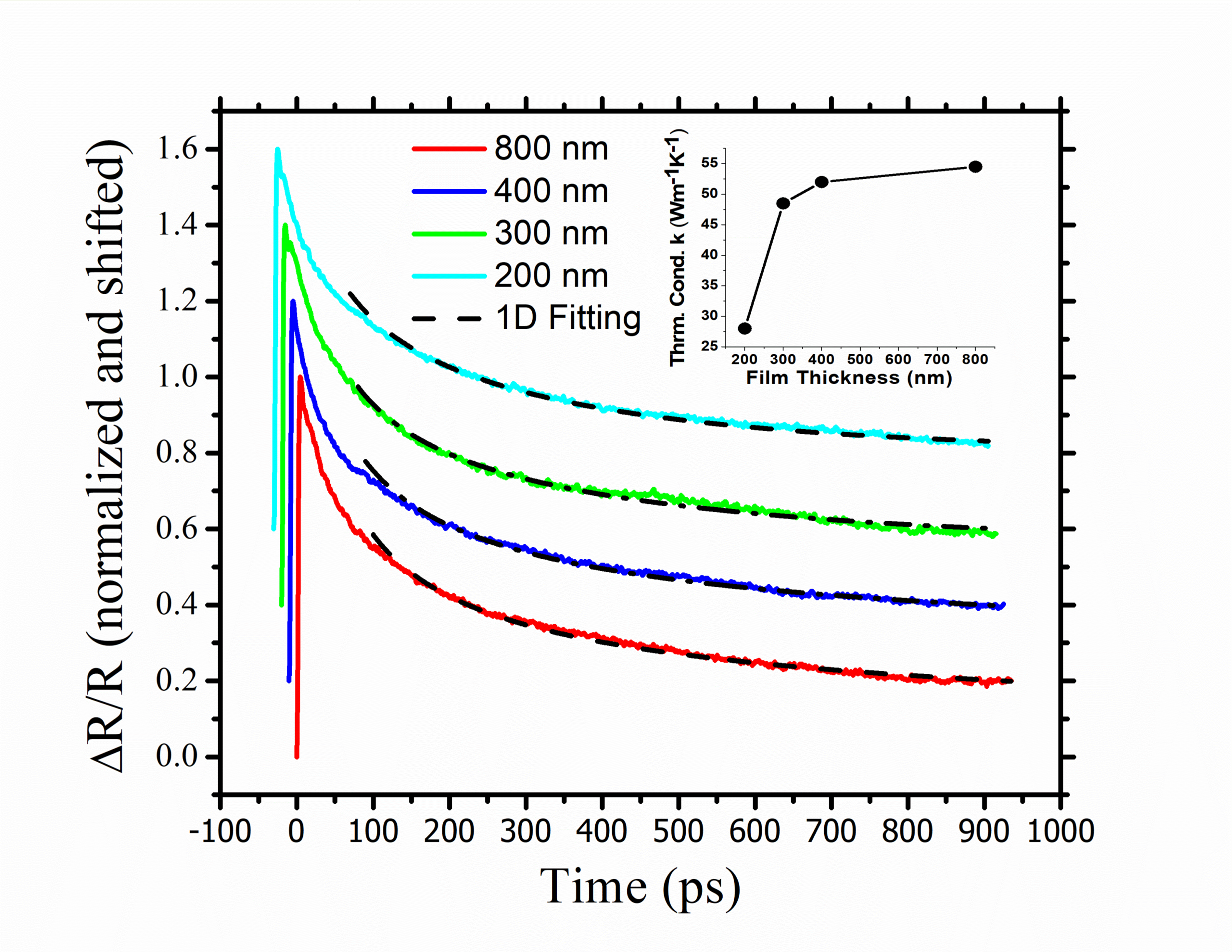


TDTR signals from 400 nm Nb on Cu

- The value of g reported is $14 \times 10^{17}\ Wm^{-3}K^{-1}$
- Thickness (**400 nm**) is much higher than optical penetration depth (**20 nm**)
- For minimal thermal diffusion thickness should be close to penetration depth.
- **Rise Time:** time needed to rise the reflectance from 10% to 90% of the total rise
- Root of discrepancy ???
- Actual pulse width of the laser might be increased after passing through so many optics.
- Pulse width must be less than e-ph relaxation time.

Source: K. M. Yoo, X. M. Zhao, M. Siddique, and R. R. Alfana, Femtosecond thermal modulation measurements of electron-phonon relaxation in niobium, Appl. Phys. lett., vol. 56, no. 19, pp. 1908-1910, 1990.

Measuring Thermal Conductivity by Fitting with TTM



Film Thickness (nm)	Thermal Conductivity ($Wm^{-1}K^{-1}$)	RMSE	R-square Measure
800	54.50	0.0078994	0.99247
400	52.00	0.0082064	0.99111
300	48.50	0.010544	0.98577
200	28.00	0.0082908	0.99127

Film thickness has impacts on grain size and distribution which are responsible for this reduction in thermal conductivity

Measuring Goodness of Fit

The root-mean-square error (RMSE) is calculated by using the following formula:

$$\boldsymbol{RMSE} = \sqrt{\frac{\sum_{i=n_1}^{n_2}(A_{Model}-A_{Exp})^2}{(n_1-n_2)}}$$

Fitting deviation measured by coefficient of determination can be calculated with two sums of squares formulas. The R-squared measure is the calculated as:

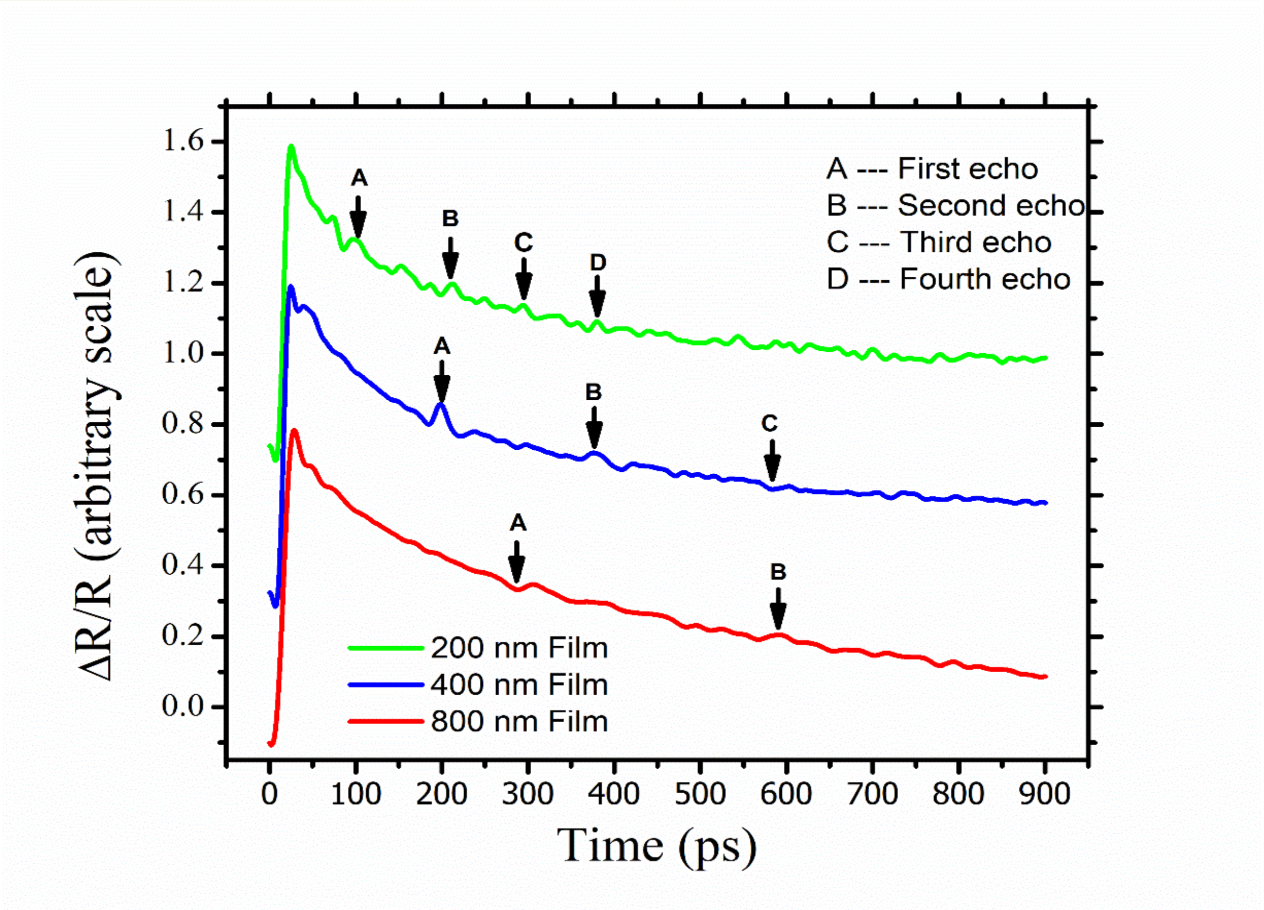
$$R^2 = 1 - \frac{SS_r}{SS_t}$$

The total sum of squares: $SS_t = \sum_i (A_{exp}(i) - \overline{A_{exp}})^2$

Where, $\overline{A_{exp}} = \frac{1}{(n_2-n_1)} \sum_{i=n_1}^{n_2} A_{exp}(i)$

The residual sum of squares: $SS_r = \sum_i (A_{exp}(i) - A_{model}(i))^2$

Strain Effect on Reflectivity



TDTR data from Nb films on Cu

Thermal expansion generates acoustic waves of ultrasonic frequency

Longitudinal component propagates perpendicular to the surface and partially **reflected at the interface**

Regularly spaced ehoes, period varied linearly with film thickness

Calculation of Longitudinal Sound Velocity Inside Niobium Film

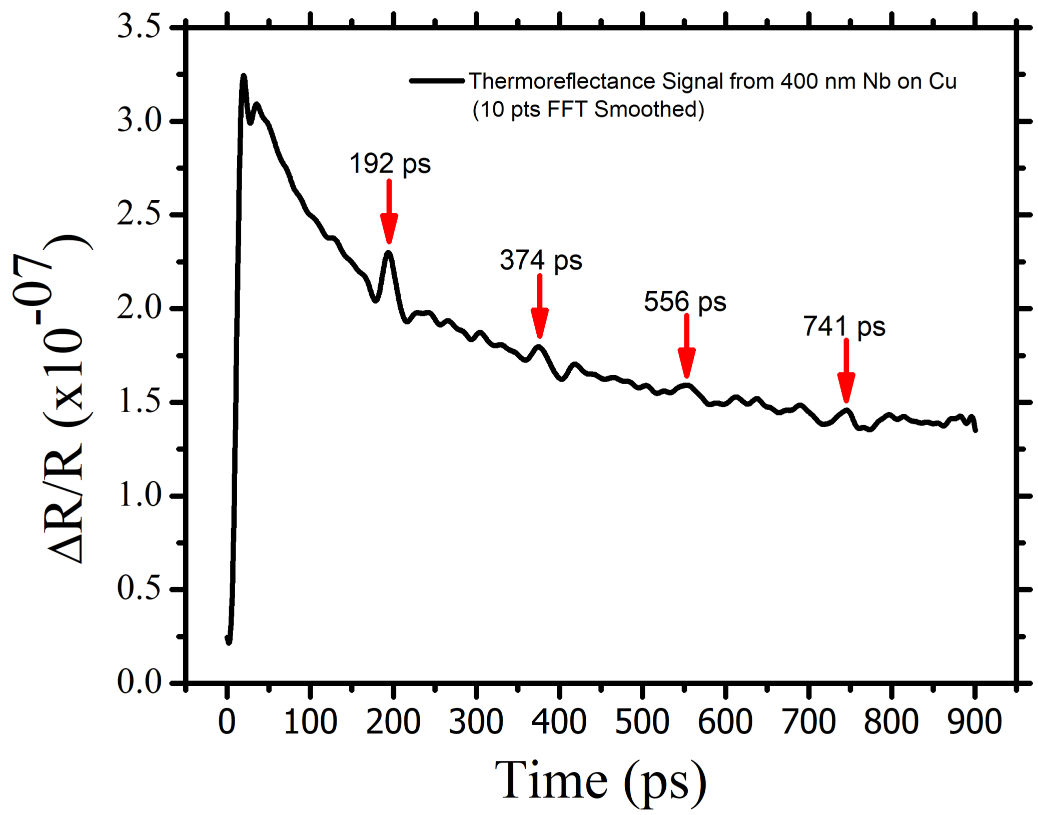
Sound velocity obtained from: $v = 2d/t$

v is longitudinal sound velocity inside film

t is the measured period

and d is the film thickness

- Period varied linearly with film thickness
- For d= 400 nm, t= 182 ps
  $v = 4395.6\ ms^{-1}$
- Reported value: 3480-4900 ms^{-1}



Source: I. L. Shabalin, "Niobium," Ultra-High Temperature Materials I: Carbon (Graphene/Graphite) and Refractory Metals, Dordrecht, Netherlands, Springer, 2014, ch. 8, sec. 8.4, pp. 539.

Concluding Remarks

- **TDTR** is a powerful and versatile technique in measuring thermal properties.
- Still improving, and its functionality has yet to be fully explored.
- **Limitations:** solution of diffusion equation suited to materials involving strong electron-phonon coupling and heat carriers having mean-free path small compared to the thermal penetration depth.
- Limitation in measuring extremely low thermal conductivity.
- **Potential Future Applications:** measuring transport properties through solid-liquid and liquid-liquid interface and heat diffusion from nanoparticle to its surroundings.


QUESTION?
ANSWER