Ultrafast laser spectroscopy and surface dynamics

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Summary I

Introduction
- Non-adiabatic processes at surfaces: Chemicurrents

Surface femtochemistry
- Surface dynamics with electronic friction
- Example: Associative desorption of H$_2$ from Ru(0001)

Time-resolved probe of structural dynamics
- Femtosecond laser spectroscopy
- Time-resolved x-ray diffraction
- Non-thermal melting and coherent phonon excitation
- Time-resolved photoelectron spectroscopy
Ultrafast laser excitation of solids

fs-laser pulse

(sample)

time [s]

$10^{-15}$

$10^{-14}$

$10^{-13}$

$10^{-12}$

$10^{-11}$

$10^{-10}$

$10^{-9}$

electron-electron-scattering:

$T_{e-h} \gg T_L$

electron-phonon scattering:

$T_{e-h} \downarrow, T_L \uparrow$

phonon-phonon scattering

$T_{e-h} \approx T_L$

heat conduction

(thermal) melting

ablation

non-thermal

thermal

CB

VB

semiconductor
Principle of pump-probe spectroscopy

Basic concept to resolve processes on ultrafast time-scales

Time resolution is determined by pulse duration
2. fs-laser plasma: "femtosecond x-ray tube"


Laser: Ti:Sa, 120 fs, 150 mJ  
Target: moving Titanium wire

fs-laser: \( \sim 100 \text{fs}, 10 \ldots 100 \text{ mJ} \)  
\( I \approx 10^{16} \ldots 10^{18} \text{ W/cm}^2 \)
Time-resolved x-ray diffraction (TXRD)
Diffraction and focussing of keV x-rax radiation

\[ \approx 3 \times 10^4 \text{ photons/pulse} \]
x-ray diffraction data

CCD camera image

Integration

Dispersion

Rocking Curve

different lattice constants of Ge and Si

integrated reflectivity
x-ray diffraction experiment...

AG von der Linde, University Essen

fs pump pulse
lead shielding
Debrie protection
fs pulse for plasma
x-ray mirror
k_α radiation
sample on x-y-θ manipulator
TiN wire
CCD
Ultrafast non-thermal melting:

Laser 0.47 J/cm²

Sample Silicon

Electronic excitation

Non-thermal melting

Ablation

Optical spectroscopy

Reflectivity vs. Wavelength [nm]

R(λ) of solid Si

Ultrafast non-thermal melting:

Intense electronic excitation

K. Sokolowski-Tinten et al., PRB 61, 2643 (2001)

> 10 % of all valence electrons!

lattice instability

P. Stampfli et al., PRB 49, 7299 (1994)

Use ultrafast melting as test case for time-resolved x-ray diffraction
X-ray diffraction: Ultrafast melting of Ge

170 nm Ge on Si; (111)-diffraction spot

Non-thermal und thermal melting and subsequent re-crystallization

K. Sokolowski-Tinten et al., PRL 87, 225701 (2001)
Analysis of x-ray pulse duration

for analysis phase transition is assumed as “instantaneous”

\[ \tau_x = (300 \pm 50) \text{ fs} \]
Lattice dynamics in Bismut

- Bi is a semimetal

- rhombohedral structure:
  - small displacement from fcc lattice
  - two atom basis

- Excitation of *coherent optical phonons* (A$_{1g}$-mode) with fs-laser pulses
  - Zeiger et al., PRB 45, 768 (1992)
  - DeCamp et al., PRB 64, 92301 (2001)
  - Hase et al., PRL 88, 67401 (2002)

**Bi-Bi** distance $a$ (0.468 $\times$ diagonal $c$) *stabilized by Peierls-Jones mechanism

A$_{1g}$-Phonon ($V = \text{const.}$)
Displacive Excitation of Coherent Phonons

pot. Energy

Distance

$\mathbf{a}_0$
geometric structure factor of Bi

→ decrease & oscillation of (111)-diffraction spot

→ increase & oscillation of (222)-diffraction spot

\[ |S(hkl)|^2 \]

\( a/c = 0.5 \)

(111)

(222)

initial equilibrium position \( a_0 \)

displaced quasi equilibrium position \( a_0' \)
Coherent optical phonons

Bi 50nm on Si, $F \approx 6 \text{ mJ/cm}^2$

$A_{1g}$ optical mode:

$\nu_{\text{obs}} = 2.14 \text{ THz (470 fs)}$

$\nu_0 = 2.92 \text{ THz (342 fs)}$

7%

softening & anharmonicity

$\Delta a \sim 0.15 – 0.25 \text{ Å}$

Coherent phonons ⇔ phase transition

Change of atomic vibrations: **periodic ⇒ aperiodic**?

Bi (111): higher excitation density \( \approx 1.1 \text{ ps} \)

**Softening of phonons** ⇔ **precursor for melting**
Phonon dynamics

Debye-Waller Eff.:

\[ DW = \exp\left(-\frac{\pi^2}{3} \frac{\langle u^2 \rangle}{d_{hkl}^2}\right) \]

coher. optical phonons \(\rightarrow\) incoh. phonons: "heat" \(\rightarrow\) coher. acoustic phonons: lattice expansion
Introduction

Non-adiabatic processes at surfaces: Chemicurrents

Surface femtochemistry

Surface dynamics with electronic friction

Time-resolved probe of structural dynamics

Femtosecond laser spectroscopy

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Questions?
Electron thermalization dynamics in metals and the Two-Temperature Model

Electron dynamics in metals following optical excitation

Fermi-Dirac Distribution

\[ f(E) = \frac{1}{e^{\frac{E_F}{kT_{el}}} + 1} \]

non thermalised electrons

W.S. Fann, R. Storz, H.W. K. Tom, J.Bokor PRB 46 (1992), 13592
time-resolved photoemission spectroscopy

$E - E_F = E_{\text{kin}} + \Phi - h\nu_{\text{probe}}$

probe pulse polarization

$p$-polarized $\Rightarrow$ bulk + surface

$E_{\text{kin}} + \Phi - h\nu_{\text{probe}}$

$p$-polarized

 delay $t$

$\frac{3}{2}$-plates

probe:

$6$ eV, $90$ fs

pump:

$1.5$ eV, $55$ fs

Gd/W(110) film preparation
Aspelmeier et al.,
JMMM 132, 22 (1994)

$\text{Gd/W(110)}$

$\text{e-beam evaporator}$

$\text{UHV chamber}$

$e^{-}$
electronic structure of the Gd(0001) surface


LDOS
charge density difference plot

surface plane

$5d_{z^2}$

Gd(0001)
$\mu = 7.56 \mu_B$

$T=80$ K

$E-E_F$ (eV)

Intensity

$5d_{z^2}$ surf. state
time-resolved photoemission of Gd(0001) bulk

$\Delta t > 100$ fs: thermalized electron distribution function in Gd bulk

s-polarized probe pulse

$\text{thermalization in } \sim 100$ fs

unoccupied

occupied DOS

$\bullet$ thermal e$^-$

$\Delta t > 100$ fs: thermalized electron distribution function in Gd bulk
electron thermalization and cooling in Gd(0001)

characteristic times
- transient changes of electron and phonon temperature
  - excitation: $< 50$ fs
  - relaxation: $\approx 1$ ps

Two Temperature Model (2TM):

$$
C_e(T_{el}) \frac{\partial T_e}{\partial t} = \nabla(\kappa \nabla T_e) - H(T_e, T_l) + S(z, t)
$$

$$
C_l(T_l) \frac{\partial T_l}{\partial t} = H(T_e, T_l) + \nabla(\kappa_{ph} \nabla T_l)
$$

H($T_e, T_l$): thermalized electron distribution
Phonons: Debye Model

good agreement with two-temperature model

TRPE of the Gd(0001) surface: p-pol. probe

$p$-polarized probe pulse

Time evolution of surface state binding energy

time-resolved binding energy of S↑

Transient binding energy of Gd(0001) surface state

\[ \Delta [E(S^\uparrow) - E_F] (\text{meV}) \]

\[ E(S^\uparrow) - E_F (\text{meV}) \]

\[ \text{pump-probe delay (ps)} \]

Gd(0001)
\[ T = 40 \text{ K} \]
\[ h\nu_1 = 1.5 \text{ eV} \]
\[ h\nu_2 = 8.0 \text{ eV} \]

\[ 3 \text{ THz} \]

LO phonon frequency
origin of the coherent mode at the surface?

LO phonon derived mode: Surface vibrates with respect to underlying bulk layers

Köhler et al., PRL 24, 16 (1970)
**Estimation of phonon amplitude**

**LO phonon derived mode:**
Surface vibrates with respect to underlying bulk layers

DFT calculations of $S^\uparrow$ binding energy as function of interplane spacing $d_{12}$

\[
\Delta E_B \approx 1 \text{ meV} \iff \Delta d_{12} \approx 0.2\% \cdot d_{12}
\]

(equilibrium value $d_{12} = 2.8 \text{ Å}$)
Charge density wave (CDW) in TaS\(_2\) or TaSe\(_2\)

TaSe\(_2\): hexagonal layered structure
strong e-ph coupling ⇒ CDW at 300 K

quasi 2D crystal
1T-TaSe\(_2\)


charge transfer
\[ \sim e/2 \]

rearrangement of electronic structure:

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>a</td>
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<td>b</td>
<td>6</td>
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<td>c</td>
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UCO
(upper cluster orbitals)
metal-insulator transition in bulk TaS$_2$

Mott transition controlled by CDW (overlap ⇔ bandwidth)


phase diagram

Crossover

insulator

metal

photoemission spectra

$\nu = 6$ eV

ARPES Intensity

$T_e / W$

$U/W$

 Binding Energy (eV)

0.4 0.0

0.1 0.01
time-resolved ARPES: $T = 30$ K

**UCO peak shift (meV)**

- **Bulk**
- **Surface**

**Pump-probe delay (ps)**

<table>
<thead>
<tr>
<th>Frequency (THz)</th>
<th>Bulk</th>
<th>Surface</th>
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<tbody>
<tr>
<td>2.2</td>
<td></td>
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<tr>
<td>2.5</td>
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<tr>
<td>2.8</td>
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See Demsar et al., PRB 66, R041101

Beating between two modes.
Coherent CDW excitation

- In phase “breathing” of the metal clusters
- Large coupling and low damping
Summary III

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Attosecond laser spectroscopy

- High harmonic and attosecond pulse generation
- Electron streak camera and Auger decay