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DPG Spring Meeting - Surface Science
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Structural Dynamics at Surfaces: Current State and Prospects of tr-RHEED

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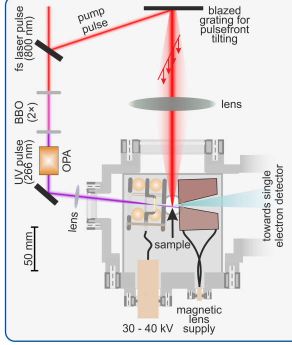
TR-RHEED: Ultrafast Electron Diffraction at Surfaces

Scientific Questions and Motivation:

- Subsequent to optical excitation and excitation of electron system the lattice system reacts on a longer timescale
- Displacive excitation ≈ 100-400 fs
- Electron-phonon coupling on ps timescale
- Thermalization in lattice system ≈ 10-100 ps
- What are techniques to study ultrafast surface dynamics?
  - Electron diffraction (tr-LEED & tr-RHEED)
  - Not yet tr-XRD, tr-STM with THz radiation
  - Indirect techniques: tr-SHG, tr-ARPES, optical reflectivity spectroscopy
  - **Here:** time-resolved reflection high energy electron diffraction



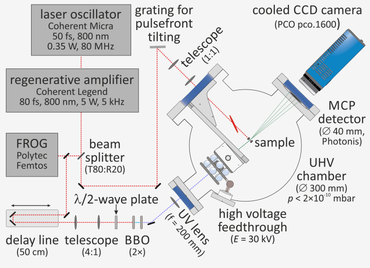
Sub-100 fs Diffraction Setup:

- Photocathode:
  - UV pulses from OPA to vary hν → Reduction of initial energy spread ΔE
  - Au film thickness variation → Optimization of work function
- Probe beam:
  - E_e = 30-40 keV
  - E_{acc} > 10 keV/mm
  - Magnetic lens behind sample → Short drift region < 5 mm
- Single electron detection (TVIPS)
- Apparatus mounted to optical stage

Future Setup Improvements:

- Modification of accessible excited electronic states by optical parametric amplifier (Light Conversion / Coherent TOPAS-Prime, λ = 1.16-2.60 µm)
- Excitation of surface systems with THz radiation
- UV laser diode to access ns - ms time scales (also in SPA-LEED)
- Single electron detection with direct detector (TVIPS TemCam XF416 on UHV DN 160 CF flange)

Experimental Setup: Laser System and UHV Chamber



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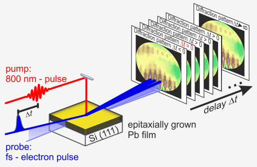
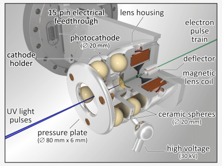
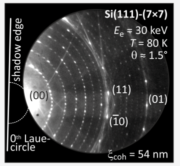


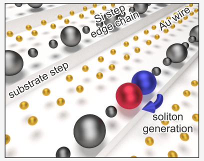


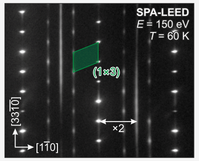


Time-resolved RHEED:

- *in-situ* sample preparation and characterization in UHV: $p < 2\times10^{-10}$ mbar, 20 K < T < 1550 K
- Pump laser at λ = 800 nm, f_{rep} = 5 kHz, τ_{pump} = 80 fs, Φ = 0-14 mJ/cm²
- Probe at E_e = 30 keV minimizes temporal broadening of e-pulse
  - Surface sensitivity by grazing incidence (1°-6°)
  - Pulsefront tilting by 71°
- Overall temporal resolution: $TIRF_{opt}$ = 330 fs FWHM
  - Focussed 3rd harmonic UV pulses matches work function of 10 nm Au/sapphire photocathode
  - Low inital energy spread ΔE = 0.1 eV
  - High acceleration field E_{acc} = 7.5 kV/mm
- Magnetic lens and XY deflector
- Ultimate pulse width ≈ 260 fs FWHM, N ≈ 500 e⁻

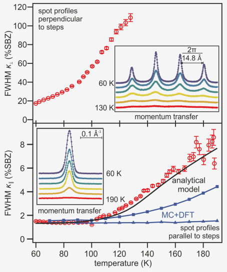
Order-Disorder Transition Driven by Charge Transfer in Au/Si(553)





Equilibrium Structural Dynamics:

- Electron transfer from dimerized Au wire (×2) partially fill dangling bonds (DBs) of Si step edge chain (×3)
- 2D-ordered ground state: 2 DBs filled, 1 DB empty along step edge, in registry with neighboring chains
- Order-disorder transition at 100 K:
  - Generation of solitonic defects
  - Disorder along step edge
  - 2D-1D dimensional crossover



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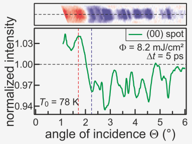
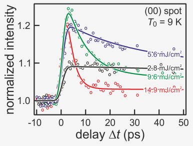
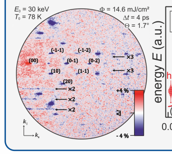
B. Hafke *et al.*, Surf. Sci. **700**, 121673 (2020)

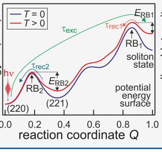
Optically Induced Surface Doping Causes Disorder-induced Metastable State:

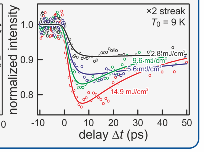
- Rise and decrease of intensity upon excitation → No Debye-Waller origin
- Excitation scenario:
  - Intensity loss of ×2 streaks: Au dimerization reduced
  - Ultrafast (τ < 100 fs) charge transfer from Au wire to Si step edge chain
  - Soliton generation induces disorder in Si step edge chain (τ < 1 ps)
- Relaxation dynamics:
  - Fast time scale determined by transient heating
  - Slow relaxation through metastable states
- Fully reversible excitation and recovery





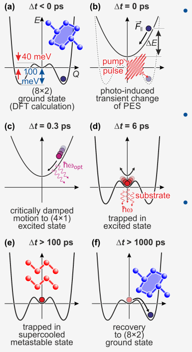




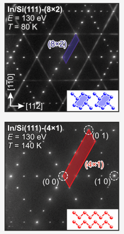


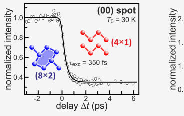
Ultrafast Dynamics of the First Order Phase Transition in In/Si(111)

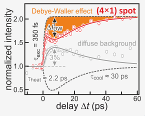
Photo-induced Excitation:



- First order Peierls-like phase transition from (8×2) to (4×1):
  - Periodicity doubling
  - Metal-insulator transition upon cooling below T_c = 130 K
  - Bandgap opening E_g ≈ 200 meV
- Transition in 350 fs:
  - Displacive excitation of ground state
  - Critically damped motion
  - Trapping in metastable state
- Heating delayed at 6 ps

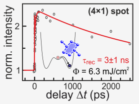


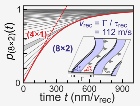


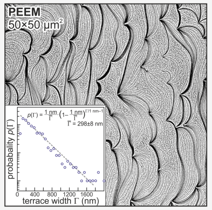


Recovery from Supercooled Metastable (4×1) to (8×2) Ground State:

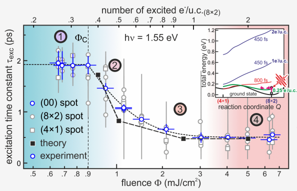
- System trapped in metastable (4×1) state for up to 10 ns
- Slow recovery to ground state
- Velocity of propagating 1D recovery front v_{rec} ≈ 100 m/s
- Recovery time τ_{rec} depends on terrace width Γ

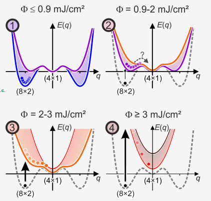






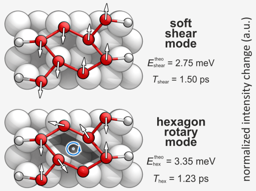
Fluence Dependence of Excitation Process:

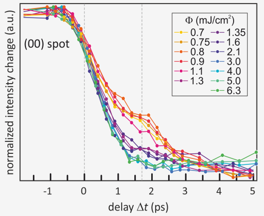




- Excitation depends on fluence Φ
- Threshold for transition at 0.9 mJ/cm²
- Speed of phase transition depends on fluence Φ

Coherent Excitation of Amplitudon Mode:





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M. Horn-von Hoegen, MRS Bulletin **43**, 512 (2018)
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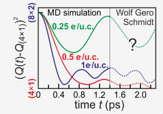
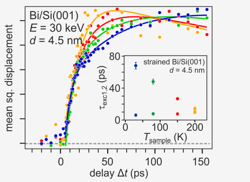
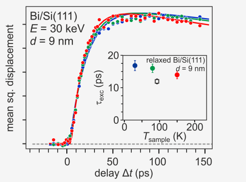
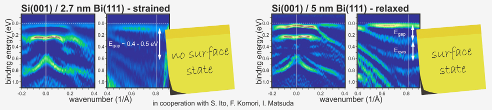


Phonon Dynamics in Bismuth Ultrathin Epitaxial Films on Si(001) and Si(111)

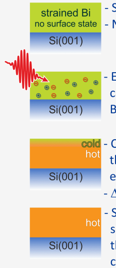
Impact of Surface State on Phonon Excitation:



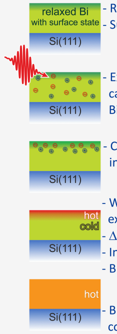




in cooperation with S. Ito, F. Komori, I. Matsuda



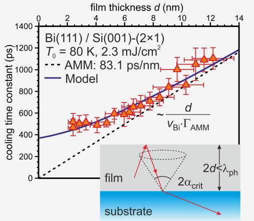
- Strained Bi(111)
- No surface state
- Excitation of carriers in Bi bulk
- Carriers heat Bi bulk through strong e-phonon coupling
- Δ*t* = 2-3 ps
- Slow excitation of surface phonons through anharmonic coupling to bulk
- Strong *T* dependence

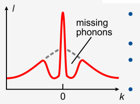


- Relaxed Bi(111)
- Surface state
- Excitation of carriers in Bi bulk
- Carriers trapped in surface state
- Weak e-ph coupling excite surface phonons
- Δ*t* = 12-15ps
- Independent on *T*
- Bulk phonons not excited
- Bulk heated through coupling to surface

Violation of Equipartition in Phonon Phase Space:

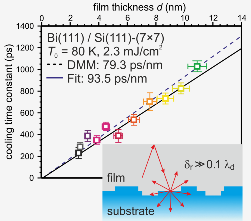
Acoustic Mismatch Model

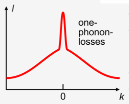




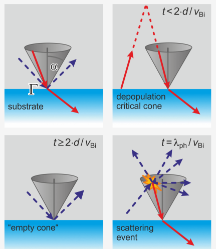
- Conservation of momentum
- Snell's law
- Refraction and total internal reflection
- Phonon losses

Diffuse Mismatch Model





- Rough interface
- Violation of momentum conservation
- Diffuse scattering
- Density of states determines transmission



Manipulation of Phonon Transport at Bi/Si Interface:

- Ballistic phonon transport for abrupt interfaces
- Depopulation of specific phonon states, so-called critical cone, after less than 3 ps
- Repopulation of empty cone by thermalization in phonon system (Umklapp and normal scattering)
- Observable in diffusively scattered intensity
- Manipulation of phonon scattering:
  - Roughening of the surface / interface
  - Adsorbates / subsorbants at surface
  - Change of interface reconstruction