Nanoscale thermal transport during ultrafast melting and crystallization of Ag and Si

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Femtosecond laser excitation

- **fs laser pulse**
- **Electronic system**
  - Electrons at thermal equilibrium
    - $\sim 100$ fs
    - $\sim$ e-p coupling
      - 0.1 to 3 ps
  - $\sim$ 100 fs
- **Phonon system**
- **Non-thermal melting ?**

- Heat transport to the bulk determines the thickness of the melt
- Little is known about transport properties in a strongly excited electronic system

Thermal melting
Outline

- Experimental details: third harmonic generation as a probe of melting and crystallization
- Ultrafast melting of Ag at 350 m/s.
- Ultrafast crystallization of Ag at 75 m/s.
- Compare and contrast with ultrafast laser processing of Si
Third harmonic (TH) probe of ultrafast phase transformations

- Third harmonic generation using circularly polarized probe light is zero from isotropic liquid and finite from a (001) oriented crystal
pump and probe beams
- wavelength 800 nm
- FWHM ~ 140 fs
Heat confinement in melting of Ag

- At low laser fluence, depth of energy deposition is known to be large ~300 nm.
- At high laser fluence, the melting threshold is independent of thickness for h>100 nm.
Heat confinement by thermally generated holes in the d-band

Near melting:
\[ T_e \sim 1.5 \times 10^4 \text{ K} \]
\[ k_B T_e \sim 1.3 \text{ eV} \]

**d-band holes**
- Strengthen e-p coupling
- Increase e-e scattering and decrease thermal diffusivity

Zhigilei et al.
Calibrate the extinction depth at high fluence

Extinction depth increases with probe fluence.

At low electron excitation, agree with the optical properties of Ag.
Melting dynamics of Ag

200 nm Ag(001) on MgO(001)

Stage I – initial melting
- $t \sim 3$ ps
- e-p coupling is fast due to the excitation of d-band electrons (Zhigilei et al. (2008), Au: Miller et al.(2007)).

Stage II – propagation of melt front into super-heated solid
- Velocity $\sim 350$ m s$^{-1}$
- Continues up to $\sim 30$ ps (a long time considering the high thermal conductivity of Ag)

Chan, Averback, Cahill, Lagoutchev PRB 78, 214107 (2008)
Weak electron-phonon coupling inhibits heat conduction at long times

Surprising result from our two temperature model: electrons are colder than the lattice temperature during stage II of melting.

Hence:
- Short time, $t < 3$ ps, $T_e >> T_{ph}$
- Long time $T_{ph} > T_e$
Control of undercooling in crystallization

- Ag film is a good heat conductor compared to the Ag/MgO interface and the MgO substrate.
- undercooling $\Delta T$ increases with film thickness $\Delta x$
- $\Delta T$ determined by solving heat diffusion equation
Slope proportional to the velocity of the solidification front
Thermally activated: \[ v(T) = C \exp\left(-\frac{Q}{k_B T}\right) \left[1 - \exp\left(-\frac{\Delta \mu(T)}{k_B T}\right)\right] \]

using \( Q = 0.12 \text{ eV} \)

Collision Limited Model:

\[ v(T) = \frac{a}{\lambda} \sqrt{\frac{3kT}{m}} f\left(1 - \exp\left(-\frac{\Delta \mu}{kT}\right)\right) \]

Chan et al., PRL 2009
Si melting and crystallization
Si melting and crystallization

- At just above threshold, can melt the top 20 nm of Si
- But we never see the melt propagate into the crystal
  - melt/crystal is a metal/semiconductor interface; thermal conductance of this interface is small (?) and any heat that can enter the crystal is rapidly conducted away.
  - optical absorption depth is longer than in a metal; non-linear effects important and hard to model.
• TH signal from Si(001) decreases with increasing temperature.

• Calibrate to T=600°C vs. thermocouple; another calibration point at melting point.
Two-photon absorption and Auger recombination in Si

- Two-photon absorption and Auger recombination in Si

- Normalized dR/R vs. Delay time (ps)

- Laser fluence vs. Carrier density (cm⁻³)

- Recombination time vs. Carrier density (cm⁻³)

- 785 nm data

- 760 nm data

- n linear at 785 nm

- n linear at 760 nm

- 1/Cn²

- Saturated, Ref. [x]
Coupling of electrons and phonons in Si changes at high carrier density

- Time-resolved incoherent anti-Stokes Raman scattering directly measures population lifetimes.
- At high carrier densities, cooling time of electron-holes and optical phonon lifetime converge to 0.4 ps, consistent with melting time.

![Graph showing lifetime vs. electron-hole pair density](image)

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Conclusions

- Third harmonic generation is a convenient probe of ultrafast phase transformation in materials.
- Thermal generation of holes in the d-band strongly confines energy deposition to the top 30 nm of Ag film.
- Weak electron-phonon coupling in Ag inhibits cooling of the lattice at long times and facilitates propagation of the melt front.
- Degree of undercooling can be engineered for fundamental studies of ultrafast crystal growth.
- Many unknowns remain in ultrafast laser processing of silicon: optical properties, electron-phonon coupling, homogenous melting(?), interface conductance of liquid-Si/c-Si interface.