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

David G. Cahill,
Wai-Lun Chan, Kwangu Kang, Wen-Pin Hsieh, R. S. Averback

Materials Research Lab and Department of Materials Science, University of Illinois, Urbana, IL

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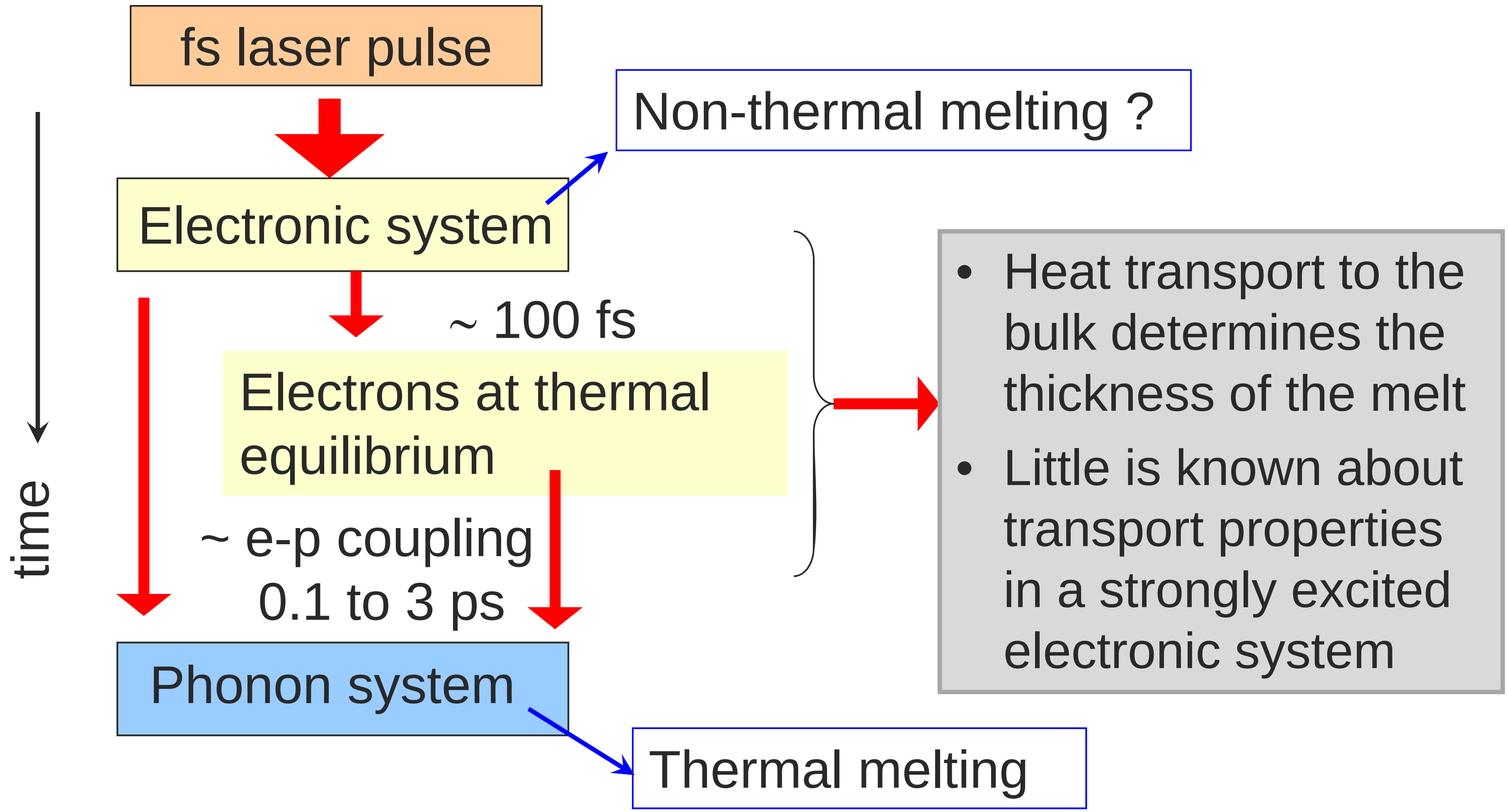
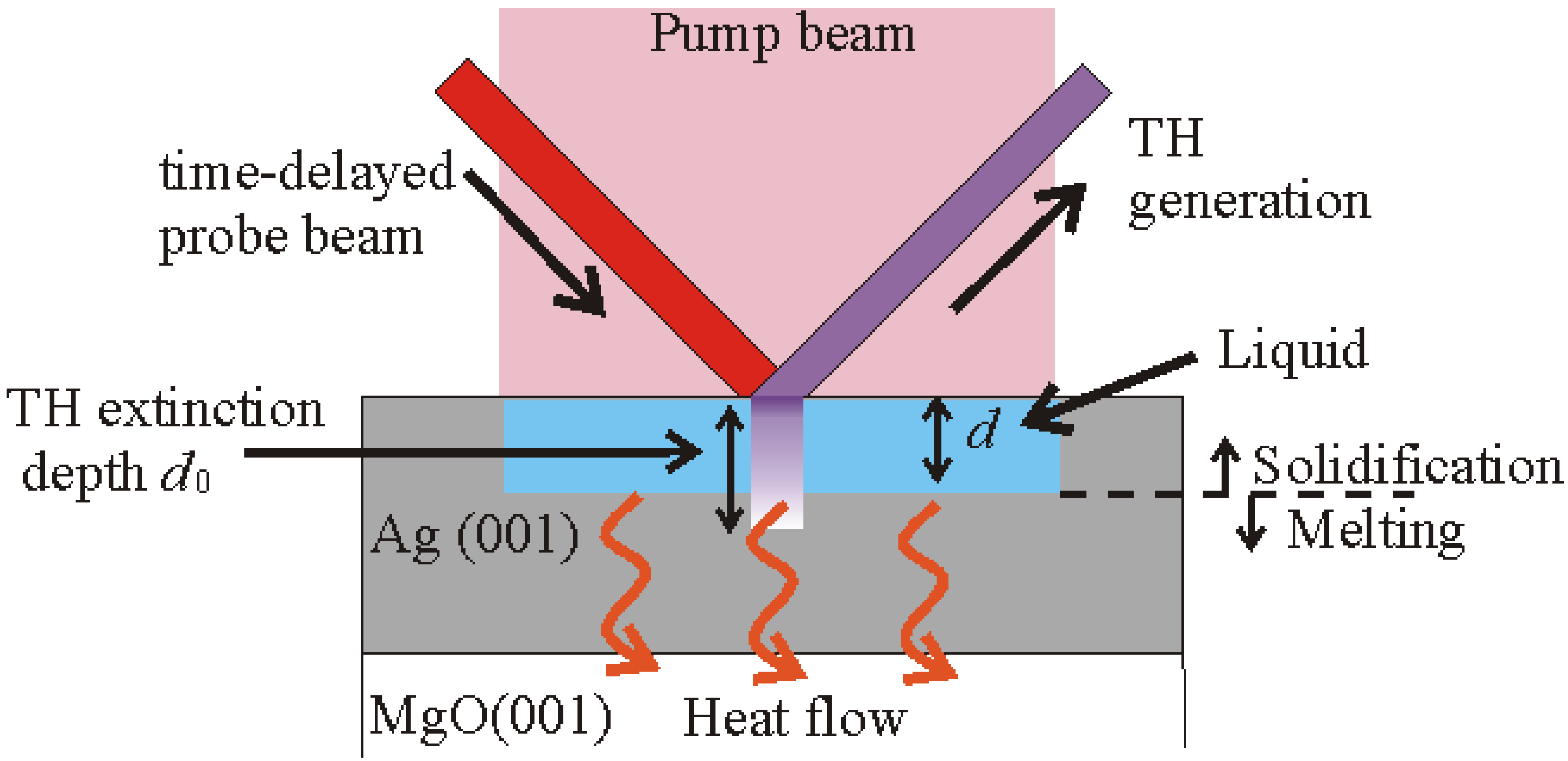
Femtosecond laser excitation



Outline

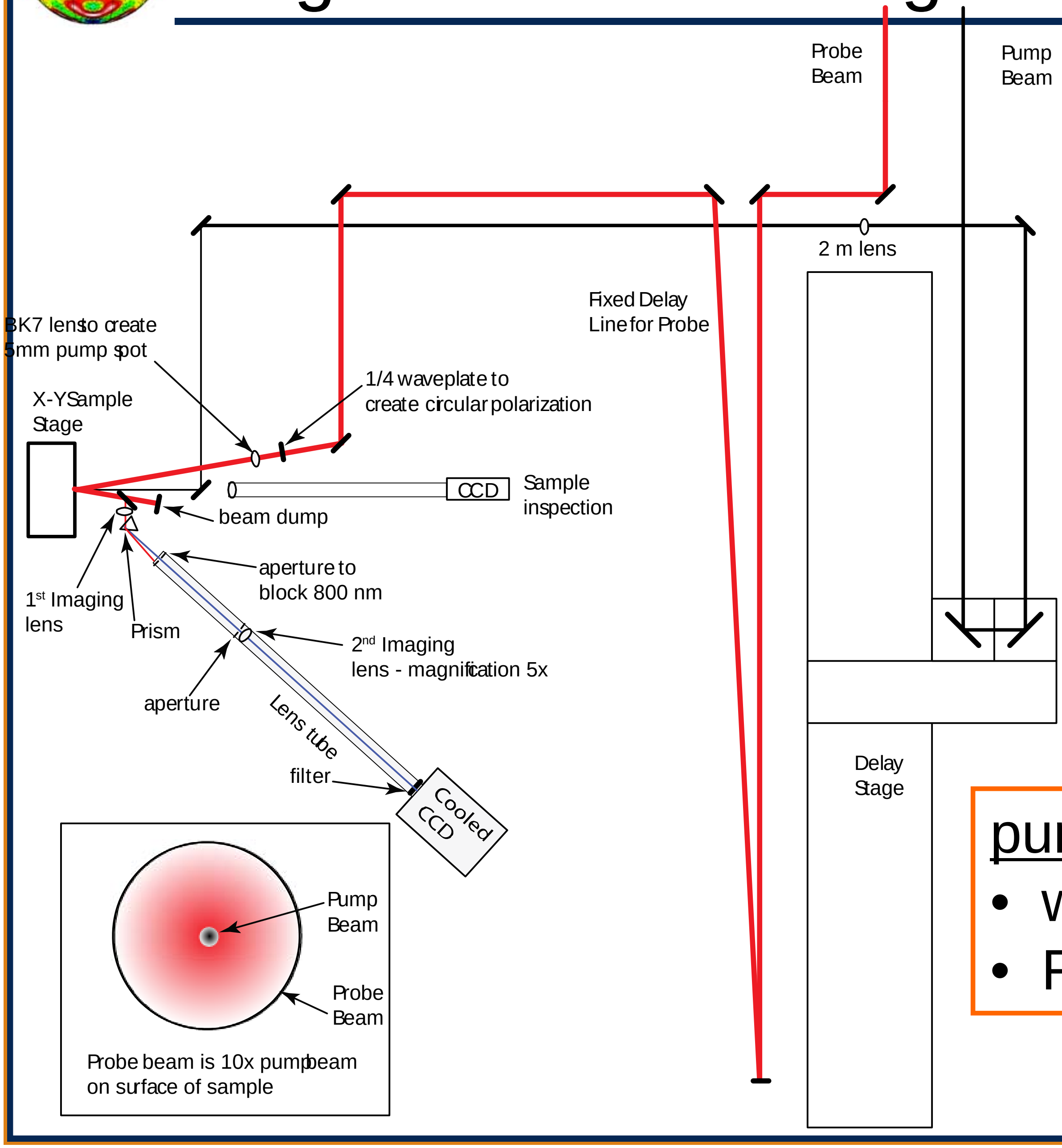
- Experimental details: third harmonic generation as a probe of melting and crystallization
- Ultrafast melting of Ag at 350 m/s.
- Ultrafast crystallization of Ag at 75 m/s.
- Compare and contrast with ultrafast laser processing of Si

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

Image third harmonic generation on CCD

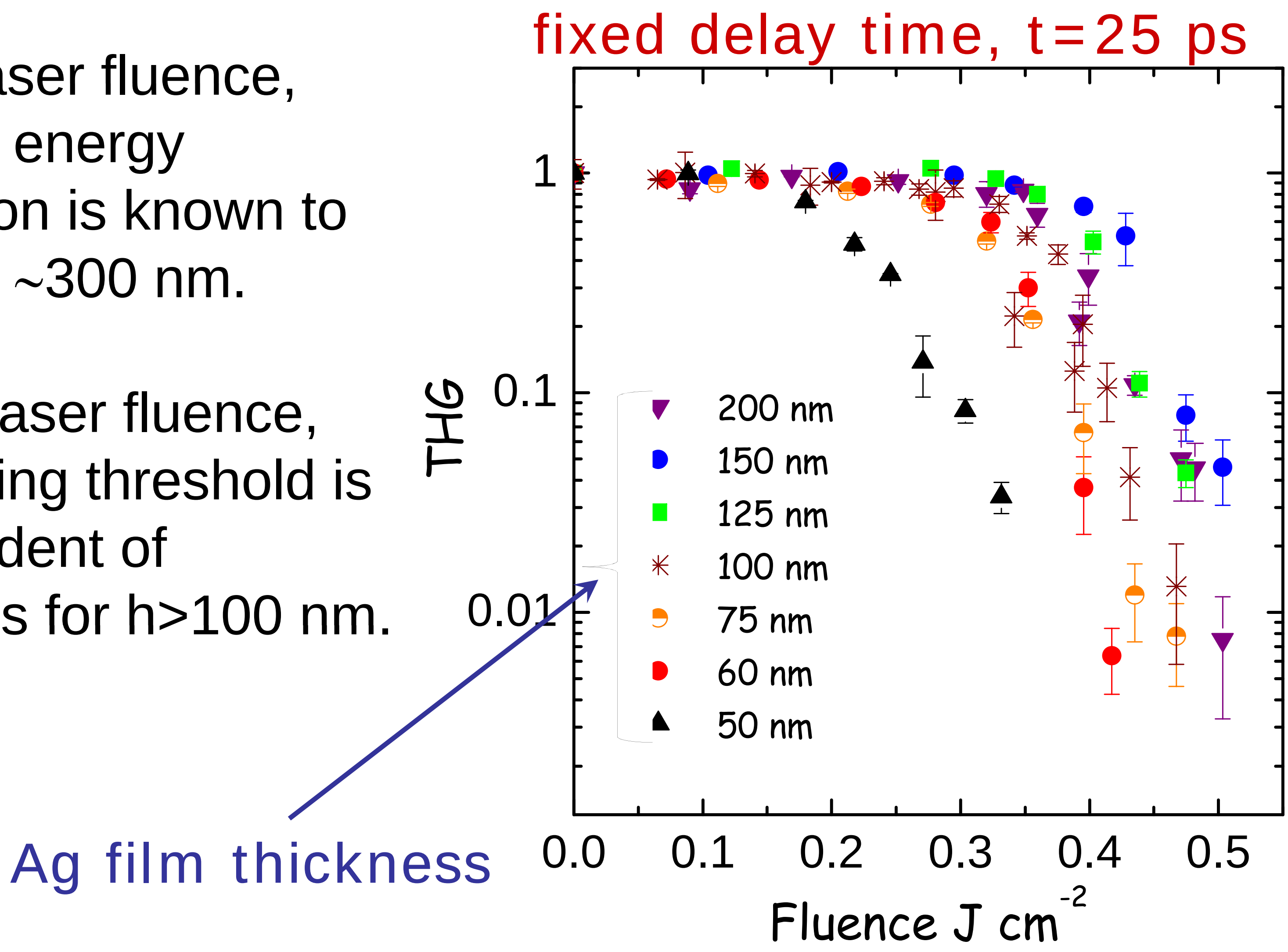


<u>pump and probe beams</u>

- 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.

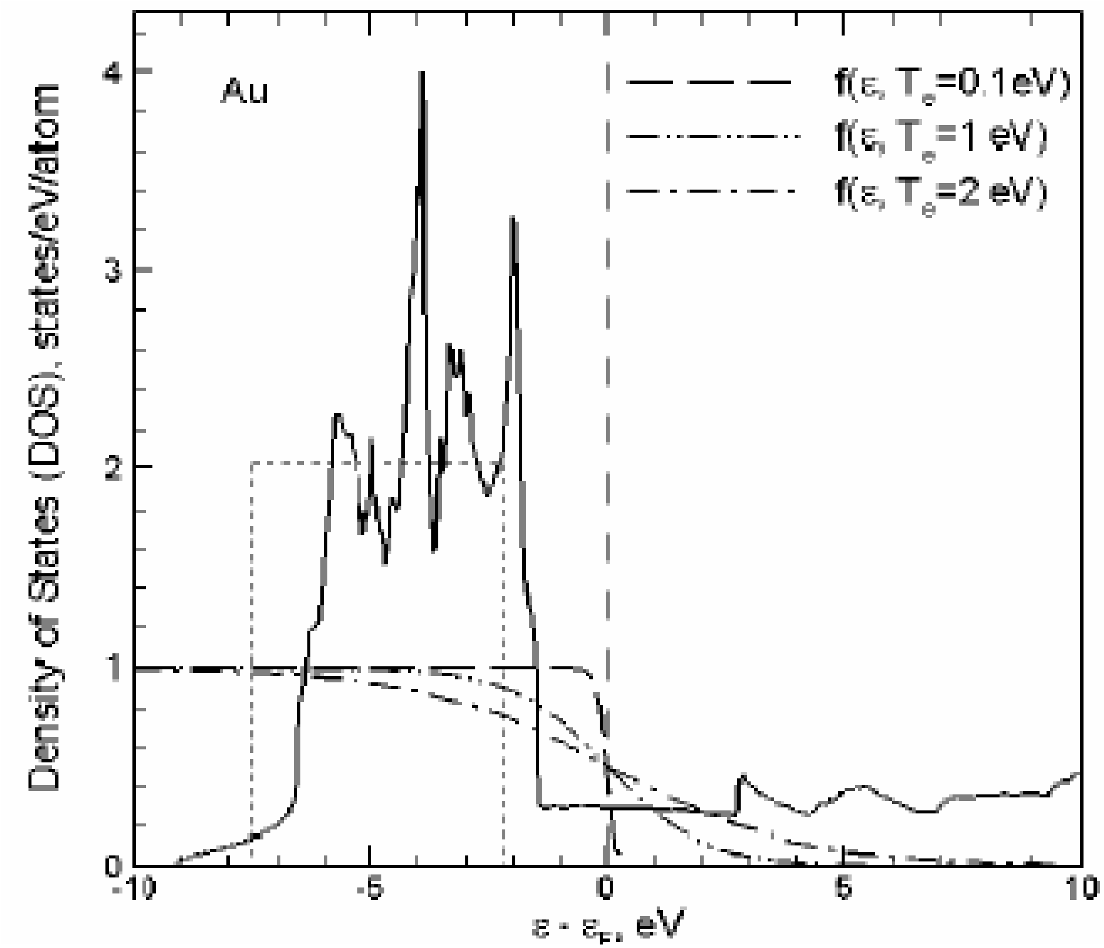


Heat confinement by thermally generated holes in the d-band

Near melting:
$T_e \sim 1.5 \times 10^4$ K
$k_B T_e \sim 1.3$ eV

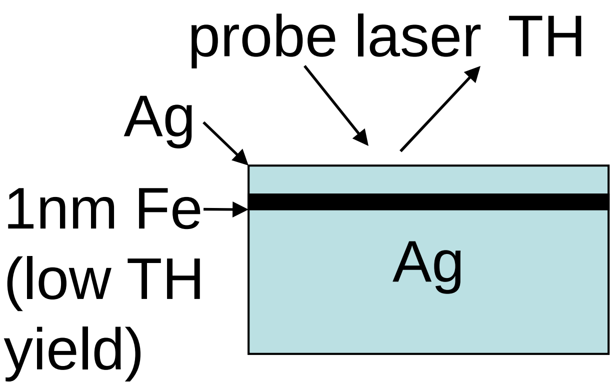
d-band holes

- Strengthen e-p coupling
- Increase e-e scattering and decrease thermal diffusivity



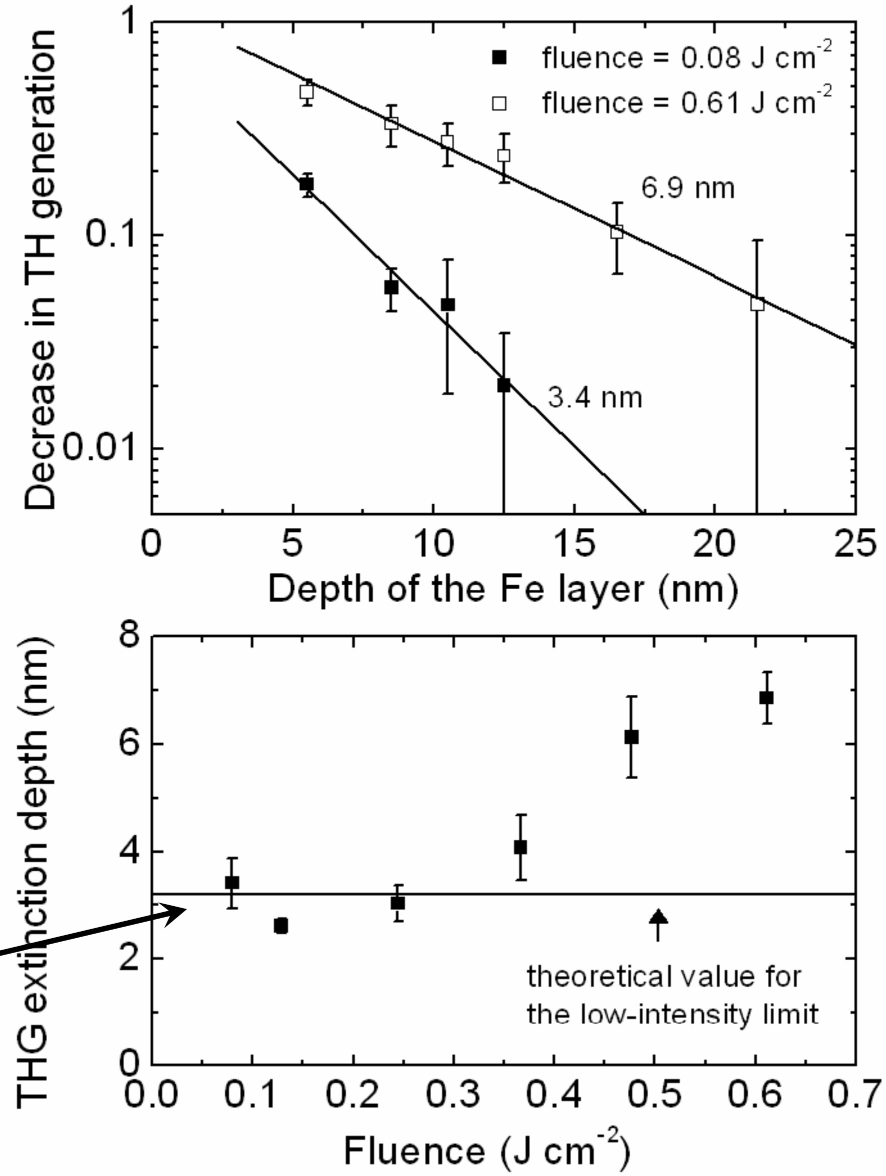
Zhigilei et al.

Calibrate the extinction depth at high fluence

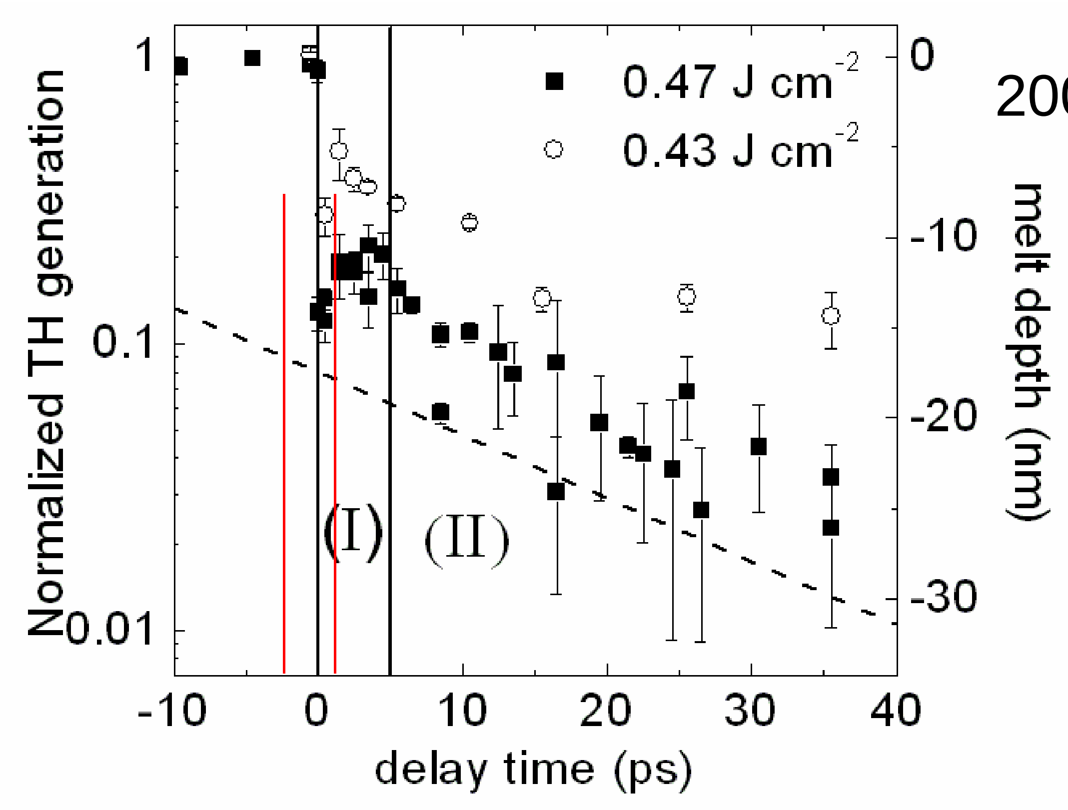


Extinction depth increases with probe fluence.

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 ~ 3 ps
- e-p coupling is fast due to the excitation of d-band electrons (Zhigilei et al. (2008), Au: Miller et al.(2007)).

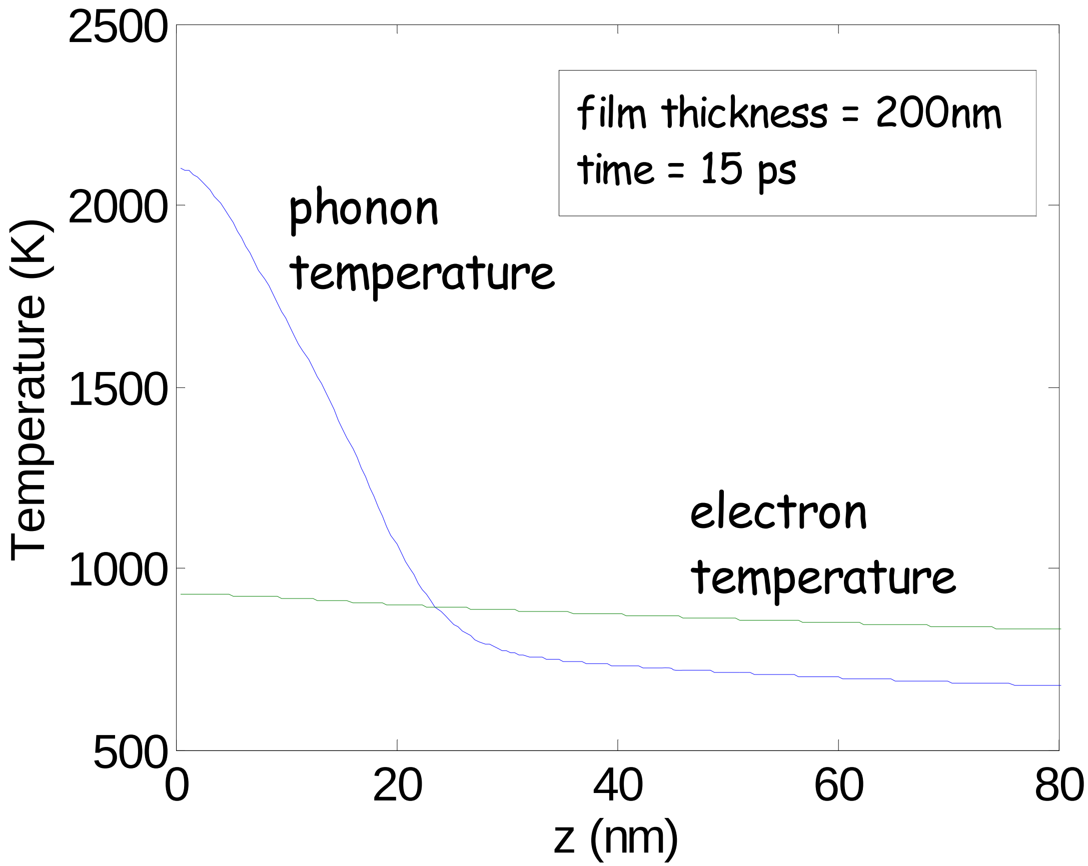
Stage II – propagation of melt front into super-heated solid

- Velocity ~ 350 m s^{-1}
- Continues up to ~ 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

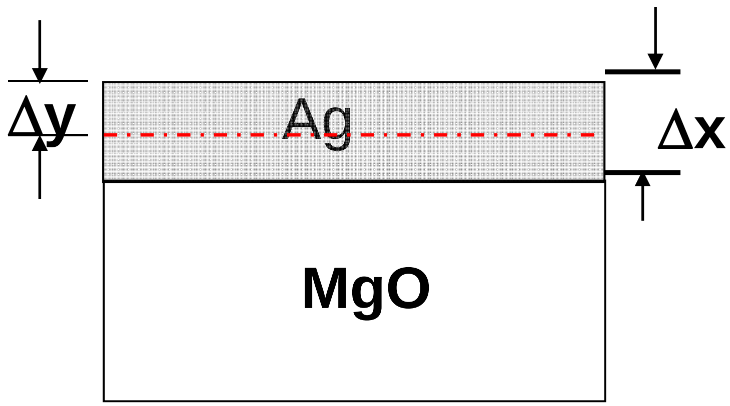
Surprising result from our two temperature model: electrons are colder than the lattice temperature during stage II of melting

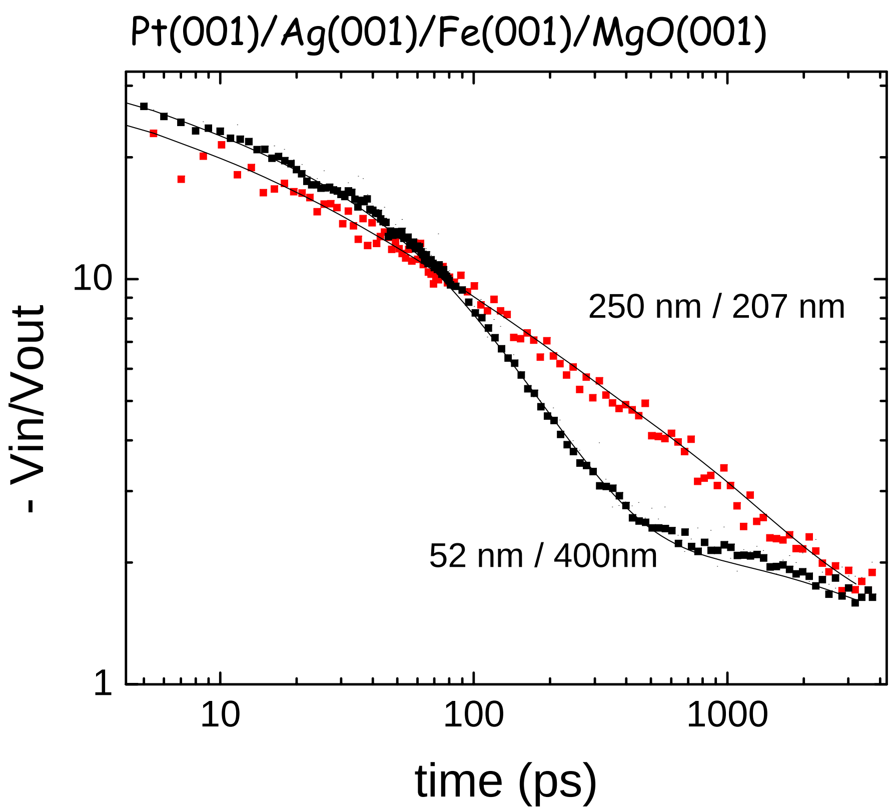


Hence:

- Short time, $t < 3$ ps, $T_e >> T_{ph}$
- Long time $T_{ph} > T_e$

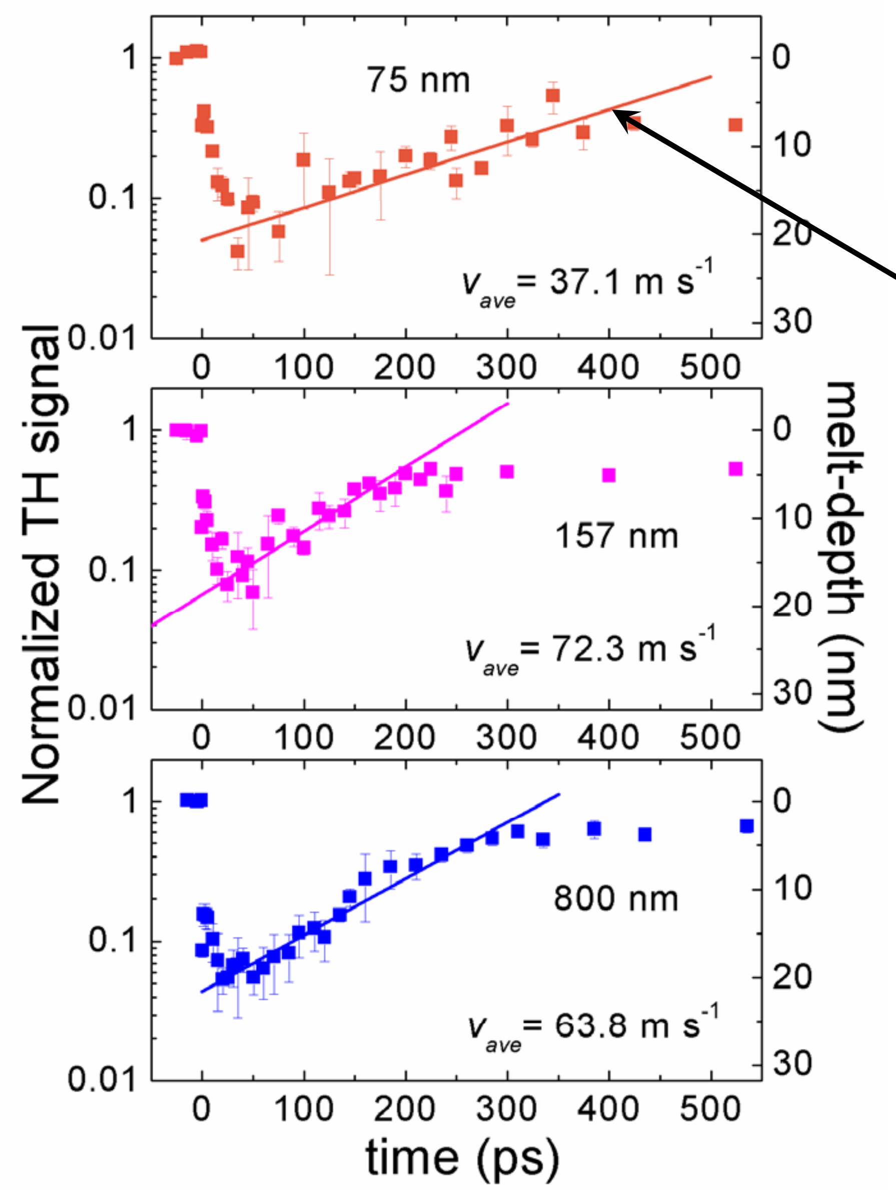
Control of undercooling in crystallization





- Ag film is a good heat conductor compared to the Ag/MgO interface and the MgO substrate.
- undercooling ΔT increases with film thickness Δx
- ΔT determined by solving heat diffusion equation

Ultrafast crystallization of Ag

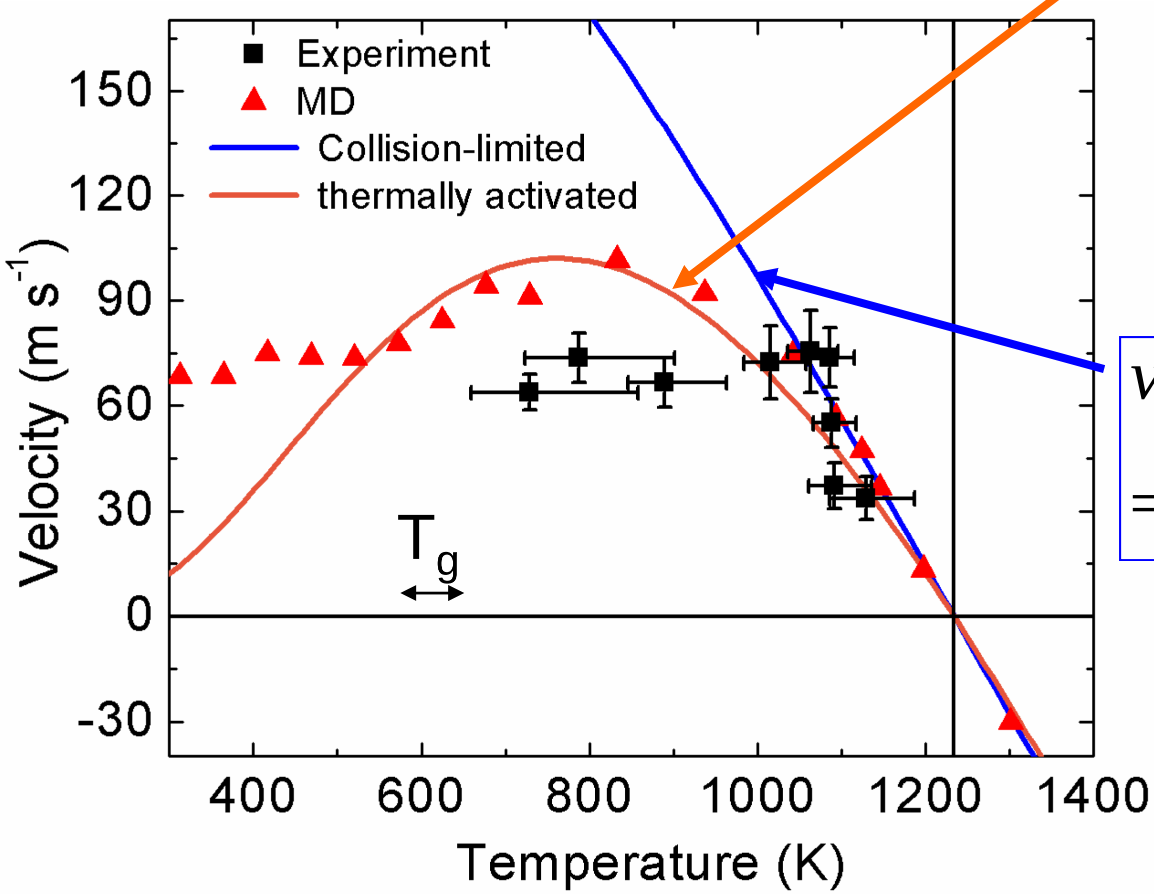


Slope proportional to the velocity of the solidification front

Solidification rate versus undercooling

Thermally activated: $v(T) = C\exp(-Q/k_BT)\left[1-\exp(-\Delta\mu(T)/k_BT)\right]$

using Q = 0.12 eV

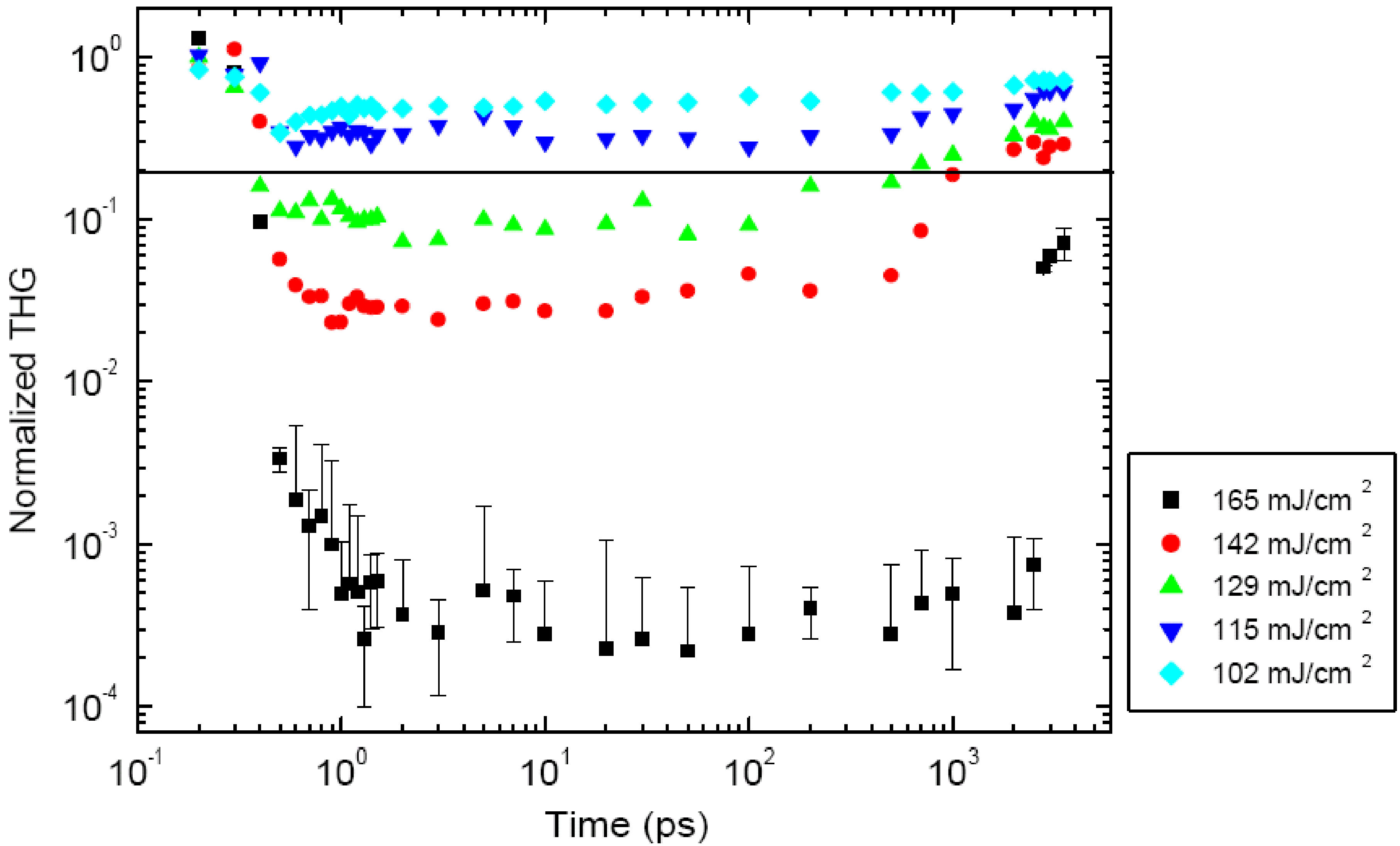


Collision Limited Model:

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

Chan et al., PRL 2009

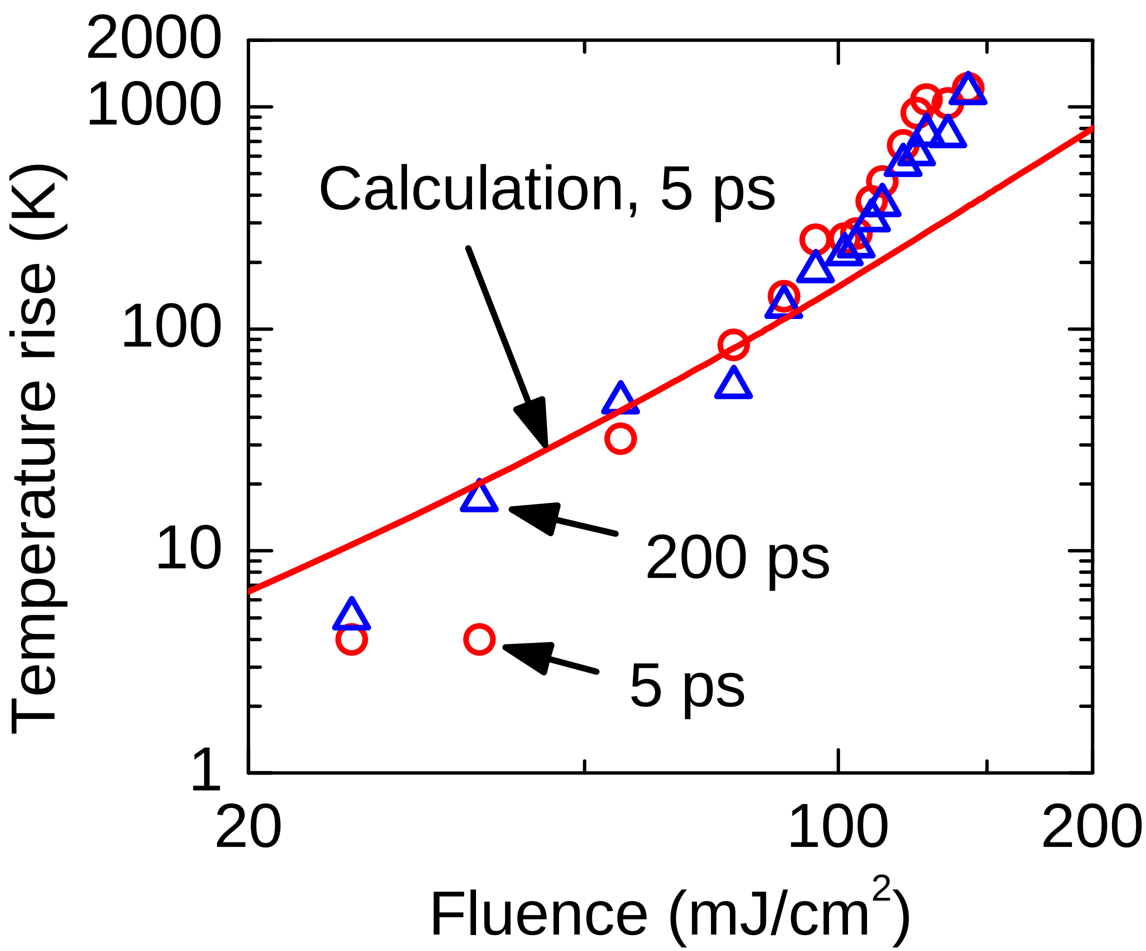
Si melting and crystallization



Si melting and crystallization

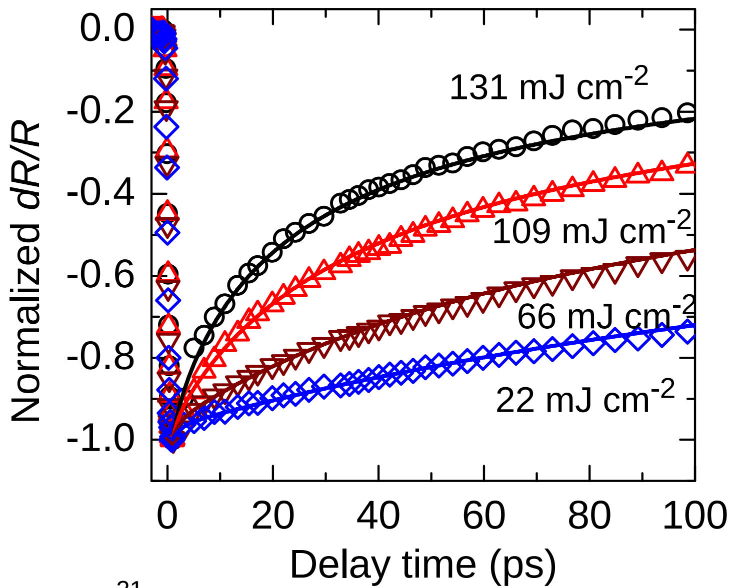
- At just above threshold, can melt the top 20 nm of Si
- But we never see the melt propagate into the crystal
  - melt/crystal is a metal/semiconductor interface; thermal conductance of this interface is small (?) and any heat that can enter the crystal is rapidly conducted away.
  - optical absorption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

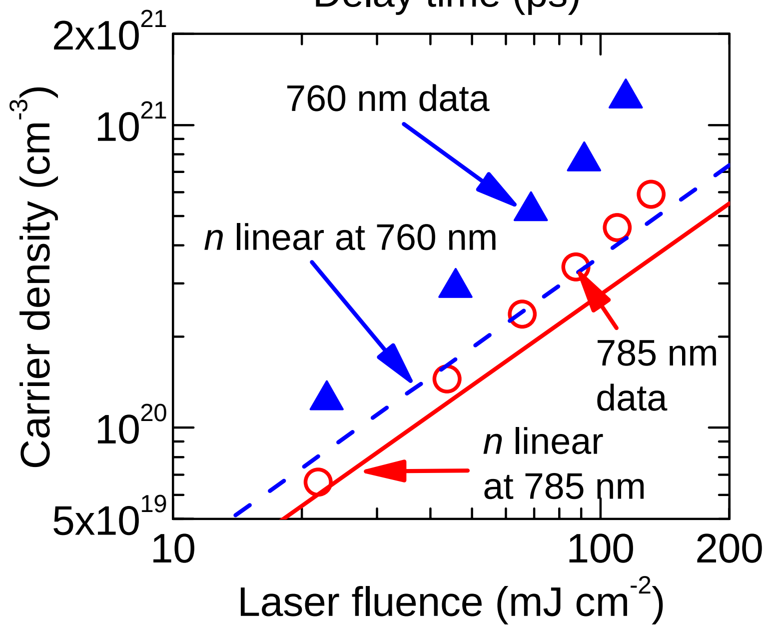
Third harmonic generation thermometry

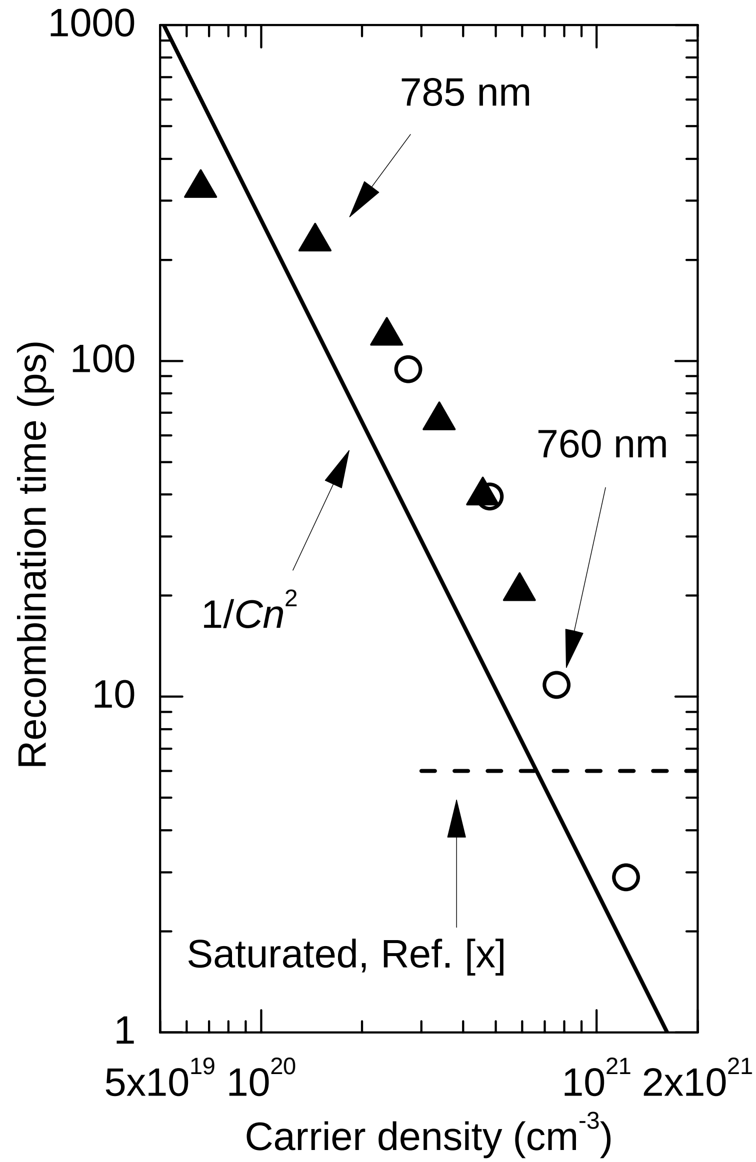


- TH signal from Si(001) decreases with increasing temperature
- Calibrate to T=600°C vs. thermocouple; another calibration point at melting point.

Two-photon absorption and Auger recombination in Si

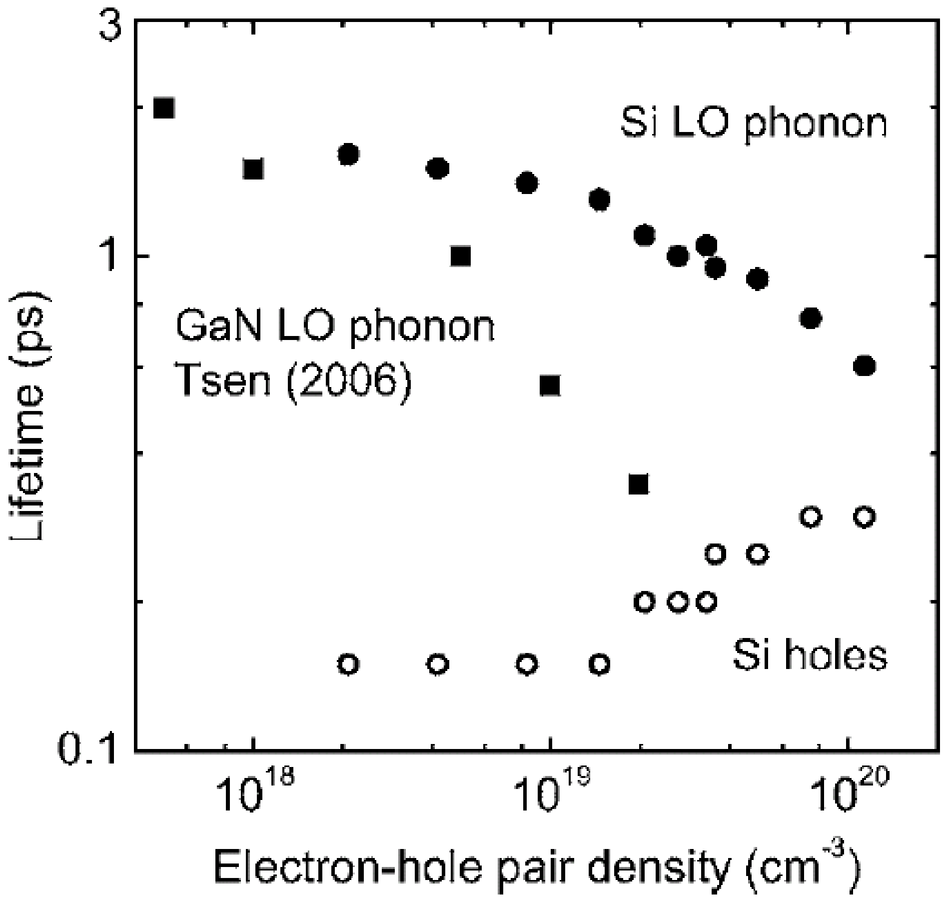






Coupling of electrons and phonons in Si changes at high carrier density

- 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.



Appl. Phys. Lett. **90**, 252104 (2007)

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.