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Phonon Scattering and Thermal Conduction in Nanostructured Semiconductors

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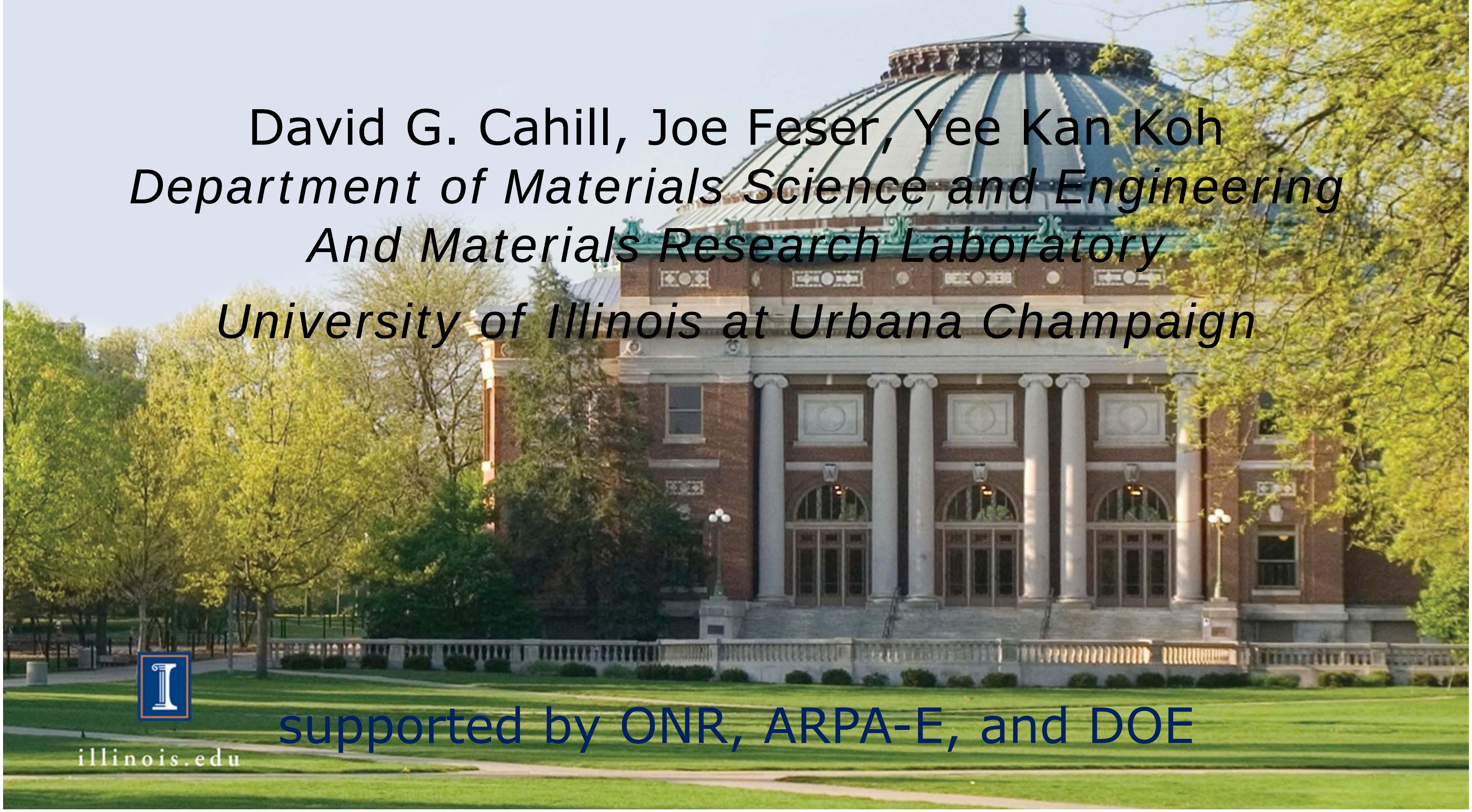

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Outline

- Distribution of phonon mean-free-paths and nanostructure effects on thermal conductivity.
- Thermal conductivity of nanostructured materials
  - GaN/AlN and oxide superlattices
  - PbSe/PbTe nanodot superlattices
  - rough Si nanowires
- Bottom line: not difficult for nanostructuring to make bad thermoelectrics into mediocre thermoelectrics, but difficult to significantly improve good thermoelectrics

Reduce lattice thermal conductivity without (significantly) reducing charge-carrier mobility

ADVANCED MATERIALS
www.advmat.de
Materials Views
www.MaterialsViews.com

Nanostructured Thermoelectrics: Big Efficiency Gains from Small Features

By *Christopher J. Vineis, Ali Shakouri, Arun Majumdar,* and *Mercouri G. Kanatzidis**

Materials Views
www.MaterialsViews.com
ADVANCED ENERGY MATERIALS
www.advenergymat.de

Thermoelectric Nanostructures: From Physical Model Systems towards Nanograined Composites

Kornelius Nielsch, Julien Bachmann, Johannes Kimling, and Harald Böttner*

www.afm-journal.de
ADVANCED FUNCTIONAL MATERIALS

Nanostructured Bulk Silicon as an Effective Thermoelectric Material

By *Sabah K. Bux, Richard G. Blair, Pawan K. Gogna, Hohyun Lee, Gang Chen, Mildred S. Dresselhaus, Richard B. Kaner,* and *Jean-Pierre Fleurial**

Heat is carried by phonons with a broad distribution of mean-free-paths

- Thermal conductivity is an integral property: difficult to understand and control.
- Simplest case of thermal conductivity where resistive scattering dominates.

$$\Lambda = \frac{1}{3}\int_0^{\omega_c} c(\omega) v_g^2(\omega)\tau(\omega)\,d\omega$$

$c(\omega)$ = heat capacity of phonon mode

$v_g(\omega)$ = phonon group velocity

$\tau(\omega)$ = scattering time

ω_c = cut-off frequency

Make a "Klemens-like" calculation

- Assume linear dispersion for $\omega<\omega_c$ and $\tau^{-1} \propto \omega^2 T$

$$\Lambda = \frac{A}{T}\int_0^{\omega_c} d\omega = \frac{A}{T}\omega_c$$

- Convert to an integral over mean-free-path $l = \frac{B}{\omega^2 T}$

$$\Lambda = \frac{A\sqrt{B}}{2T^{3/2}}\int_{l_c}^{\infty} \frac{1}{l^{3/2}} dl$$

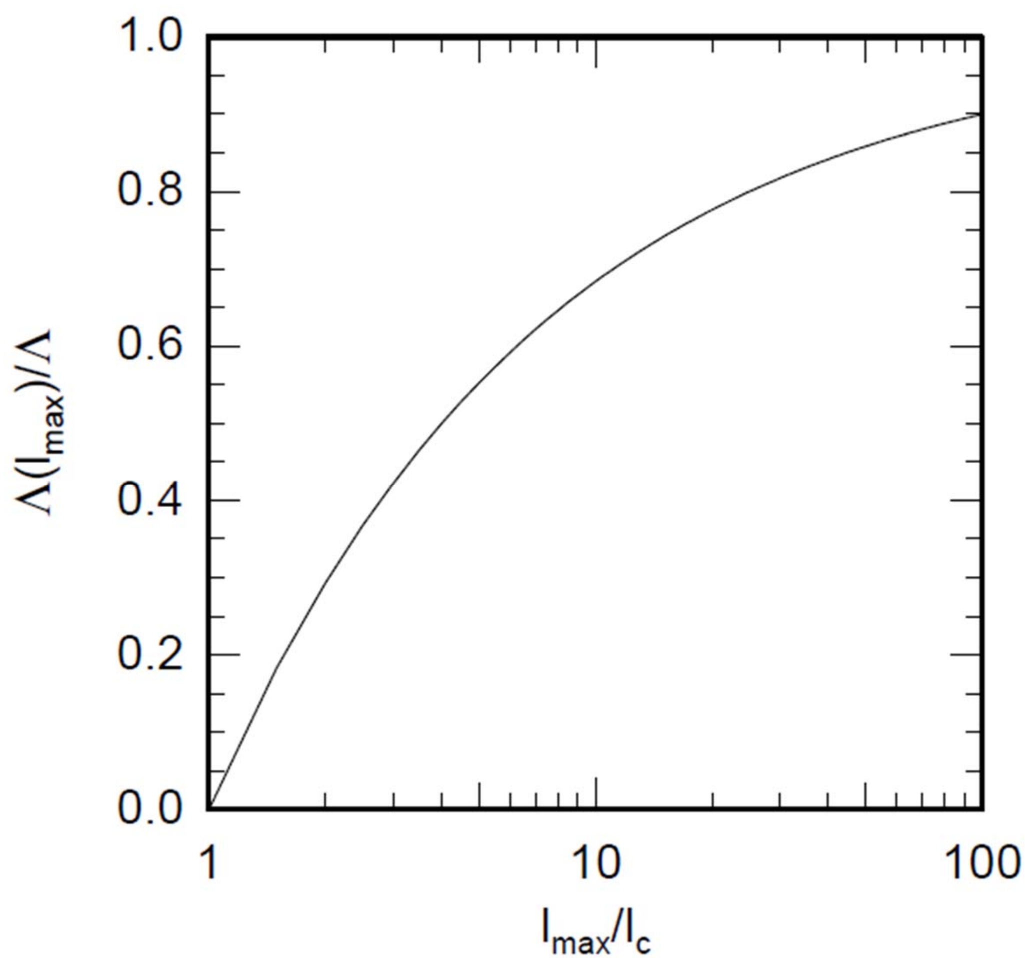
$$\frac{\Lambda(l_{\max})}{\Lambda} = 1 - \left(\frac{l_c}{l_{\max}}\right)^{1/2}$$

ℓ_c is the mean-free-path at the cut-off frequency

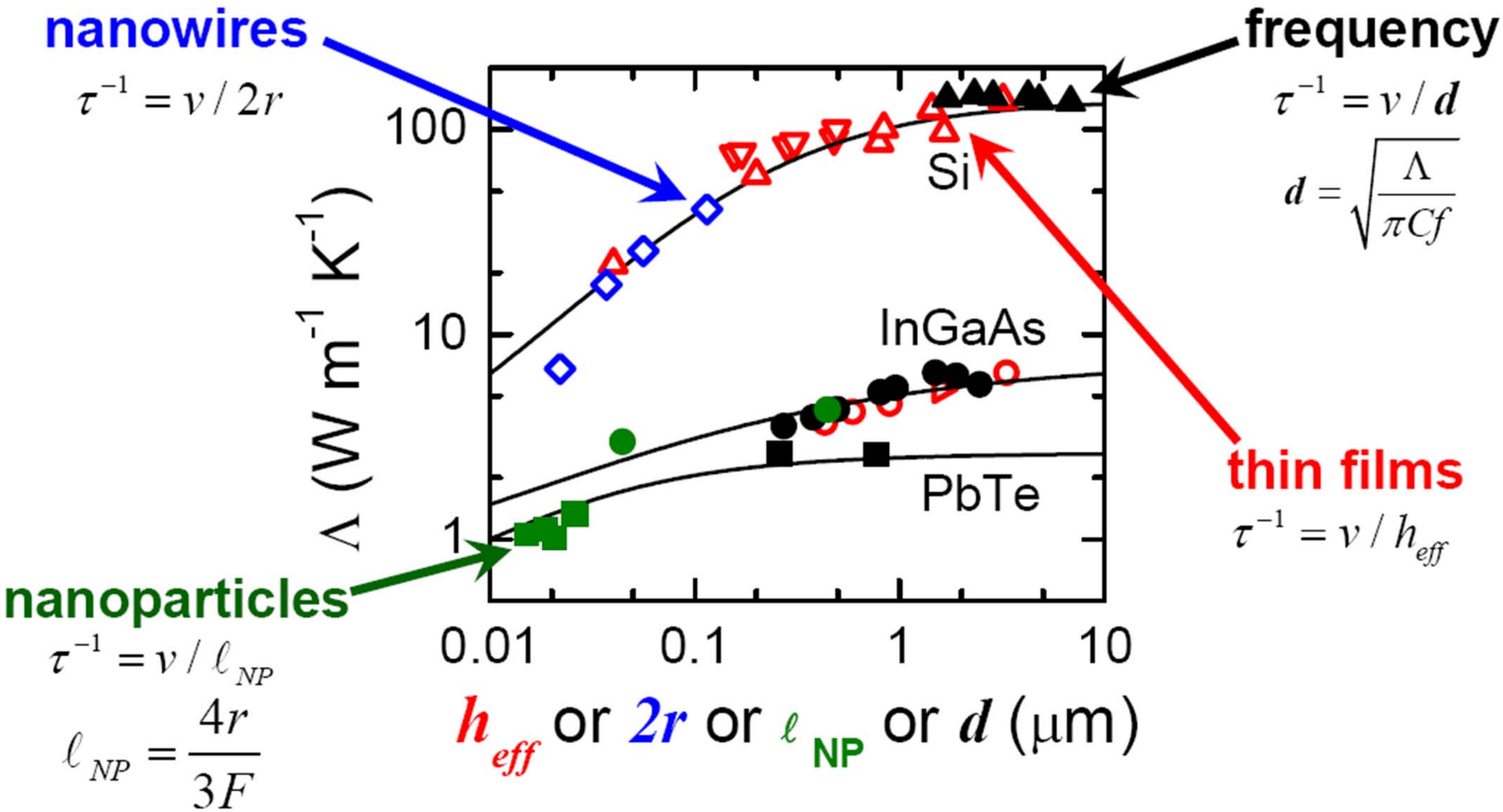
ℓ_{max} is the maximum mean-free-path that contributes to Λ

Heat is carried by phonons with a broad distribution of mean-free-paths

- Phonon scattering by charge carriers or boundaries will narrow the distribution.
- Alloying and point defects will broaden the distribution.
- Relaxational damping will eventually be a limiting factor.
- Details are probably important (scattering rates, normal processes, dispersion…)



Summary of nanostructure effects

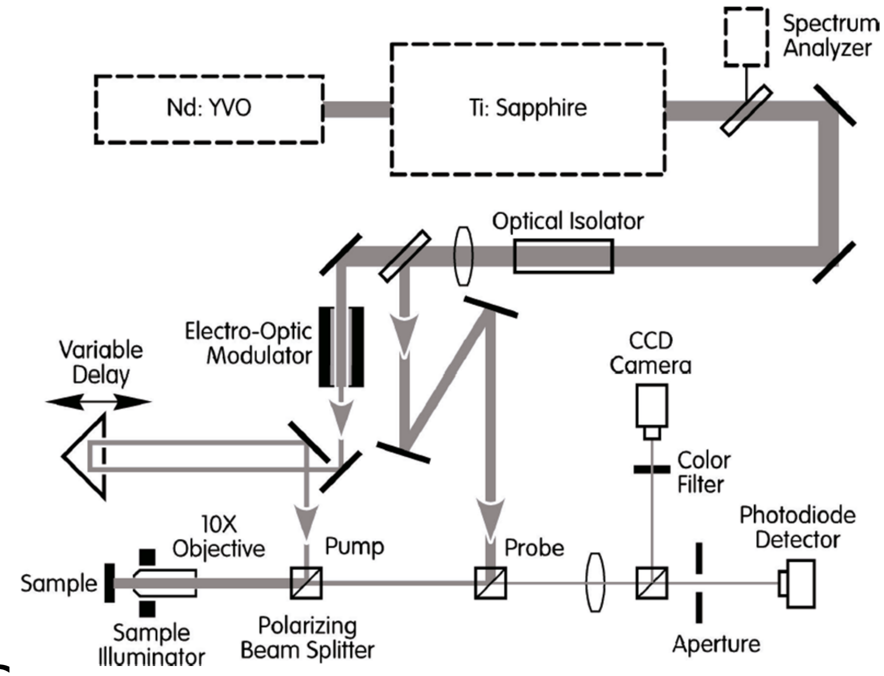


F=volume fraction, r=radius

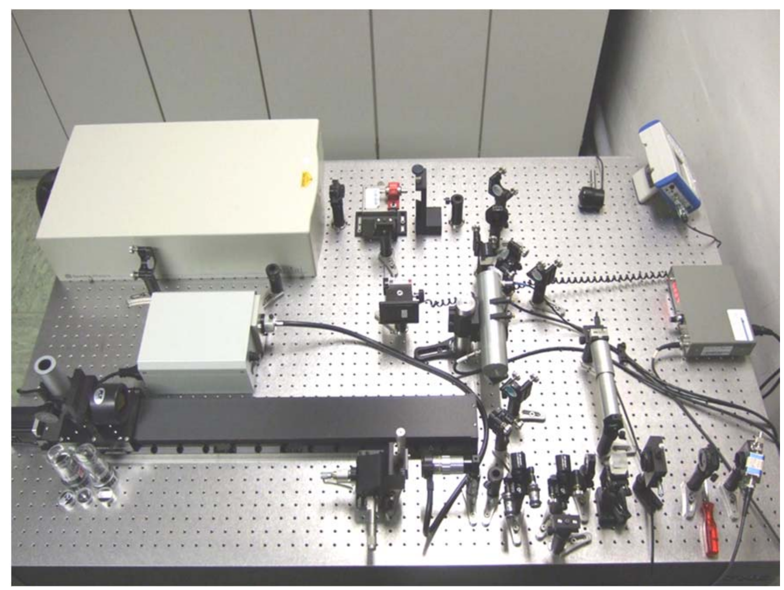
Yee Kan Koh, unpublished

Time domain thermoreflectance since 2003

- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

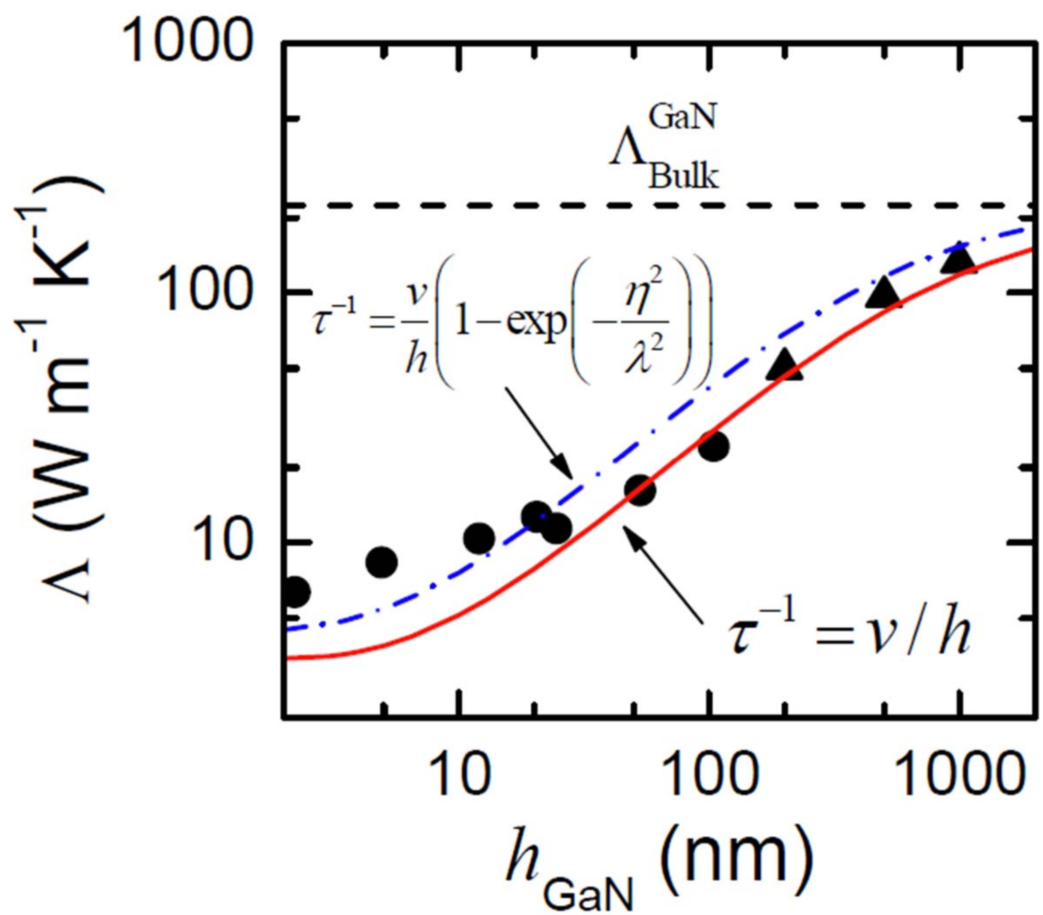


Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008



AlN/GaN superlattices

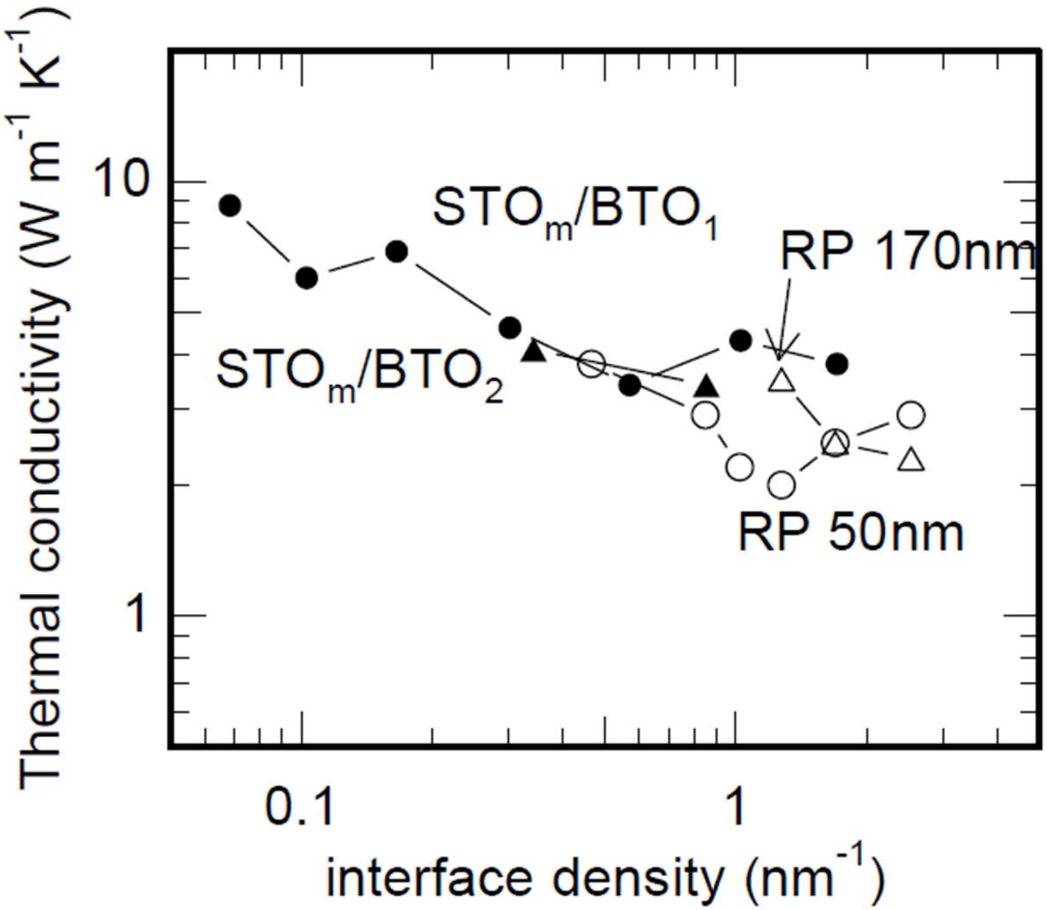
- Strained AlN 4 nm
- Vary GaN thickness 2 < h_{GaN} < 1000 nm
- Data suggest that long wave-length end of phonon distribution is not diffusively scattered
- No evidence of coherent phonon scattering (e.g., minimum created by reduction in group velocity)



Collaboration with D. Jena, Koh *et al*., Adv. Funct. Mater. (2009)

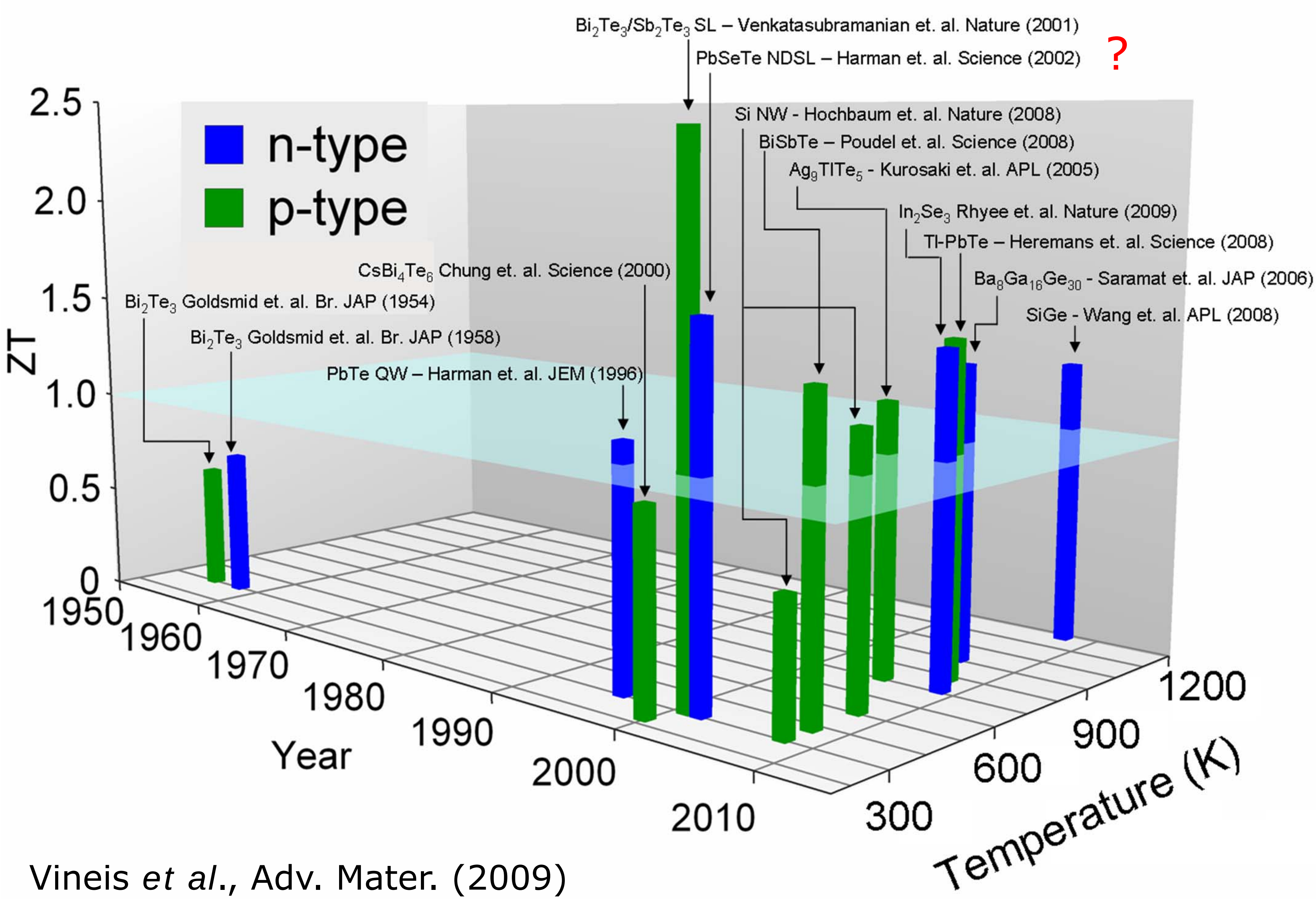
Work in progress: short period perovskite superlattices and RP phases.

- No evidence (yet) of coherent phonon scattering (e.g., minimum created by reduction in group velocity)



Collaboration with Mark Zurbuchen (UCLA) and D. Schlom's group (Cornell)

Progress in increasing figure of merit ZT



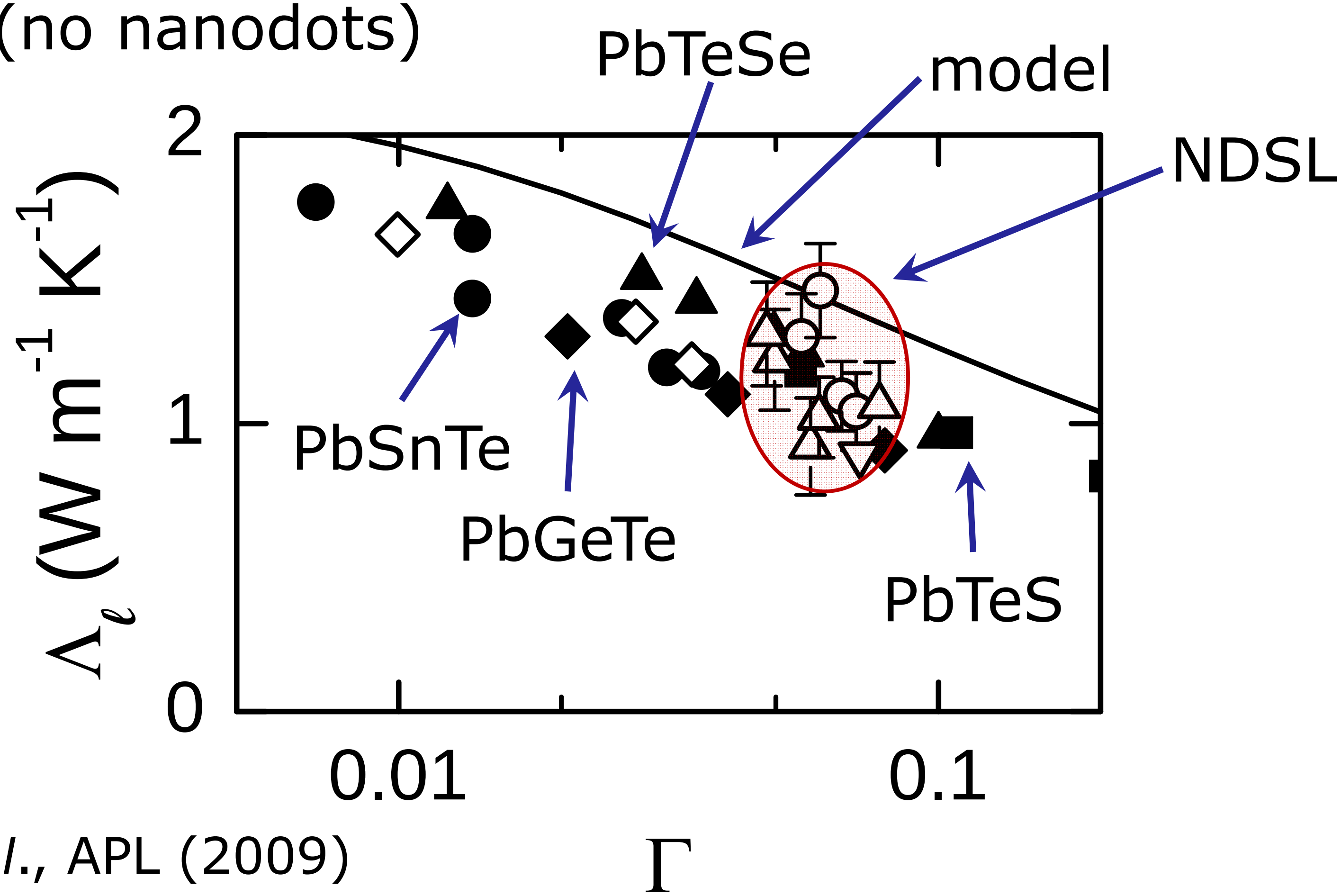
Vineis *et al*., Adv. Mater. (2009)

ZT=1.6 reported for PbTe/PbSe nanodot superlattices (NDSL) thermoelectric materials

- Power factor is not enhanced so lattice thermal conductivity is assumed to be very small
- Limited data for thermal conductivity
- Use TDTR to measure the total thermal conductivity in the top ~0.5-μm of a large number of ~5-μm-thick NDSL samples grown at MIT/Lincoln-Lab
- In-plane electrical measurements (conductivity, Hall) give estimate of electrical thermal conductivity, $\Lambda_{lat} = \Lambda_{total} - \Lambda_{elec}$
- Assume that anisotropy is "not too strong"

NDSL and superlattice PbTe do not significantly beat the alloy limit

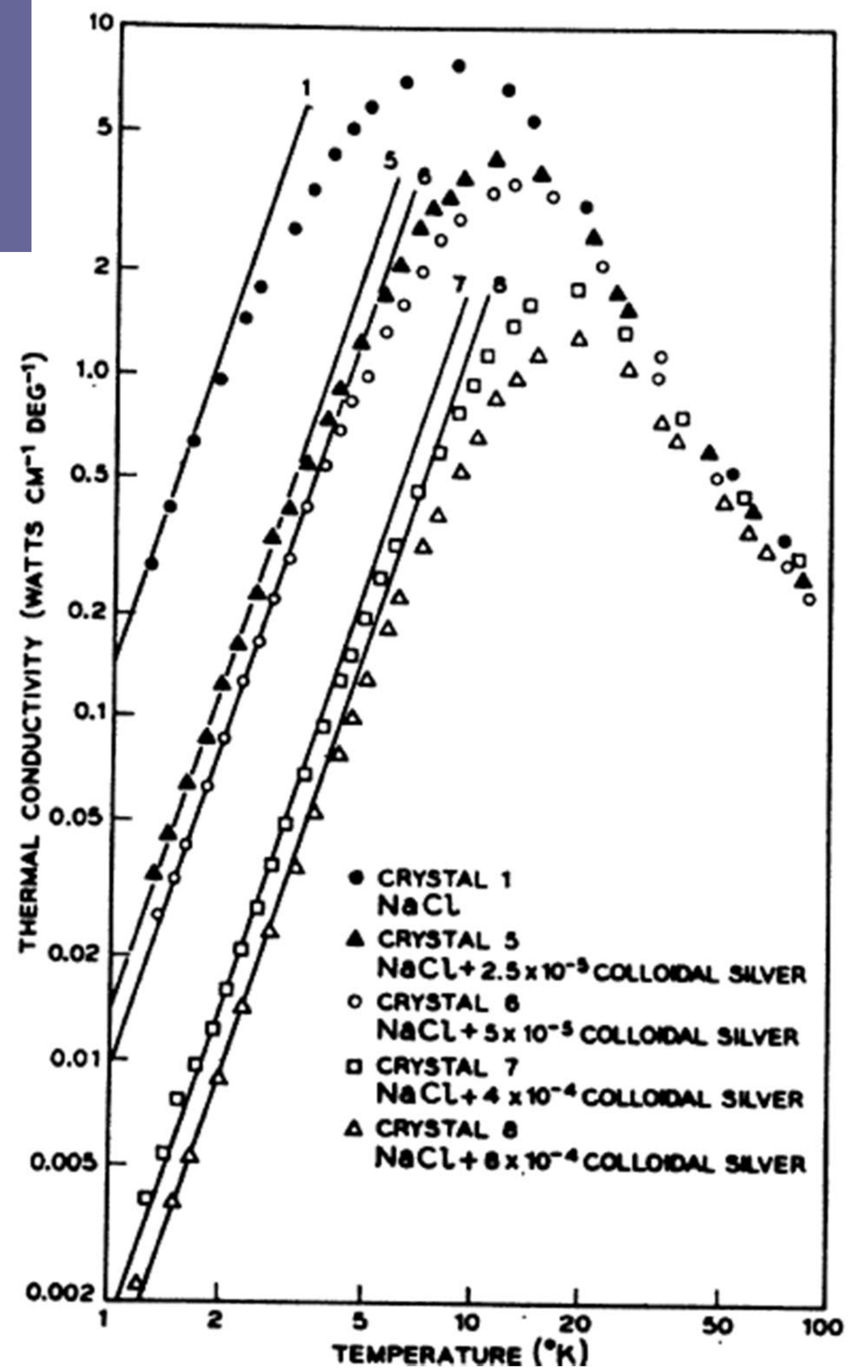
- nanostructured (open symbols); random alloys (filled symbols);
- Rayleigh scattering strength Γ calculated for random alloy (no nanodots)



Koh *et al*., APL (2009)

Need high densities of precipitates to make a difference at high temperatures

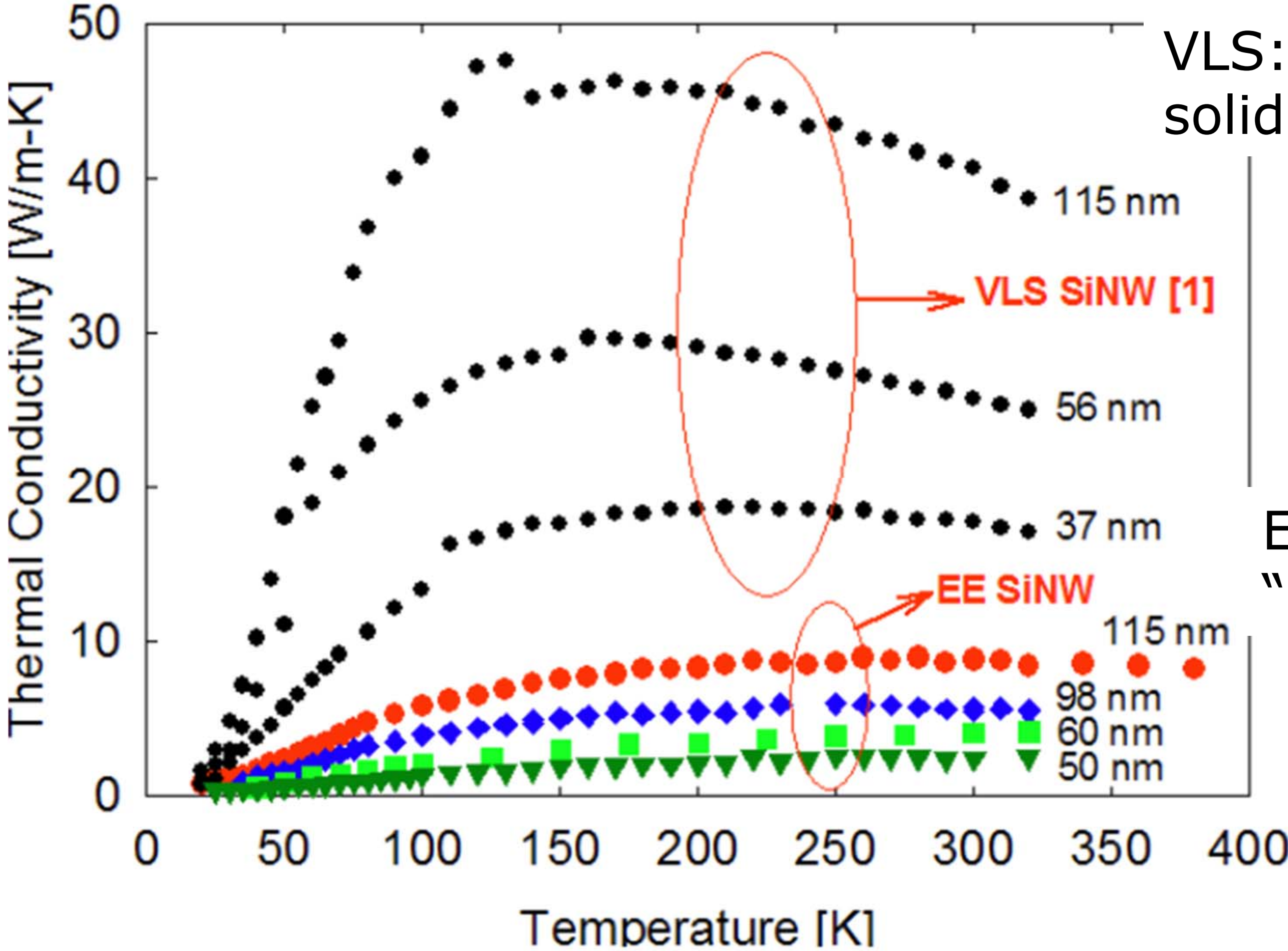
- Reduction of NaCl:AgCl mixed crystal in K vapor at 600 °C.
- Ag particle radii $r \approx 15$ nm
- Mean-free-path is $\ell = 40$ μm at the highest volume fraction $F \approx 10^{-3}$
- Reasonable agreement with expected $l_{NP} = \dfrac{4r}{3F}$



Worlock, PR 147, 636 (1966)

New phonon physics in roughened nanowires?

Single Si nanowire measurements by Majumdar, Yang, and co-workers (2008)

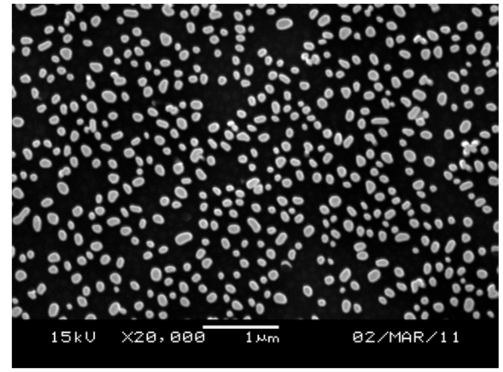


VLS: vapor-liquid-solid “smooth”

EE: electroless-etched “rough”

Sample Process Flow for Si nanowire arrays

Pre-Fabrication Image Analysis (SEM, TEM)

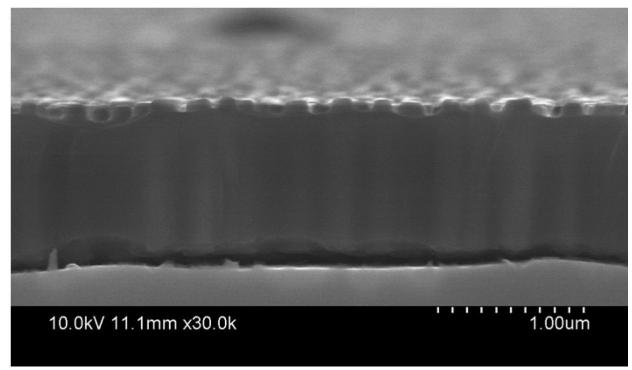


Spin-On Glass
Fill and Cure

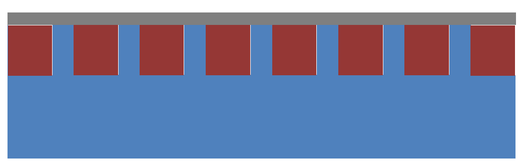
S. Sinha and co-workers

Post Fabrication Image Analysis

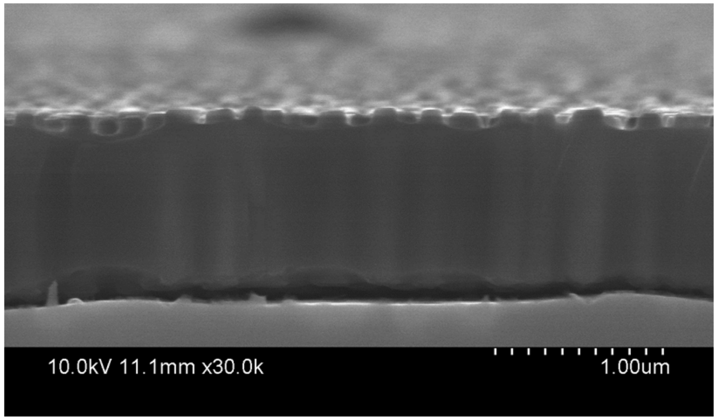
Wire exposure
(RIE Etch)



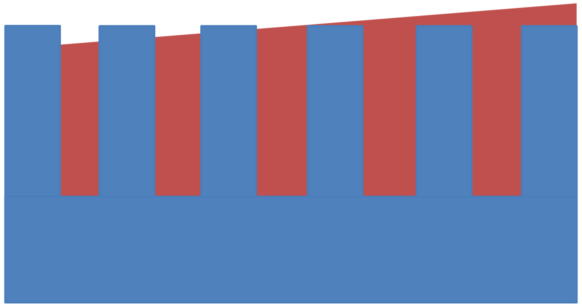
Aluminum
Sputtering

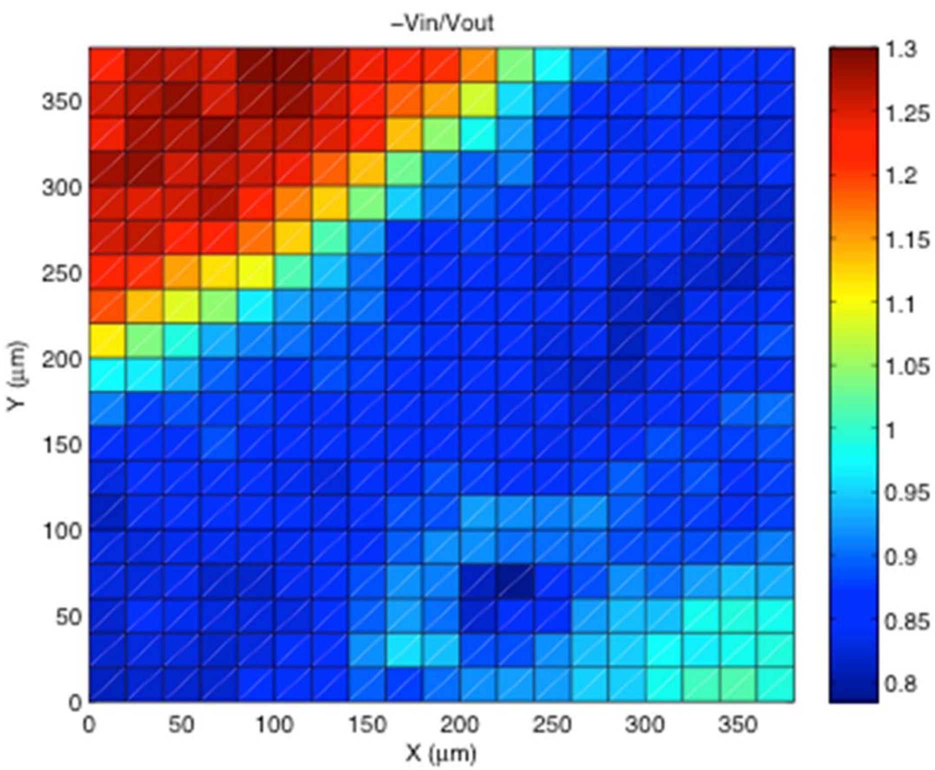


Make use of high spatial resolution of TDTDR



Penetration Depth at 10 MHz in Spin-On Glass: ~50nm

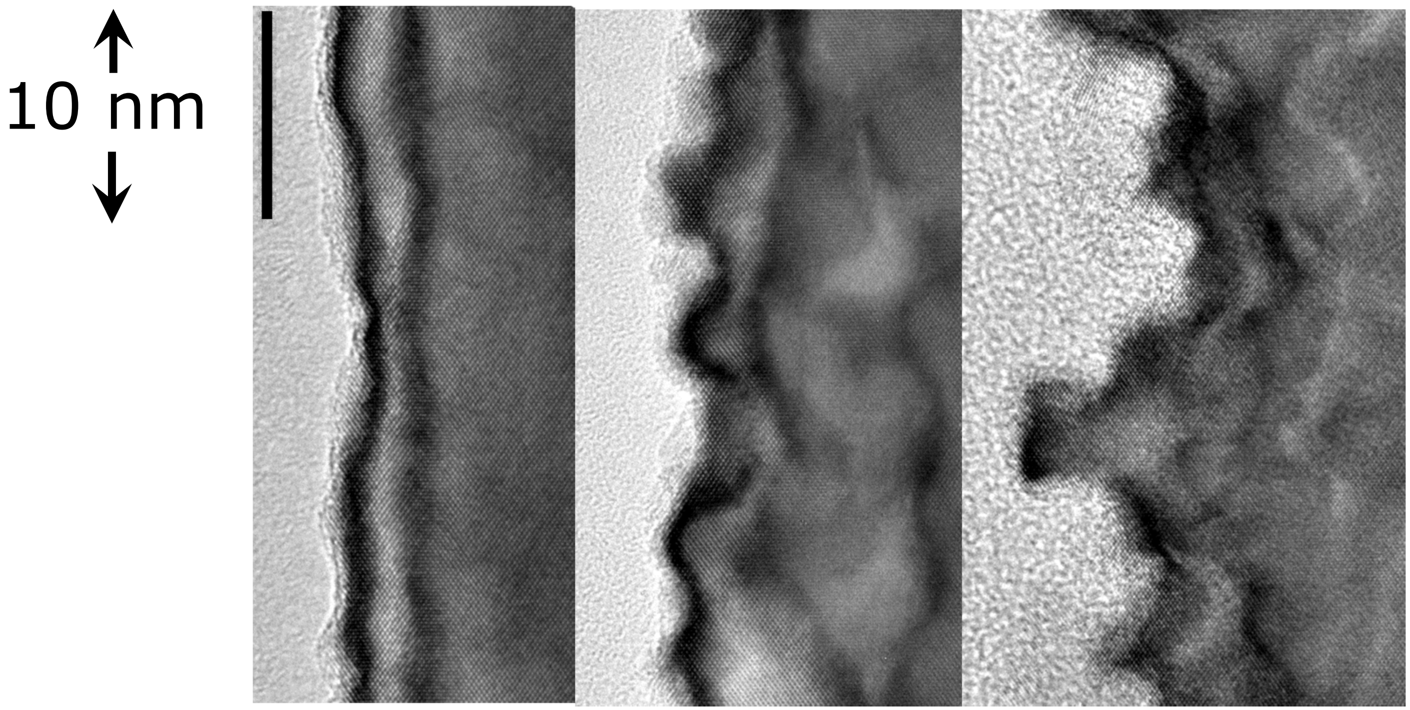




All measurements are taken beyond the transition to the higher thermal conductivity regions

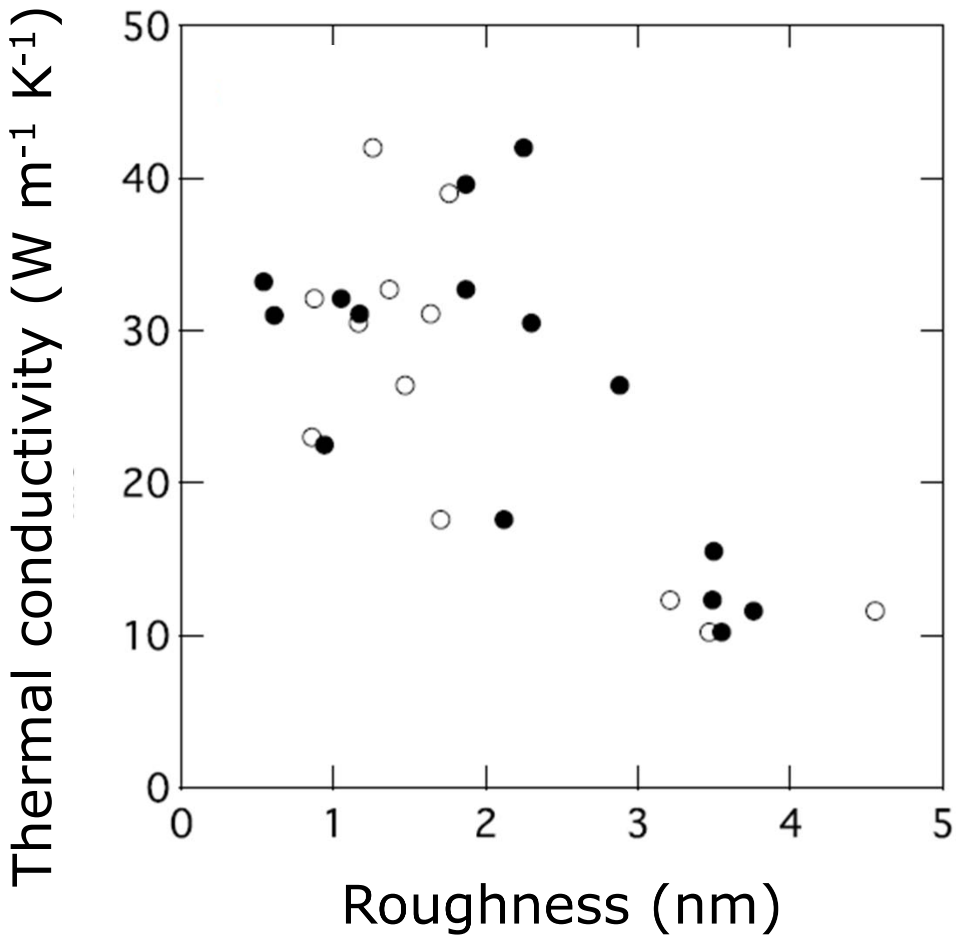
≈100 nm diameter Si nanowires by metal-assisted etching, Au and HF/H_2O_2

- Post-fabrication roughening using Au sputtered onto sidewalls and wet-chemistry
- Characterize roughness by TEM



≈100 nm diameter Si nanowires by metal-assisted etching, Au and HF/H_2O_2

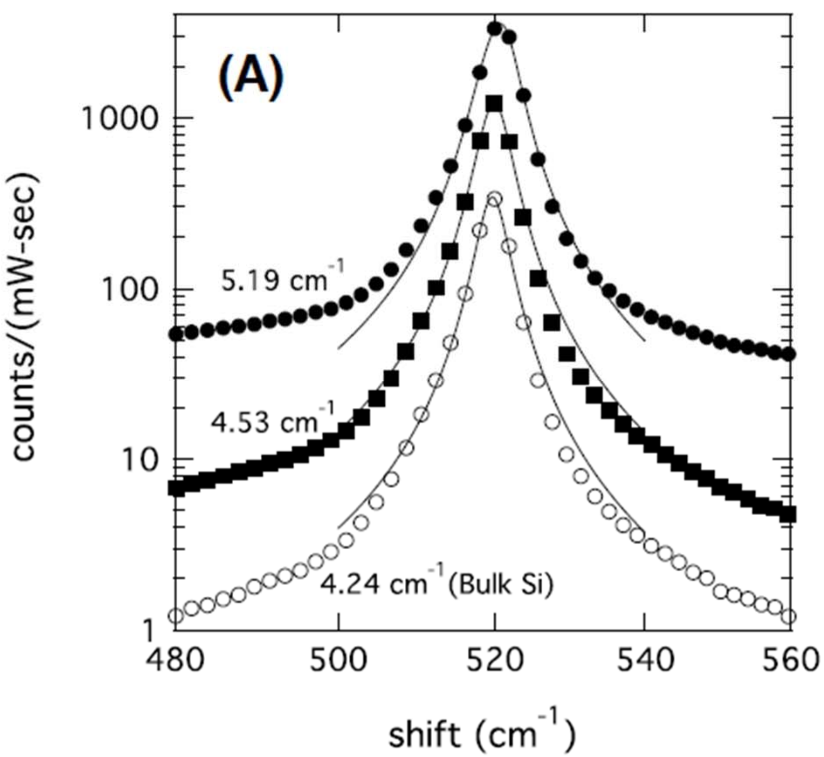
- The \$64k question: are we witnessing new physics or do the etched harbor defects that are not apparent by TEM.
- TEM is typically great for extended defects but not that sensitive to point defects or clusters of point defects.

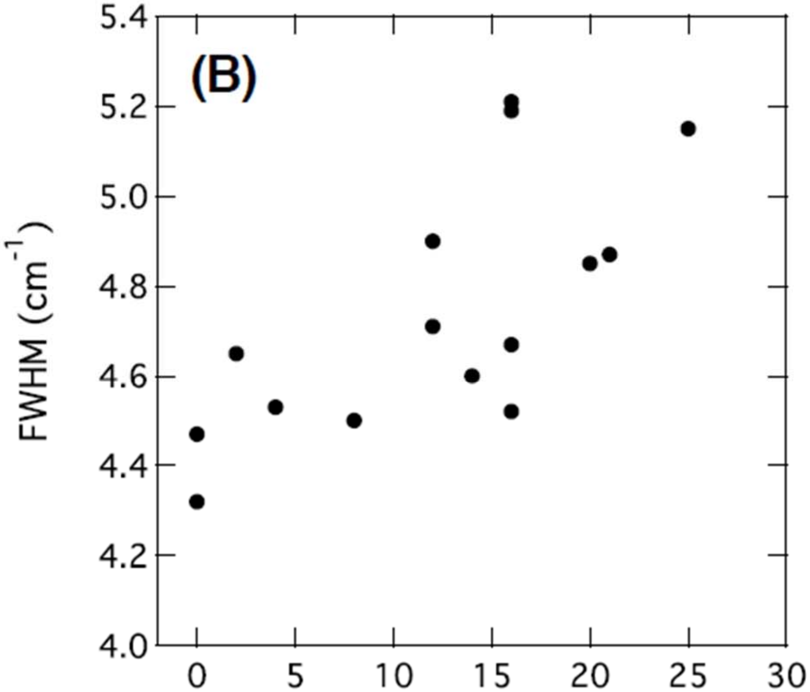


Feser *et al*., submitted

Raman peak broadens with etching time

- Consequence of roughness (e.g., inhomogeneous strain fields, confinement) or does etching inject defects?





Post-fabrication etching time (sec)

Feser *et al*., submitted

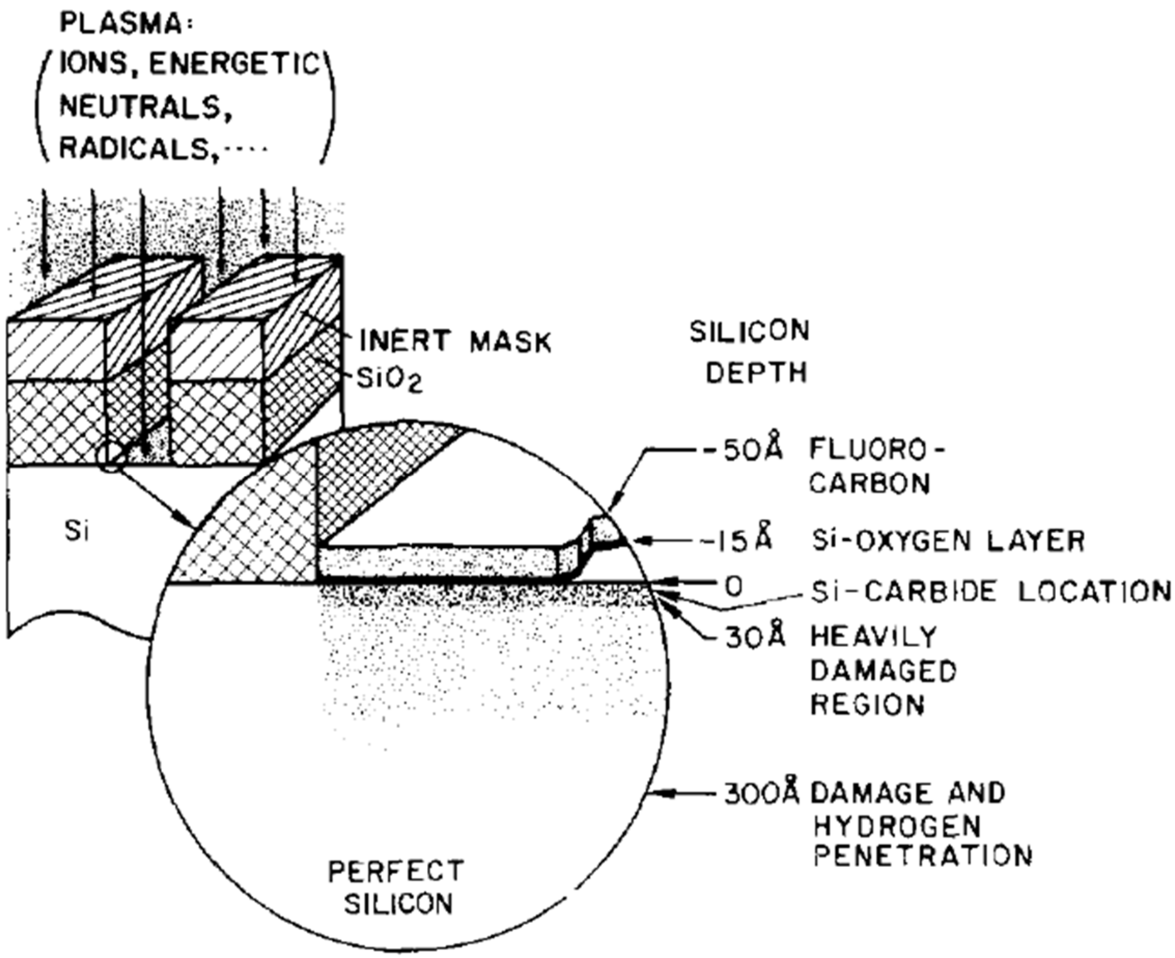
Defects happen…

- Not the same, of course, but extensive damage from dry etching of Si was not expected either

Dry Etching Damage of Silicon: A Review

GOTTLIEB S. OEHRLEIN

IBM Research Division, Thomas J. Watson Re:



Conclusions

- Superlattice interfaces can be used to reduce thermal conductivity but lowest conductivity is typically above the amorphous limit. Even the best superlattice interfaces are diffuse to most thermal phonons at room temperature.
- PbSe nanodots are not very effective in lowering the thermal conductivity of PbTe. Essentially the same thermal conductivity is observed in alloys with the same average composition. This can be understood based on strong anharmonicity and short intrinsic phonon mean-free-paths in of PbTe.
- Jury is still out on the question of new physics in rough nanowires. But we can conclude that the low thermal conductivities observed in single nanowire measurements are not easy to reproduce. Does metal-assisted etching create damage, e.g., vacancy/hydrogen complexes or clusters?