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Surpassing the High-Temperature Thermoelectric Figure-of-Merit by Nano-Structured Phononic Crystals

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Objective High-ZT:

ZT – a 3D dilemma!

The ZT-Problem:

The task is to min κ and max S & σ :

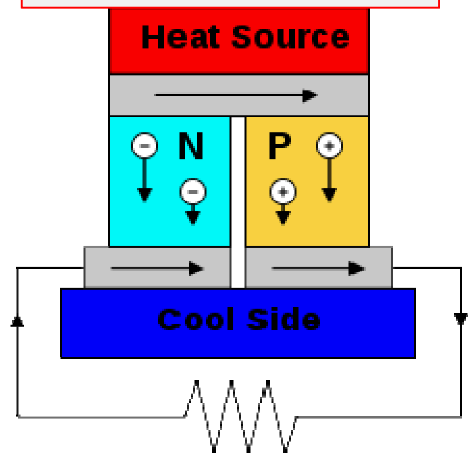
- The κ-σ Problem:
  - In semiconductors, "κ" is dominated by the phonon contribution
  - ➔ to reduce "κ", we need to increase phonon scattering!
  - ➔ leads to an increase in electron scattering
  - ➔ $\kappa\downarrow \Leftrightarrow \sigma\downarrow$
- The S-σ Problem:
  - S: is like a measure of the electronic entropy (disorder/scattering) in the system
  - σ: is a measure of how fast we can propagate a current ➔ decreases with increasing disorder!
  - Mott Equation:

$$S \sim \left.\frac{d\ln(\sigma(\varepsilon))}{d\varepsilon}\right|_{\varepsilon=\varepsilon_F} = \frac{1}{\sigma}\left.\frac{d\ln(\sigma(\varepsilon))}{d\varepsilon}\right|_{\varepsilon=\varepsilon_F}$$

  - ➔ $S\uparrow \Leftrightarrow \sigma\downarrow$

TE Peltier Effect:

TE Generator



- Cooler: Apply DC voltage ➔ heat moves from cold-side to hot-side
- Generator: Heat gradient ➔ current flow
- Efficiency: Quantified by the dimensionless quantity ZT
- Figure of merit : $Z = S^2\sigma/\kappa$
- S: Seebeck coefficient ($\Delta V/\Delta T$)
- σ: Electrical conductivity
- κ: Thermal conductivity ($= \kappa_e + \kappa_{ph}$)

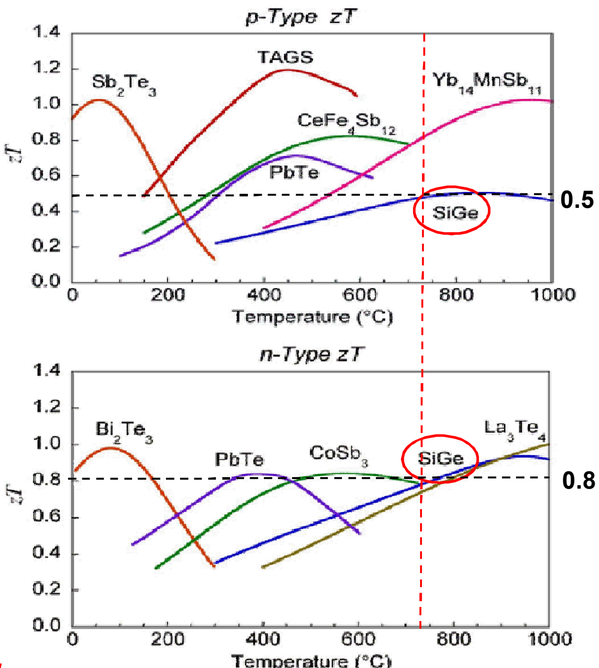
Z is a 3D problem in nature, meanwhile almost all literature attempts deal with one parameter at a time!

Objective High-Temperature High-ZT :

"Traditional Approaches" and their Drawbacks

Bulk TE Materials:

G. Jeffrey et. al., Nature Materials, Feb 2008



Issues:

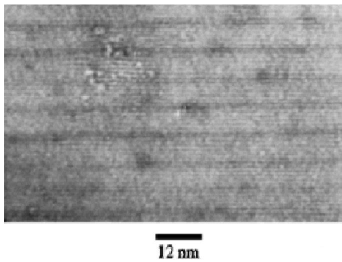
- **Fabrication/Integration:**
  - Compatibility with standard Fab.
  - Need p-n junction ➔ SiGe
- **Common Literature Mistake:**
  - Mention only n-type or p-type ZT
  - ZT_{SiGe-n}~0.8 & ZT_{SiGe-p}~0.5
  - $ZT_{SiGe-pn}$~0.7 (@1000K) low!

$$Z\bar{T} = \frac{(S_p - S_n)^2 \bar{T}}{[(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2}]^2}$$

Super Lattices:

- **κ-σ Problem:**
  - "Hard interfacial boundary" ➔ Lots of electron scattering
- **Fabrication:**
  - "Small layer thicknesses" ➔ ALD: Non scalable!
- **Integration:**
  - "Small separation between hot and cold sides" ➔ low performance!

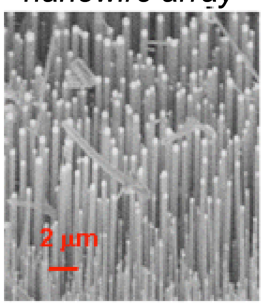
10Å/50Å Bi2Te3/Sb2Te3 Structure



Nano-Wires:

- **κ-σ Decoupled:**
  - "Unimpeded transport of electrons"
- **Fabrication:**
  - "Too many wires" ➔ lose quantum effects and approach thin films
- **Integration:**
  - "Requires vertical integration" ➔ Practically impossible

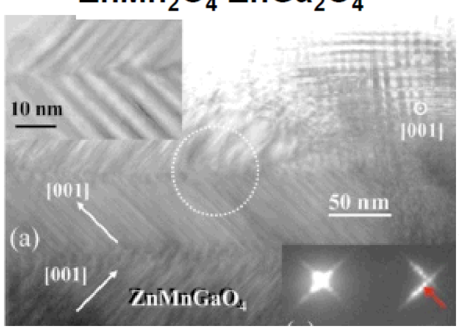
Doped Si nanowire array



Ceramics (Oxides):

- **κ-σ Problem (low κ ~10w/mK& low σ):**
  - "Incoherent scattering" ➔ Affects both electrons and phonons
- **Fabrication:**
  - "Nanostructures self-assembly" ➔ Nondeterministic outcome
- **Integration (vertical):**
  - "very thin films~0.5µm" ➔ Questionable!

$ZnMn_2O_4$-$ZnGa_2O_4$



Reducing κ:

Phononic Crystal Approach A lateral (planar) Device

- The thermal conductivity is given by

$$\kappa = \frac{1}{6\pi}\sum_j \int_q \frac{\hbar^2\omega_j^2(q)}{k_B T^2} \frac{\exp\left[\frac{\hbar\omega(q)}{k_B T}\right]}{\left(\exp\left[\frac{\hbar\omega(q)}{k_B T}\right]-1\right)^2} \upsilon_j^2(q)\tau_j(q) q^2 dq$$

$\omega(q)$ is the phonon dispersion

$\upsilon(q) = \partial\omega(q)/\partial q$ is the phonon group velocity

$\tau(q)$ is the scattering time of the phonons

q is the wavevecto r

$j = 1, 2, 3$ (1 longitudin al, and 2 transvers e)

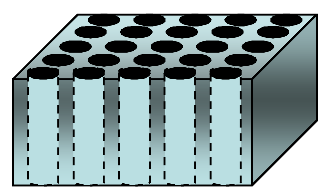
L is the minimum feature size

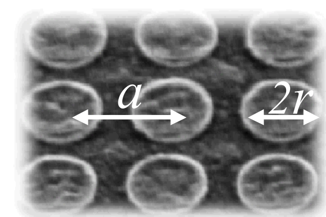
$$\frac{1}{\tau_j(q)} = \frac{1}{\tau_{Umklapp,j}} + \frac{1}{\tau_{impurity,j}} + \frac{1}{\tau_{boundary,j}}$$

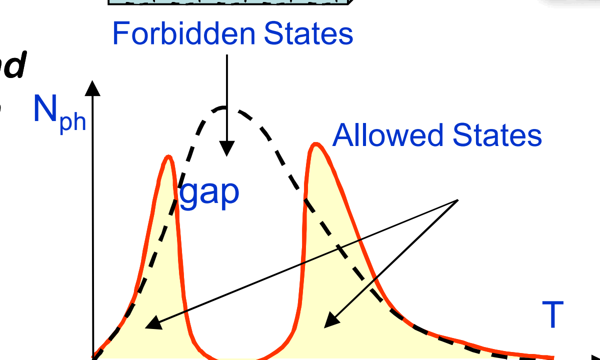
$$\tau_{boundary,j} = \frac{L}{\upsilon_j(q)}$$

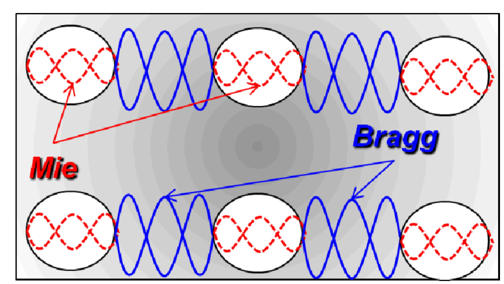
- To change κ need to change :
  - a. Dispersion "ω(q)"
  - b. Minimum feature size "L"

PnC





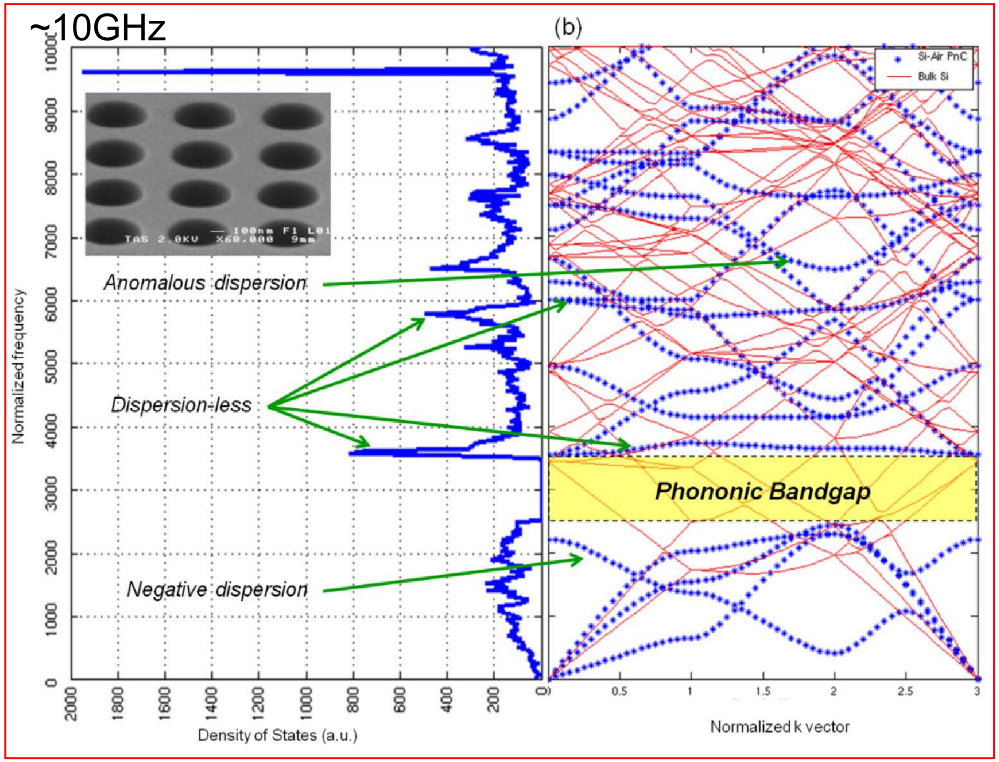


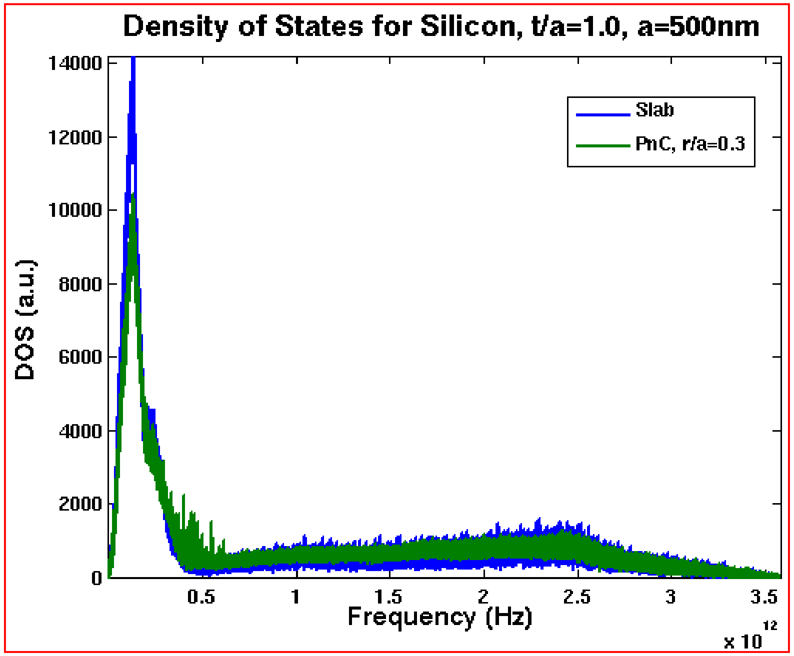


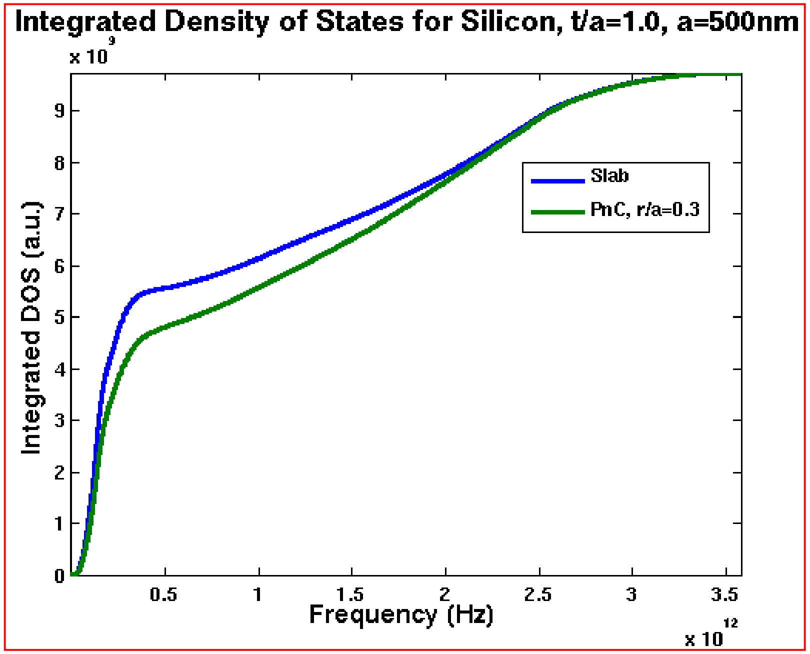
- **What is a Photonic Crystal?**
  - ***Created** by superposing Mie and Bragg resonant scattering by a periodic arrangement of scattering centers in a lattice.*
  - ***Requires** sufficient acoustic impedance mismatch.*

Reducing κ:
Planar PnC Approach

- *Dispersion Engineering: How Coherent Scattering Works*



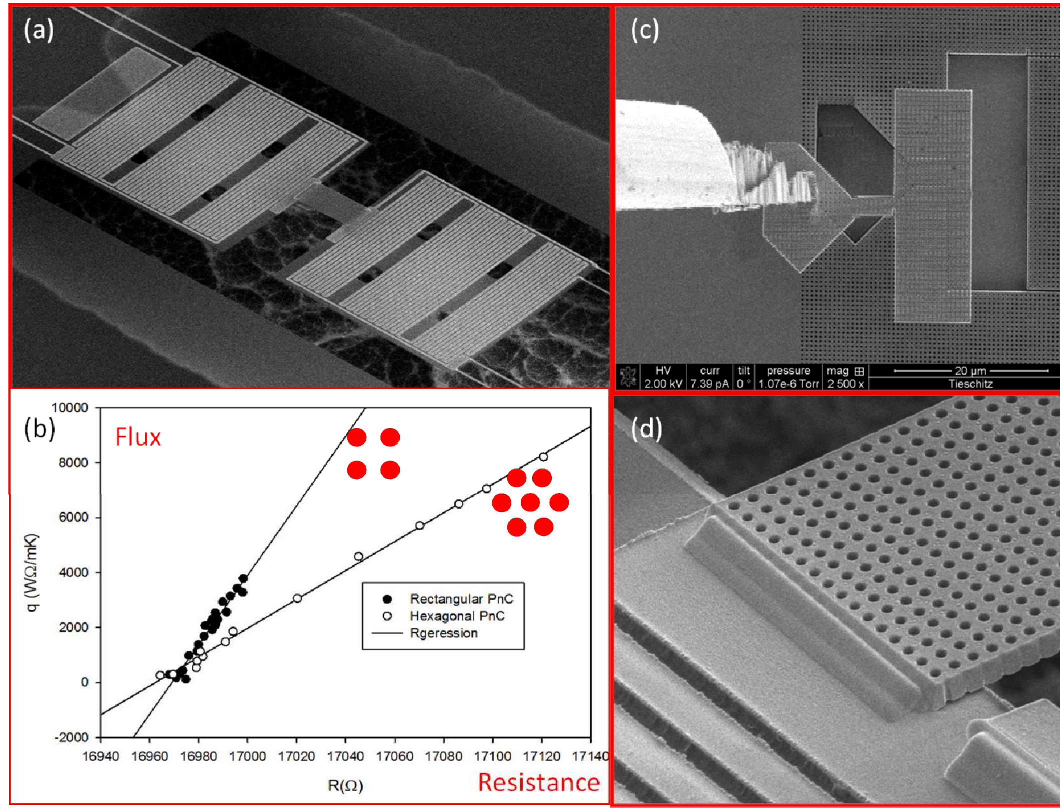




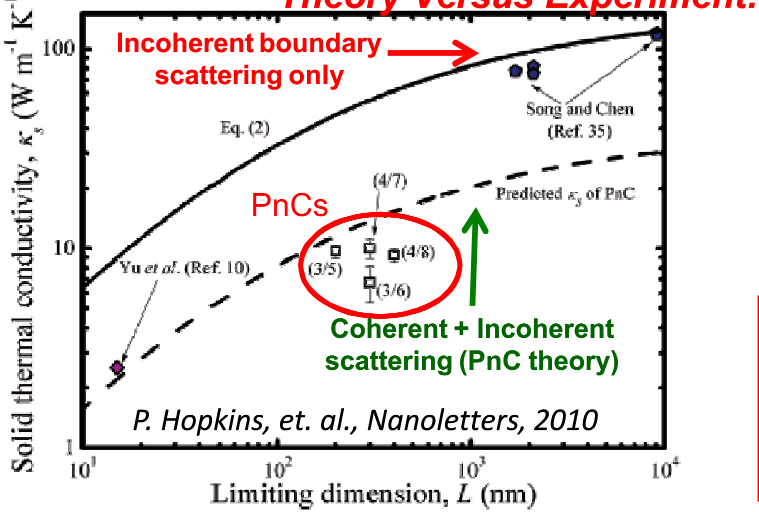
- *Bragg Resonance ➔ Creation of gap (long wavelength acoustic phonons)*
- *Flat Bands ➔ Less in number but higher in density ➔ Reduced group velocity*
- *Negative Bands ➔ Backward propagation (backward scattering)*

Reducing κ:
Planar PnC Apprach

- *Additional Evidence of Coherent Scattering*
- *Suspended-island technique:*
  - *The only thermal path between the heating stage and the detector stage is the PnC sample.*
  - *Pick-and-place technique using a Omniprobe needle tip used to place the PnC samples between the suspended islands.*
  - *SEM close-up showing the quality of the FIB welding of the PnC sample to the islands using platinum.*
  - *Comparison of the square PnC lattice with a triangular PnC lattice of the same thickness, hole diameter, critical dimension L (minimum feature size).*



Theory Versus Experiment:



- *2D Air Fraction:*

$$ff_{sq} = \frac{\pi r^2}{a^2} \qquad ff_{hex} = \frac{2\pi r^2}{\sqrt{3}a^2}$$

- *Ratio:*

$$\frac{ff_{hex}}{ff_{sq}} = \frac{\frac{2\pi r^2}{\sqrt{3}a^2}}{\frac{\pi r^2}{a^2}} = \frac{2}{\sqrt{3}} = 1.155$$

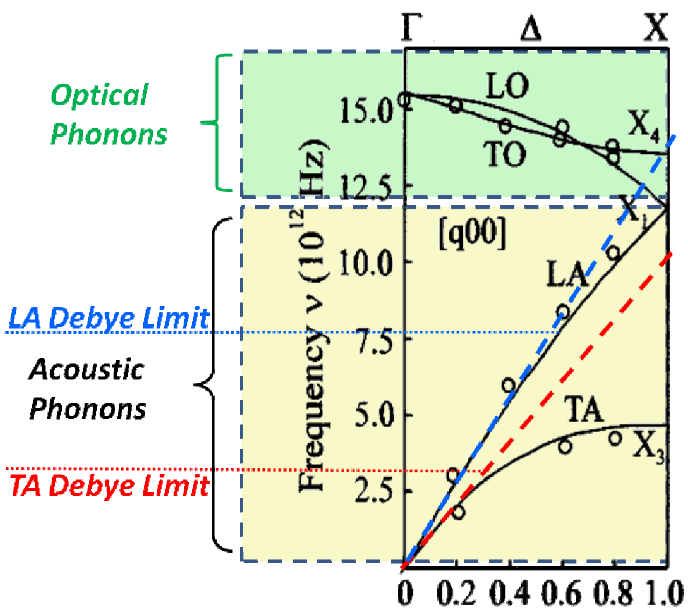
- *Since all other parameters are constant:*
  - *Same hole size*
  - *Same slab thickness*
  - *Same critical length*
  - *Same material*
- *Then:*

$$2.88 \leftarrow \frac{\kappa_{Sq}}{\kappa_{Hex}} = \frac{ff_{Hex}}{ff_{Sq}} \rightarrow 1.15$$

- *Off by a factor of 2.5!*
  - ➔ *Must be topology!*
  - ➔ *Dispersion !*
  - ➔ *Coherent !*

Reducing κ:
How can such widely spaced holes affect high frequency phonons?

- *When do our predictions breakdown?:*
- *Sensitive to the lattice periodic topology*



Si Phonon Dispersion **LA:** Longitudinal Acoustic Mode; **TA:** Transverse Acoustic Mode.

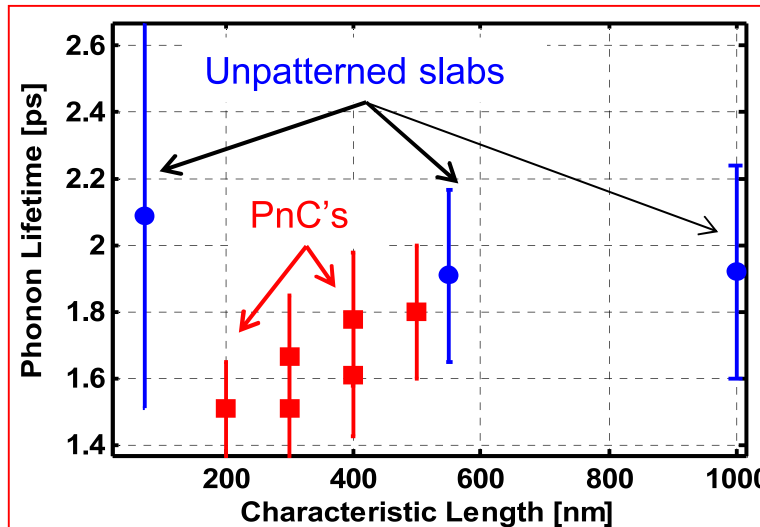
PWE –PnC theory predictions remain:

- ***Quantitatively valid :***
  - ***In the Debye Limit portion of the dispersion:***
  - ***~7.5THz for LA***
  - ***~3.5 THz for TA***
- ***Qualitatively valid :***
  - ***In the linear/slow portion of the material dispersion***

- *Reduction Mechanism:*

1. *PnC-coherent scattering directly affects low frequency acoustic phonons*
2. *PnC-coherent scattering affects high frequency optical phonons in an indirect manner:*
   - *Optical Phonons are responsible for upto ~27% of cross-plane κ [Sellan, et. al, , JAP 108, 113524 (2010)].*
   - *~30% of all optical phonon scattering involves an acoustic phonon mode [Broido*, PRB 81, 085205 (2010)].
   - *PnC anomalous dispersion affects low laying acoustic modes*
3. *Incoherent PnC boundary scattering affects high frequency acoustic and optical phonon modes*

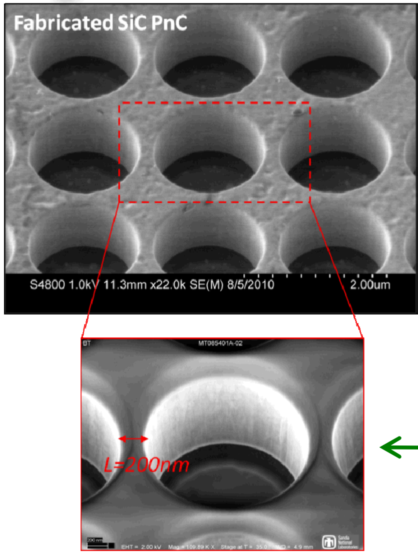
End result: *Is a reduction in the overall thermal conductivity*

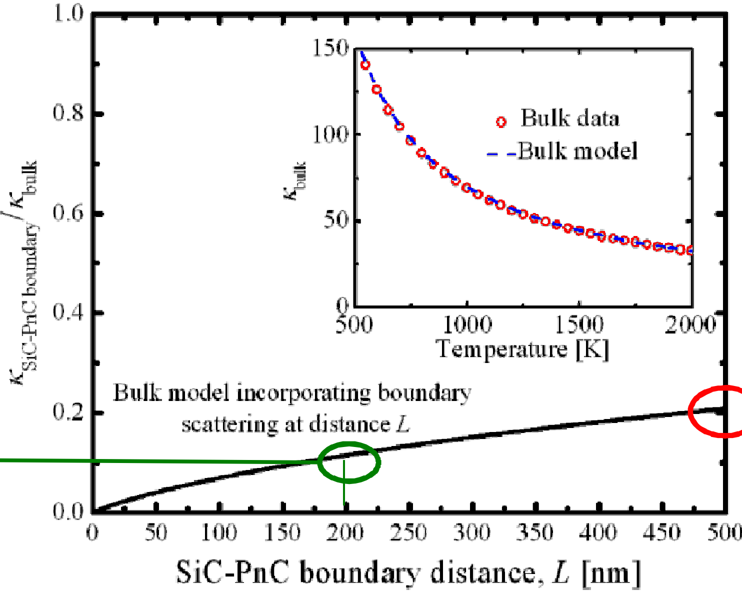


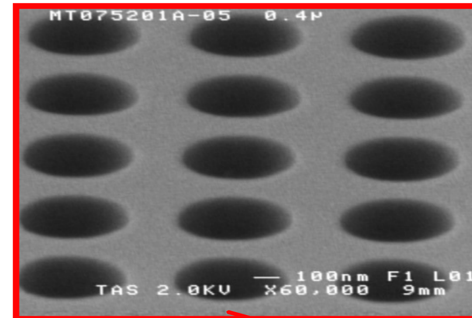
Anticipated Performance

Semiconductor-Air PnC ZT Estimate

- *Predicted κ Reduction: Holland-Callaway Equation*







Controlled Oxidation
a=1μm, r=250nm, L=500nm

Standard Photolithography
a=1μm, r=250nm, L=500nm

- *Ok, but what happens to the electrons @ L~500nm?*
- *Mean free path of the electrons is ~10nm or less @1000K ➔ σ should be affected at most by the porosity factor*

$$\text{For } a = 1\mu m \ \&\ r = 250\ nm$$

$$\Rightarrow\ ff_{air} \sim 0.2\ \&\ L = 500\ nm$$

$$\sigma_{PnC} \approx (1 - ff_{air})\sigma_{SC-Bulk} \approx 0.8\sigma_{SC-Bulk}$$

$$\kappa_{PnC} \sim 0.2\kappa_{SC-Bulk}$$

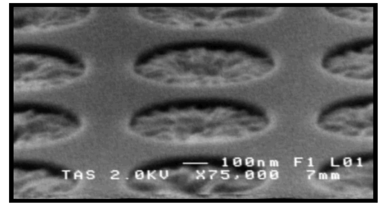
$$S_{PnC} \sim S_{SC-Bulk}$$

A factor of 4 enhancement in ZT@1000K!

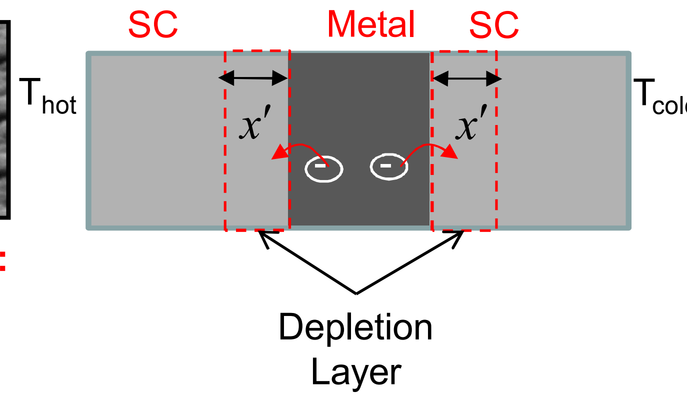
Increasing σ While Maintaining Low κ

Semiconductor/Metal PnC

- <u>Effective σ:</u>
  - Increased doping
    ➔ decreases the interface potential width
    ➔ Electron tunneling
  - "**Ohmic Contact**"!



Fabricated Example:
Si/W PnC

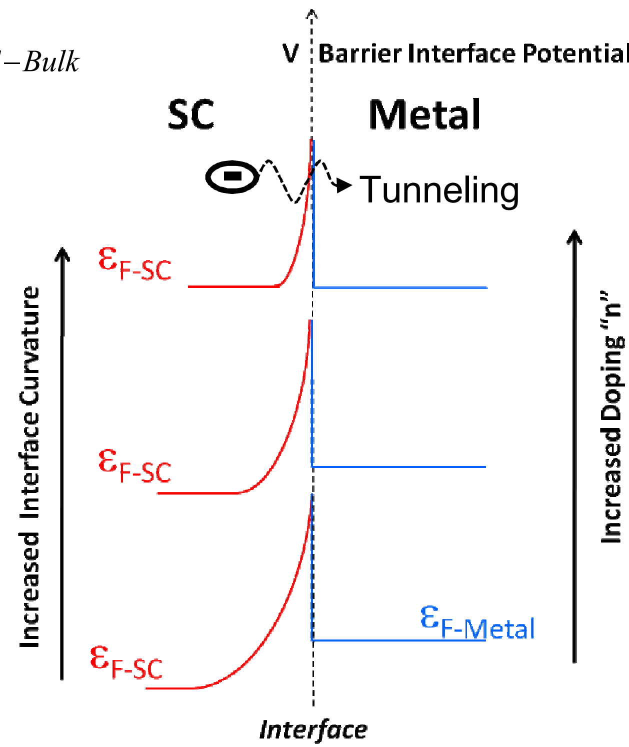


- At degenerate doping:

$$\rho_{PnC+Metal} \approx ff_{Metal}\rho_{Metal} + (1-ff_{Metal})\rho_{SC-Bulk} \approx (1-ff_W)\rho_{SC-Bulk}$$

- <u>Effective κ ($^1/_{\Re}$):</u>
  - What happens to the <u>thermal resistance</u> now that we have plugged the holes with "metal"?
    - Mechanical impedance mismatch is still very high
    - Incoherent scattering almost unaffected
    - Coherent scattering slightly enhanced

$$\Re_{PnC+W} \approx ff_{Metal}\Re_{Metal} + (1-ff_{Metal})\Re_{PnC}$$
$$\approx (1-ff_{Metal})(5\Re_{SC-Bulk}) \approx \Re_{SC-Bulk}$$



- <u>Effective ZT:</u>
  - Assuming: $a = 1\mu m \;\&\; r = 250nm \Rightarrow ff_W \sim 0.2 \;\&\; L = 500nm$

$$\Rightarrow \kappa_{PnC+Metal} = \frac{1}{\Re_{PnC+Metal}} \approx \frac{1}{\Re_{SC-Bulk}} \approx \kappa_{SC-Bulk}$$

$$\Rightarrow \rho_{PnC+Metal} \approx 0.2\rho_{SC-Bulk}$$

A factor of 5 enhancement in ZT@1000K!

Increasing S (quadratic)

Metallic Nano-Particle implantation

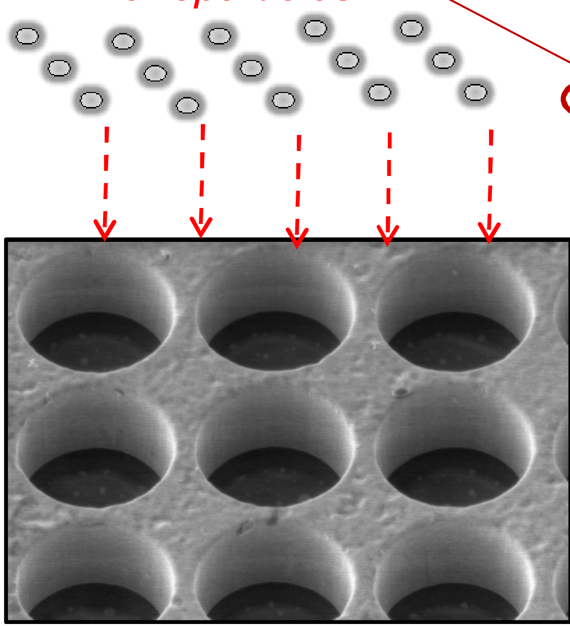
(Up to a factor of 8 total enhancement!)

Additional Factor ≥ 2 enhancement in ZT@1000K

- *If W effect on κ is drastic:*
  - *We can increase S and mildly affect σ and κ by ion implantation of metallic nanoparticles:*
    - *Al ions implanted in SiC-PnC at IBL-SNL*
    - *Anneal ➔ congregate islands ~5-20nm*
    - *Conceptual proof data is for PbTe: same arguments hold for a highly-doped SC, although quantum mechanical treatment would be best (SNL-California)*

SiC-PnC + Metalic-nanoparticles

R=1.5nm; x=5%



Solid circles:

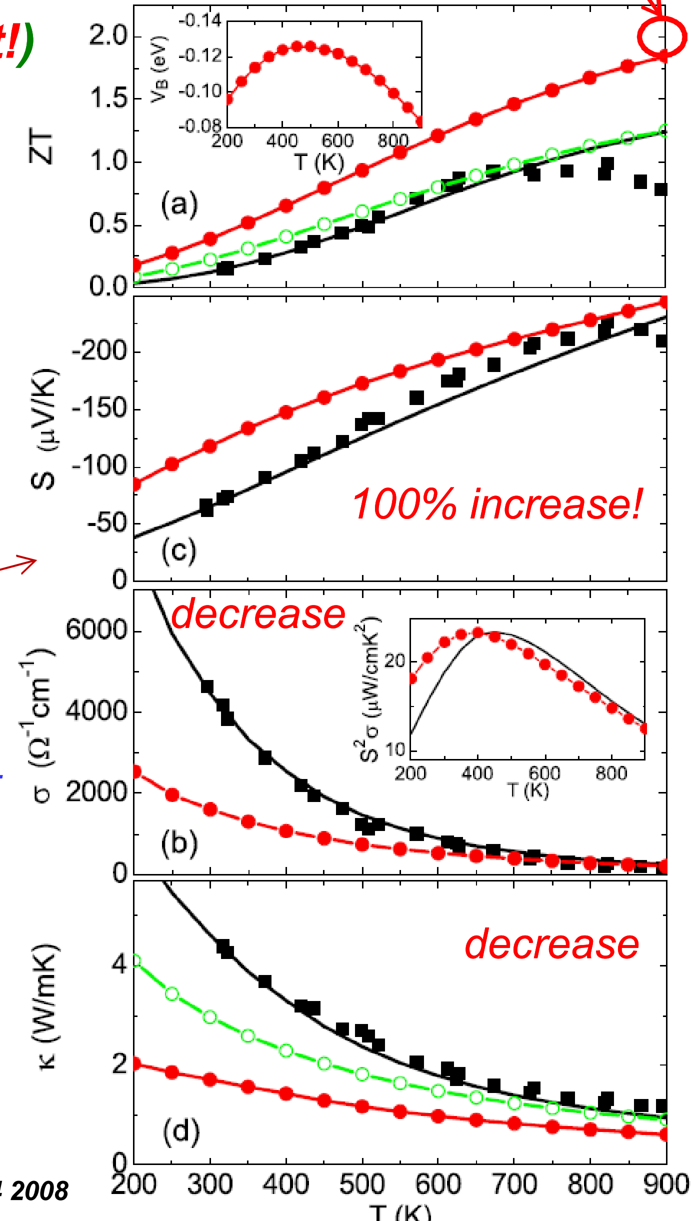
Electron & phonon scattering on the inclusions;

Open circles:

Include electron scattering on the inclusions but with bulk values of κ;

Solid lines (filled squares):

Experimental & calculated Bulk values



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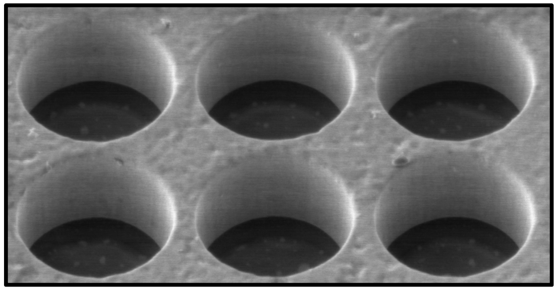
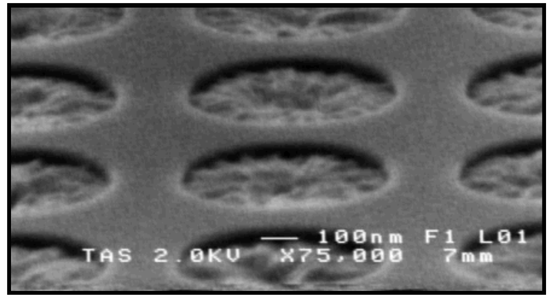
Overall Picture: 3 Possible Approaches in Order of Difficulty

#1 SC/Air PnC



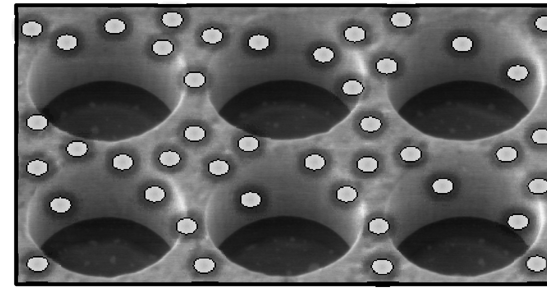
ZT up by 4 @1000K

#2 SC/Metal PnC



ZT up by 5 @1000K

#3 SC/Air PnC + MNPs



ZT up by 8 @1000K

These are NOT independent routes, but rather different post-processing techniques for the same PnC device with different optimal parameters!

Possible Material Systems (test beds)

- Si/Air & Si/W:
  - ✓Easy to process
  - ✓CMOS fab. compatible
  - ✓Cheap!
  - ✓Provides a proof of concept!
  - ✓Si has a large power factor
  - ✓Suitable for room T applications

- SiC/Air & SiC/W:
  - ✓Corrosion resistant
  - ✓Resilient in harsh environments
  - ✓Withstands cycling at high T
  - ✓CMOS fab. compatible
    - ✓Know how to process well and control minimum feature size
  - ✗Hard to dope (p-type)

Surpassing the High-Temperature Thermoelectric Figure-of-Merit by Nano-Structured Phononic Crystals

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- Dan Catalin Spataru (First Principles Calculations - 8656)
- Charles Reinke (PnC Dispersion Engineering - 1725)
- Alan McGaughey (Molecular Dynamics - Carnegie Mellon U.)
- Mahmoud Hussein (Lattice Dynamics - UC-Boulder)

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- Blythe Clark (High Resolution TEM - 1111)
- Zayd Leseman (ZT Temperature-Dependant Characterization – U. New Mexico)
- Patrick Hopkins (Pump Probe thermal conductivity measurements – U. Virginia)

Fabrication:

- Roy Olsson (MDL – Fab - 1749)
- Khalid Hattar (Nanoparticle Implantation and Lattice Defects using FIB - 1111)
- Bongsang Kim (Electronic Characterization and Device Layout - 1749)

Device Models:

- Darren Branch (PNC – TE Device Multi-Physics Modeling - 1714)

Reducing κ:
Planar PnC Approach

- *Evidence of Coherent Scattering:*
- *Sensitive to the lattice periodic topology*