WCPM Seminar Series, Feb. 12, 2015 - Warwick

Electronic, thermal, and thermoelectric transport in nanostructures

Neophytos Neophytou

School of Engineering, University of Warwick, Coventry, U.K.

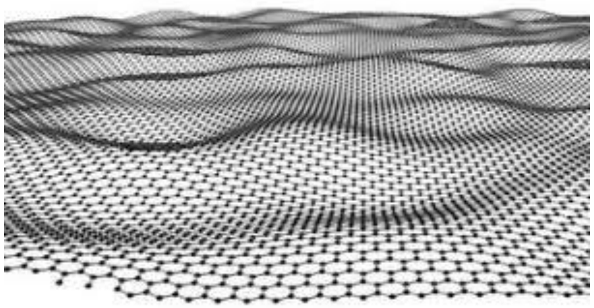
Outline

- Introduction – design at the nanoscale
  - Nanoscale thermoelectrics – design targets
- Low-dimensional TEs (atomistic tight-binding + BTE)
- Gated thermoelectrics: control scattering
- Phonons transport for low-D (Modified Valence Force Field)
  - *ZT* figure of merit for low-D channel
- Nanostructured thermoelectrics
- Other studies: Nanomeshes (MC), Graphene (NEGF)
- Future directions and conclusions

Why nano ?

New low-dimensional materials:

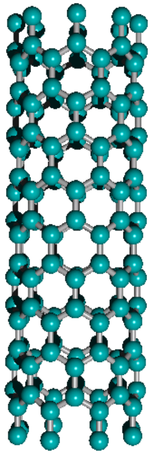
- 2D ultra thin layers
- 1D nanowires
- 0D quantum dots
- 2D graphene, 1D carbon nanotubes

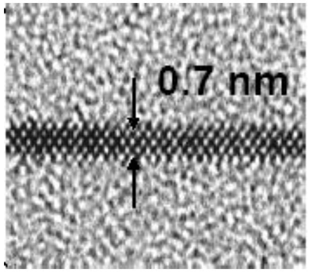


2D graphene

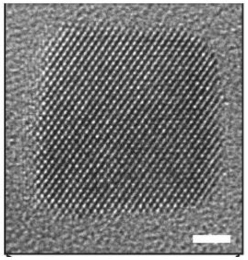
Design degrees of freedom for design:

- Length scale - geometry
- Quantum effects (electrons behave differently)
- Atomistic effects

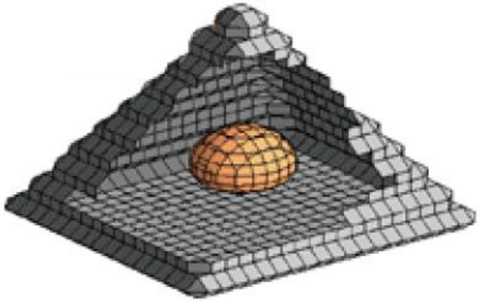




thin layers
Uchida et al., IEDM 03



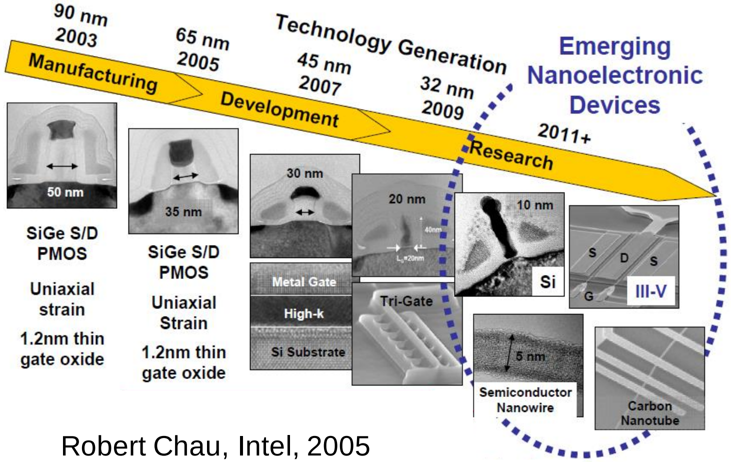
nanowires
Trivedi, 2011



quantum dots

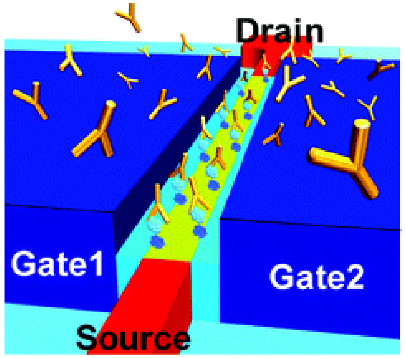
nanotube

Applications for nanodevices



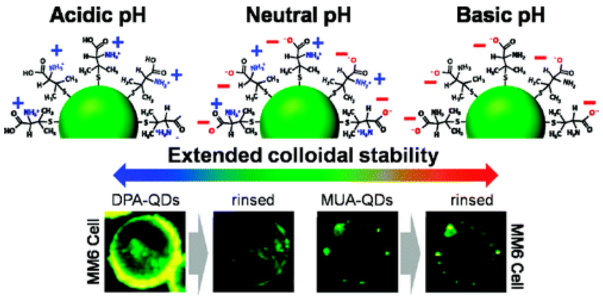
Robert Chau, Intel, 2005

Nano-transistors



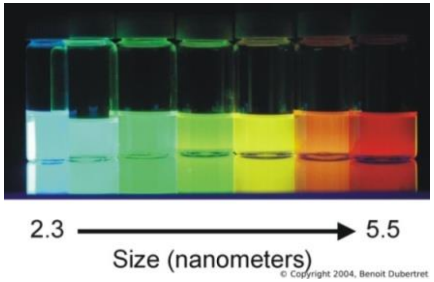
Ahn *et* al., Nano Lett., 2010

Bio-sensors

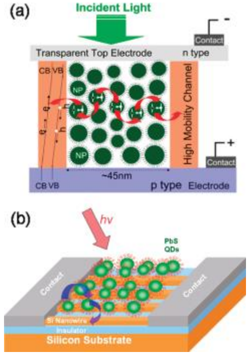


Breus *et* al., Nano Lett., 2009

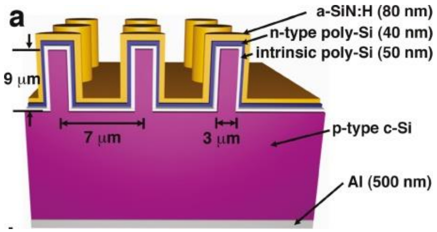
Bio-illumination / drug delivery



Optoelectronics

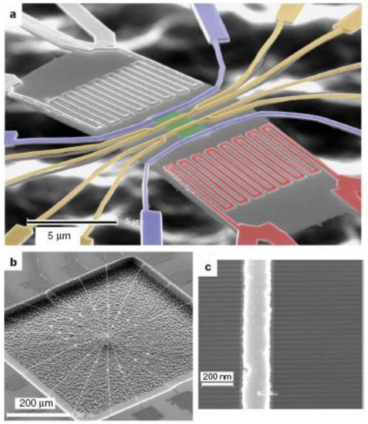


Lu *et* al.,
Nano Lett., 2009



Kim *et* al., Nano Lett., 2011

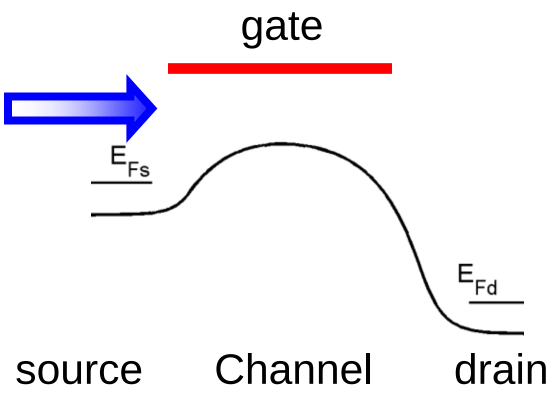
Photovoltaics



Boukai *et* al., Nature 2008

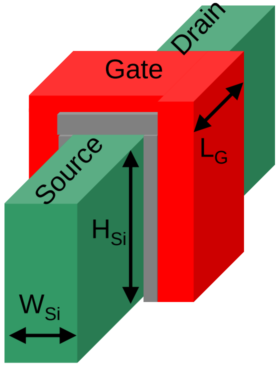
Thermoelectrics

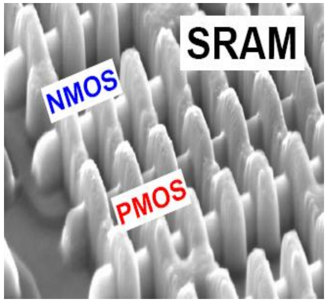
Nano-design for transistors



$$\tau = \frac{L_{ch}}{\langle v_e \rangle}$$

Length scale (the shorter, the faster)

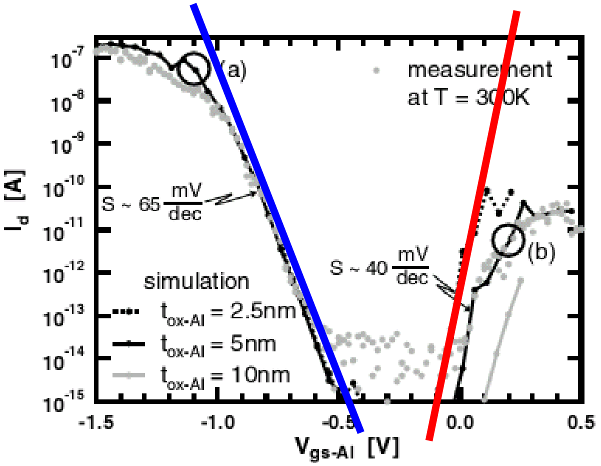


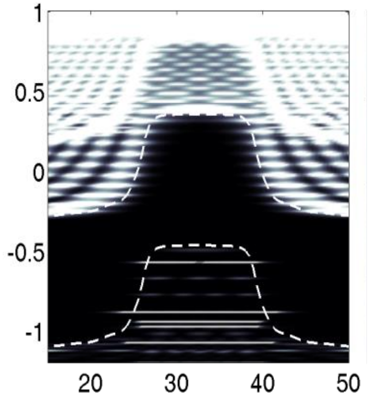


3D geometry (better electrostatics)

60mV/dec

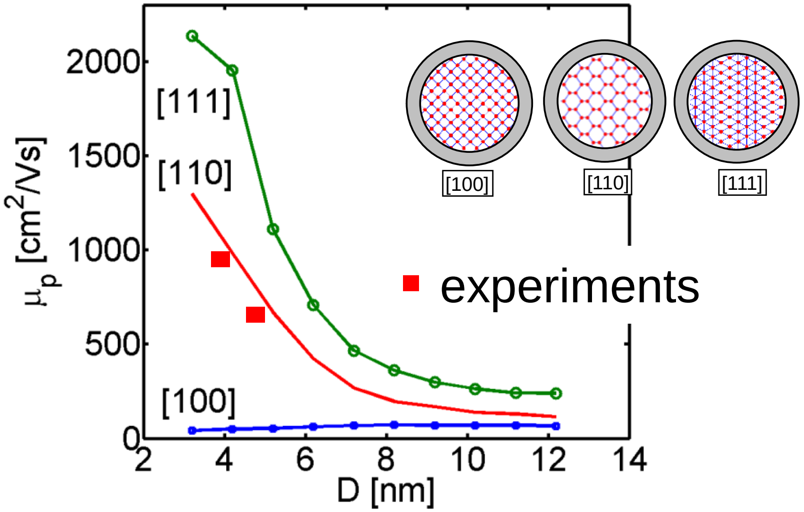
<40mV/dec





Appenzeller, PRL, 2004 (IBM)

Quantum effects (band to band tunneling)



Neophytou, Nano Lett., 10, 4913, 2010, APL 2011

Atomistic effects (bandstructure)

Outline

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    - Nanoscale thermoelectrics – design targets

- Low-dimensional TEs (atomistic tight-binding + BTE)

- Gated thermoelectrics

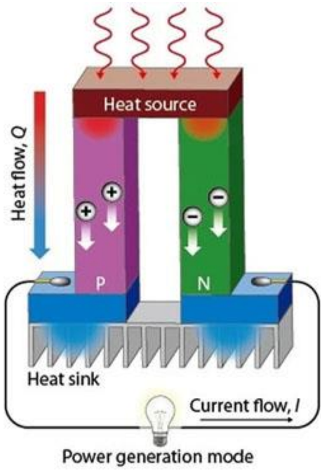
- Phonons transport for low-D (Modified Valence Force Field)
    - *ZT* figure of merit for low-D channel

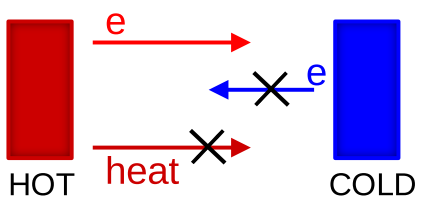
- Nanostructured thermoelectrics

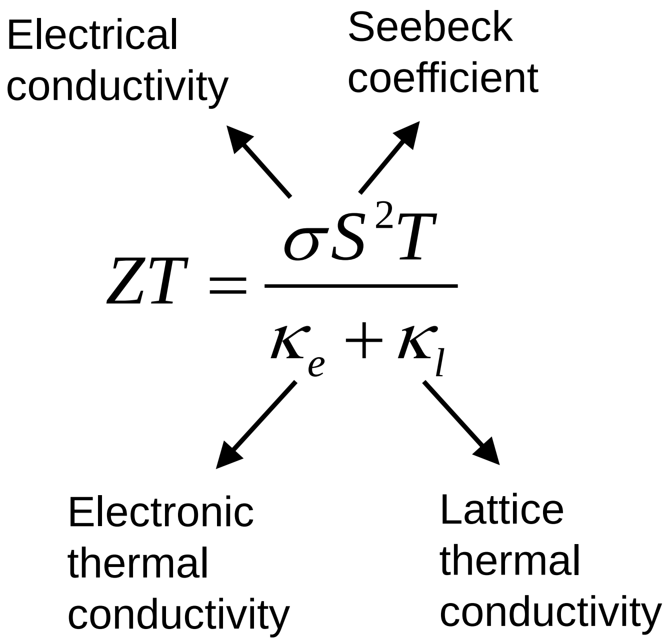
- Other studies: Nanomeshes (MC), Graphene (NEGF)

- Future directions and conclusions

Attempt similar design for thermoelectrics







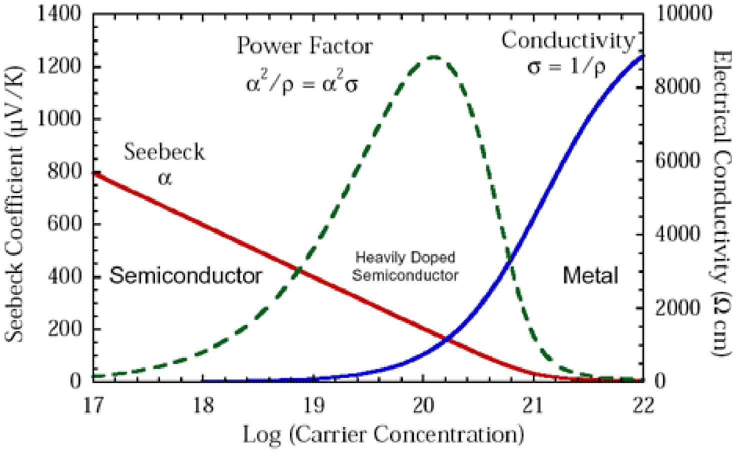
Electrical conductivity

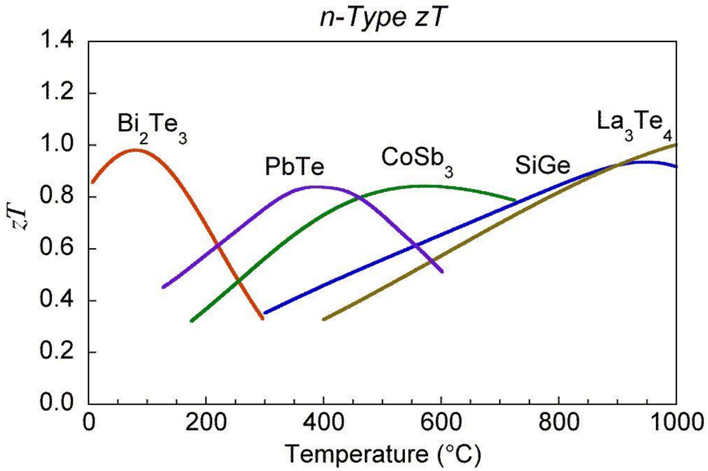
Seebeck coefficient

$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l}$$

Electronic thermal conductivity

Lattice thermal conductivity

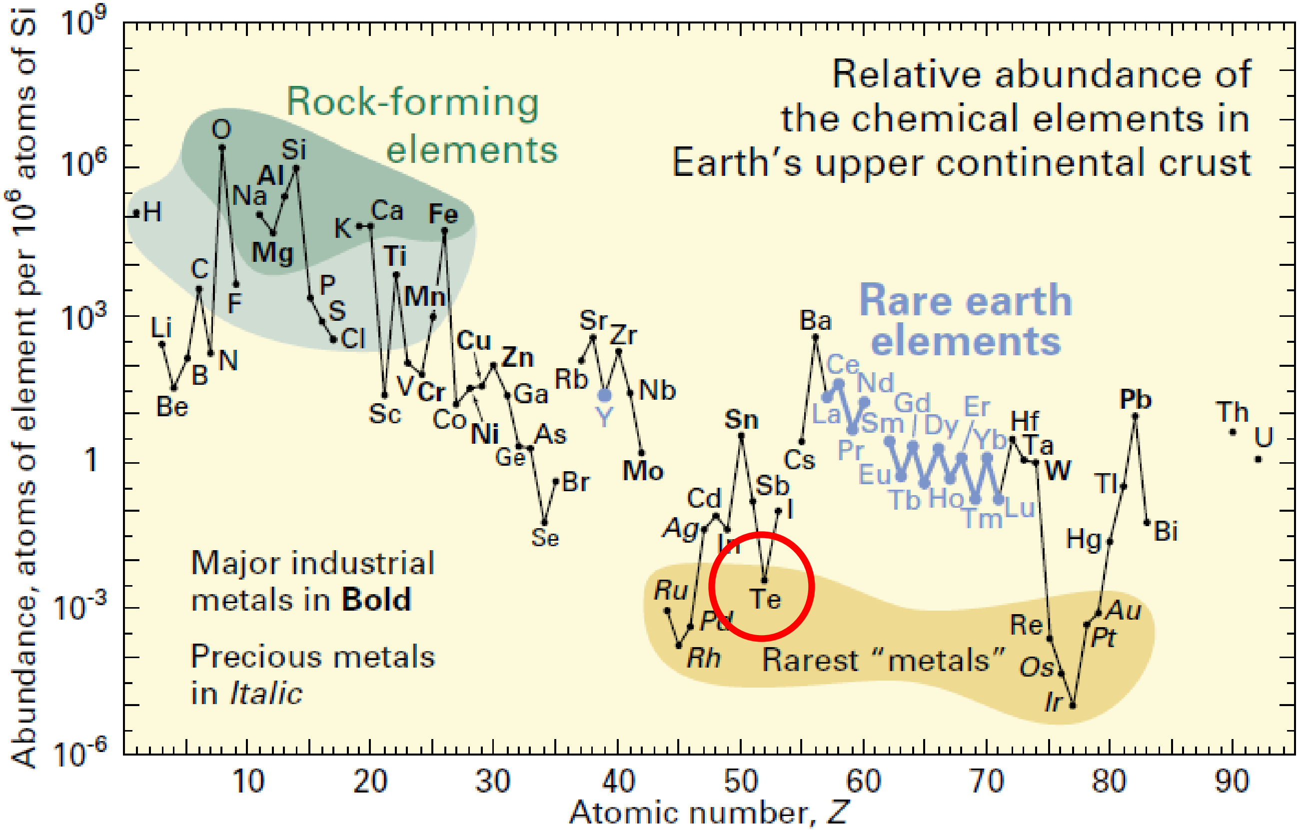




Snyder *et al.*, Science, 2008, Nat. Mat., 2008.

- 15 TWatts of heat are lost, but
- State of the art: *ZT*~1.5 (need *ZT*~4)
- Rare earth, toxic, expensive materials

Abundance issues with good TE materials



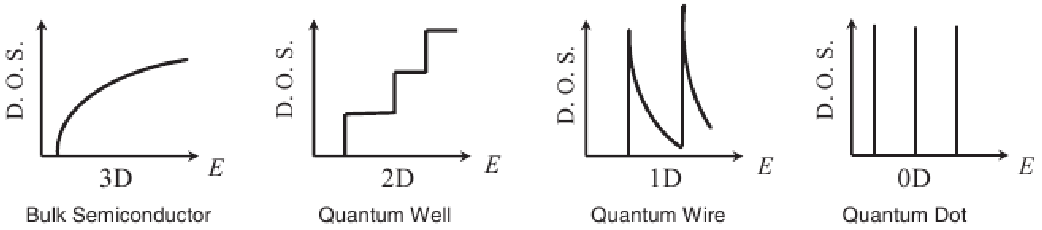
http://pubs.usgs.gov/fs/2002/fs087-02/

Abundance issues for Te, toxicity for Pb

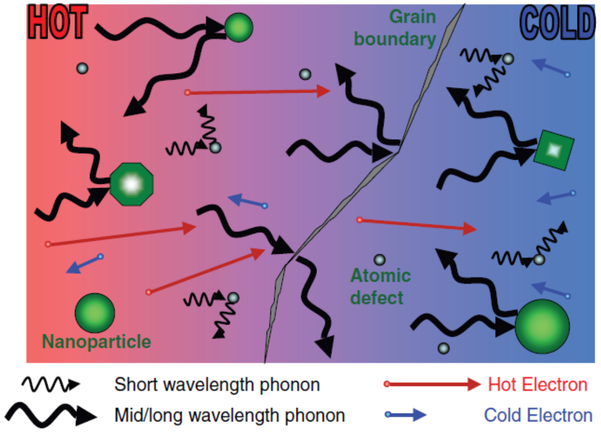
Design targets for nano-TE materials

<u>Sharp peaks in *DOS(E)*</u>

$$S \sim \frac{d}{dE} DOS(E)$$



Hicks and Dresselhaus -1993, Dresselhaus - 2001

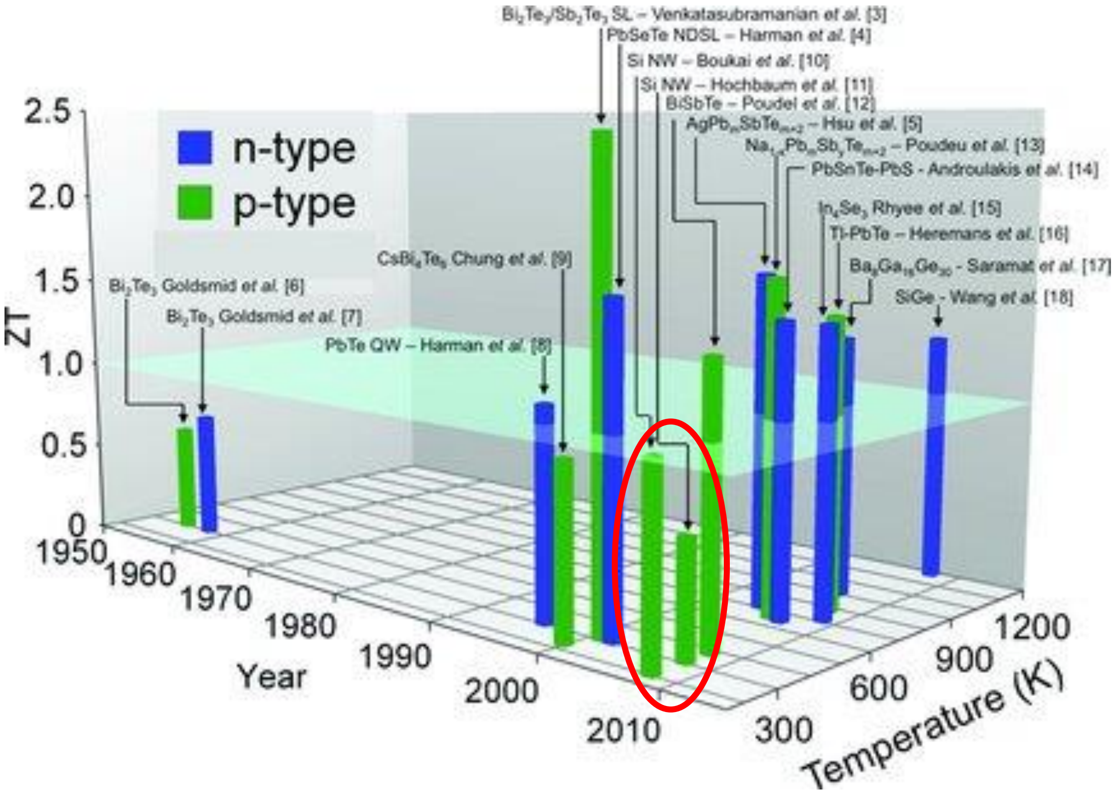


- ➢ Low dimensionality – improves *S*

- ➢ Nanostructuring - phonon engineering
- ➢ Scatter phonons only

$$ZT = \frac{\sigma S^2 T}{k_e + k_l} \downarrow$$

How to proceed further ?



Vineis et al., Adv. Mater. 22, 3790, 2010

Case for Si:

Bulk : 140 W/mK, ZT=0.01

NWs: 1-2 W/mK, ZT~1

- κ_l reduction benefits are reaching their limits (easily)
- we need to look into σS^2

This talk’s focus

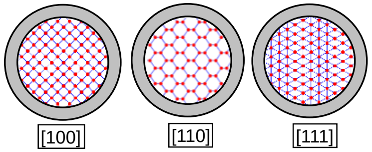
(1) Electronic properties: model and simulations

Interplay between σ, S at the nanoscale

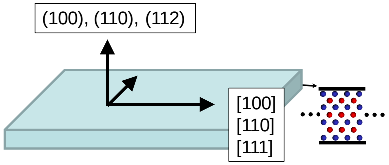
(Si @ T=300K)

(2) Phonon properties: model and simulations

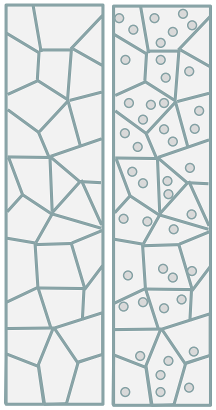
Possibility of further reduction in κ_l



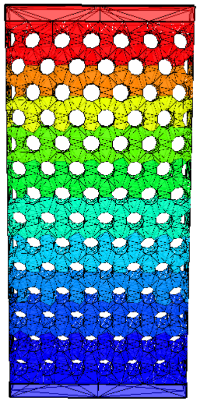
nanowires



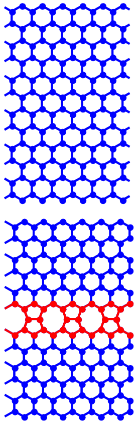
thin layers



nano-crystalline



nanomeshes



graphene

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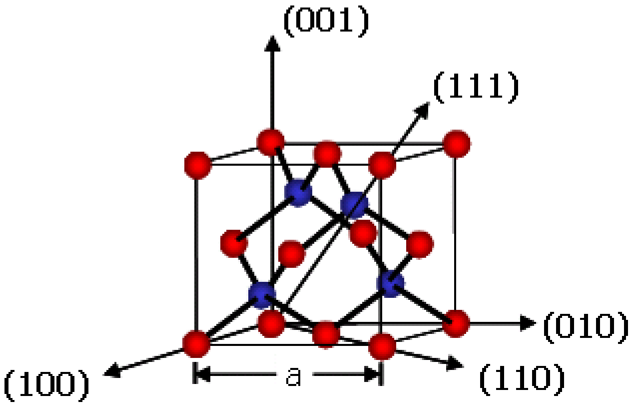
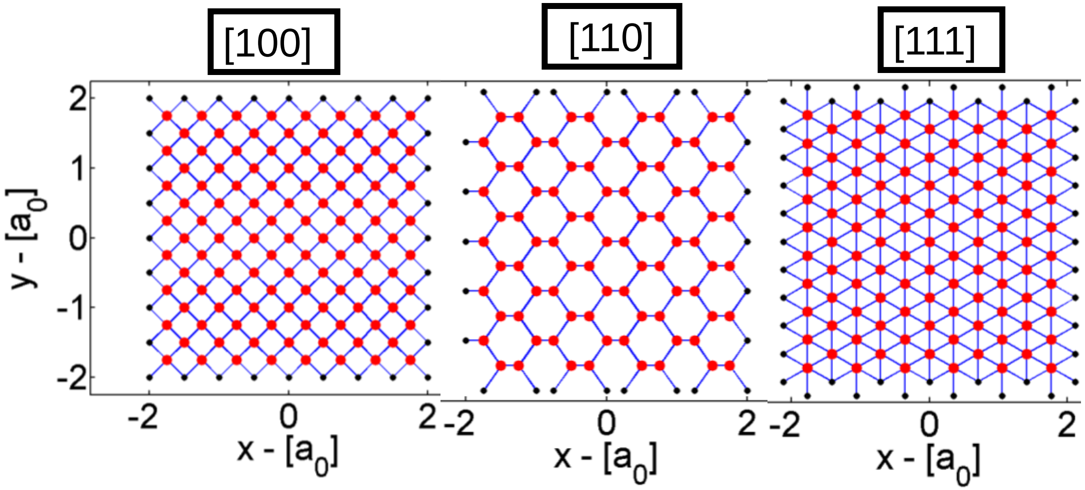
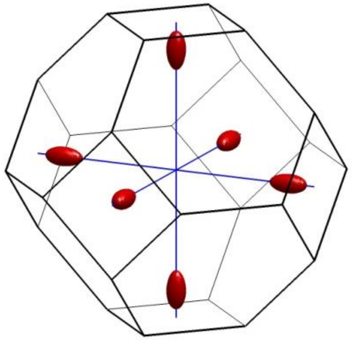
Channel description: Atomistic Tight-Binding



NN $sp^3d^5s^*$-SO





The bulk bandstructure

Based on Localized Atomic Orbitals

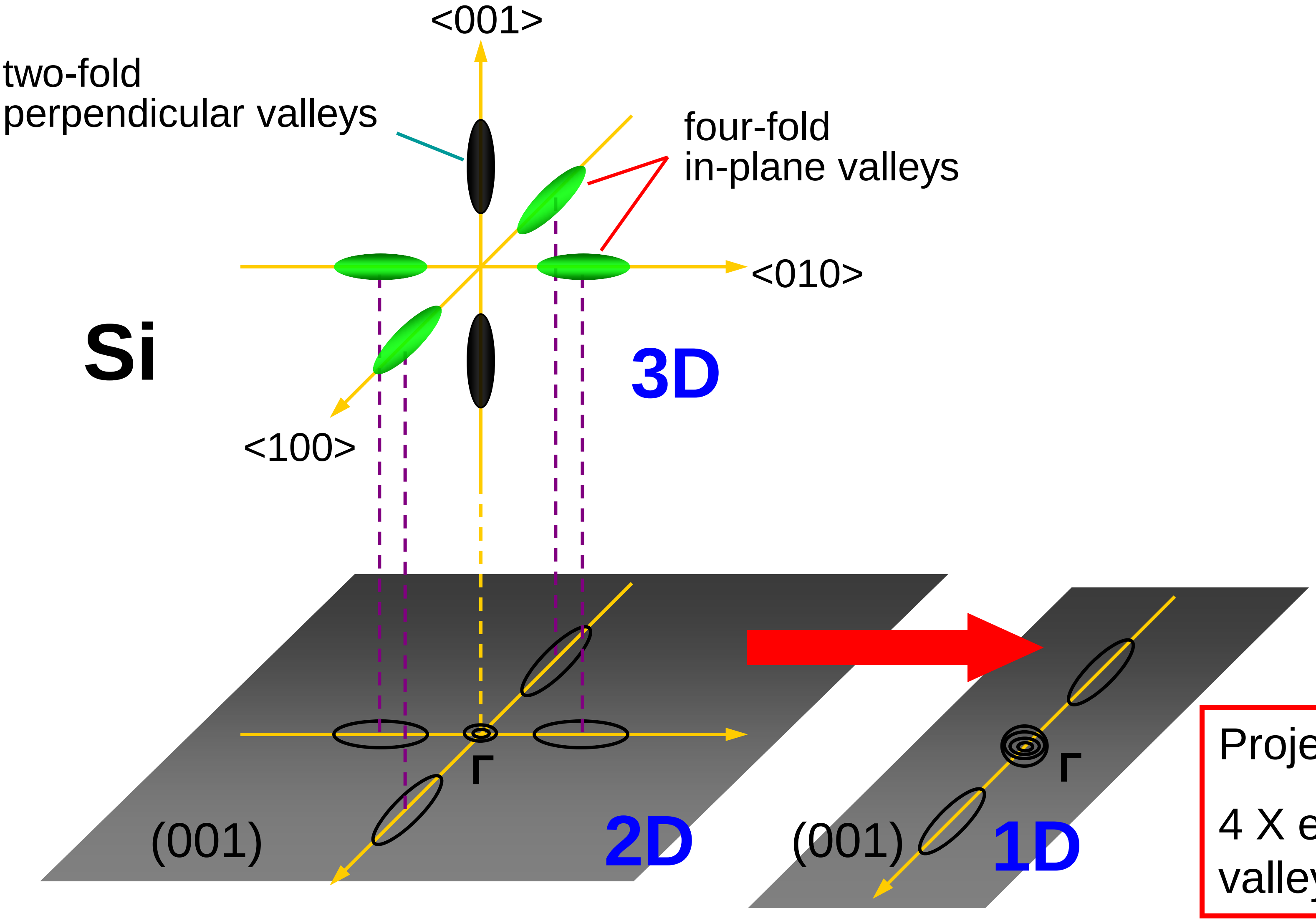
<u>Suitable for:</u>

- Structure deformations, strain
- Material variations, heterostructures

- Needs a set of fitting parameters
- Computationally expensive

- Compromise: between ab-initio methods and continuum methods
- Able to handle 10s of thousands of atoms

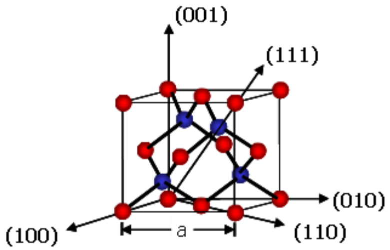
Valleys-from bulk, to quantum wells, and to NWs



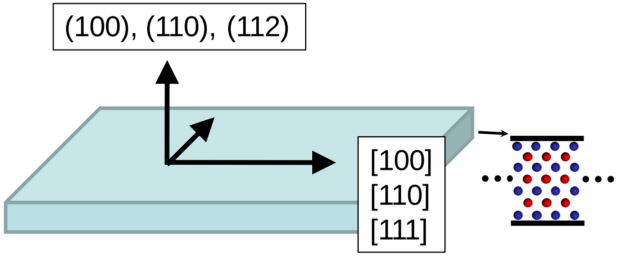
Projection to 1D

4 X equivalent valleys at **Γ**

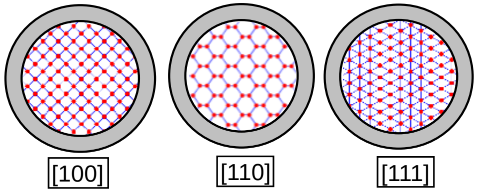
Electronic structure examples

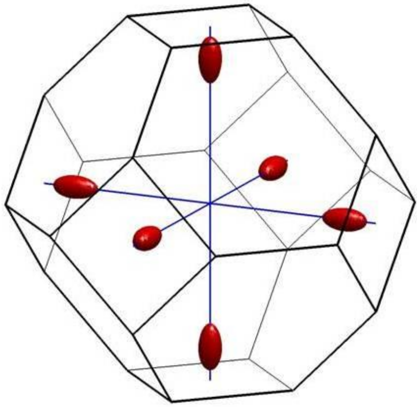


NN $sp^3d^5s^*$-SO

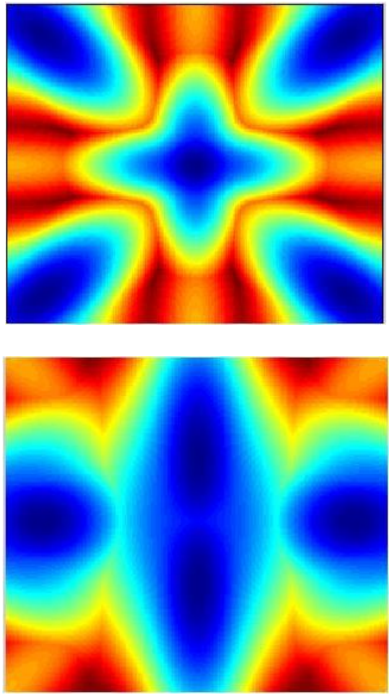

(100), (110), (112)

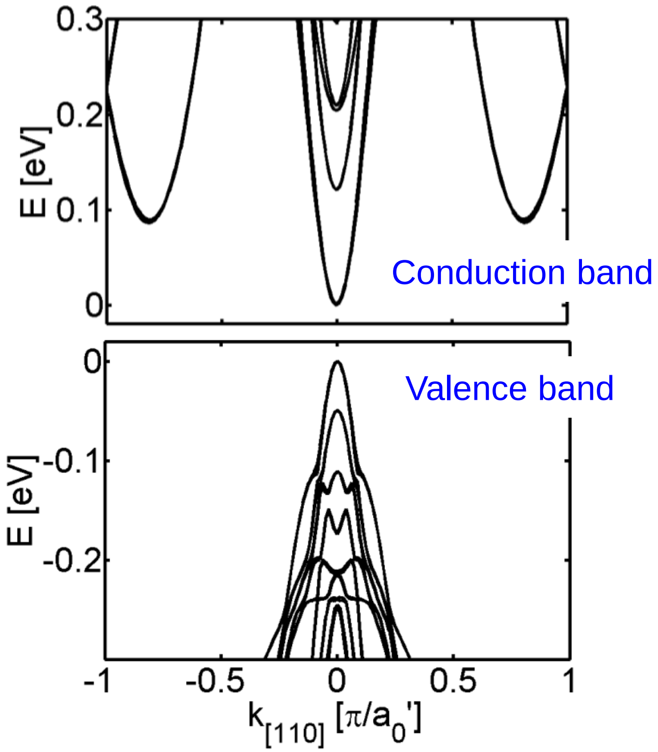
[100]
[110]
[111]





1st Brillouin Zone

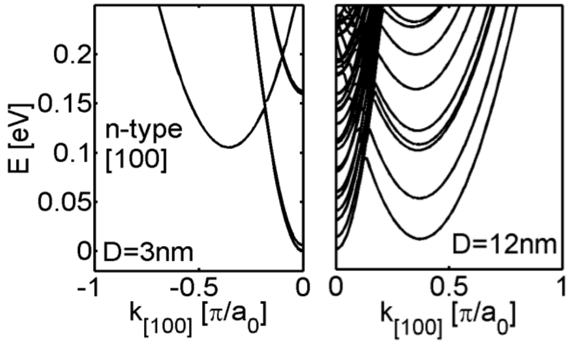




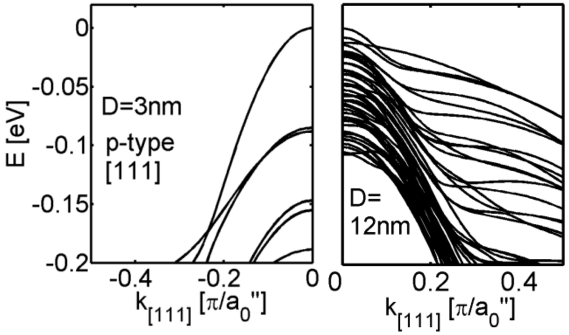
Length scale dependent properties

D=3nm D=12nm

[100]

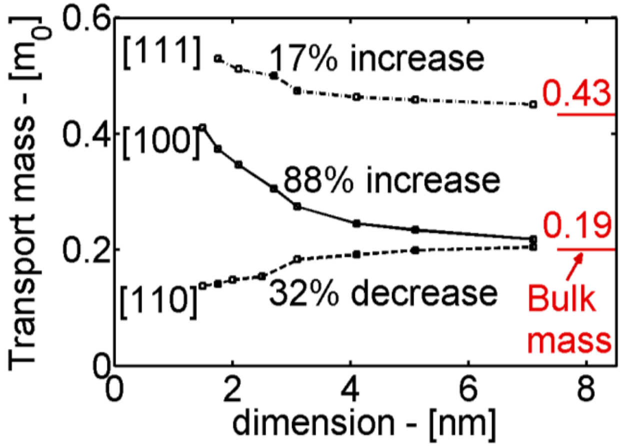


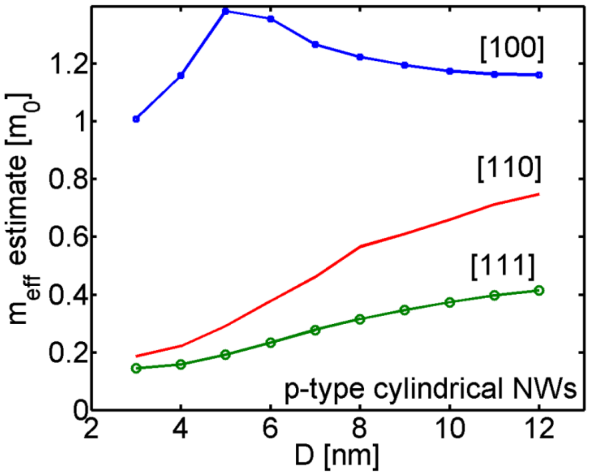
[111]



- Electronic structure is geometry dependent

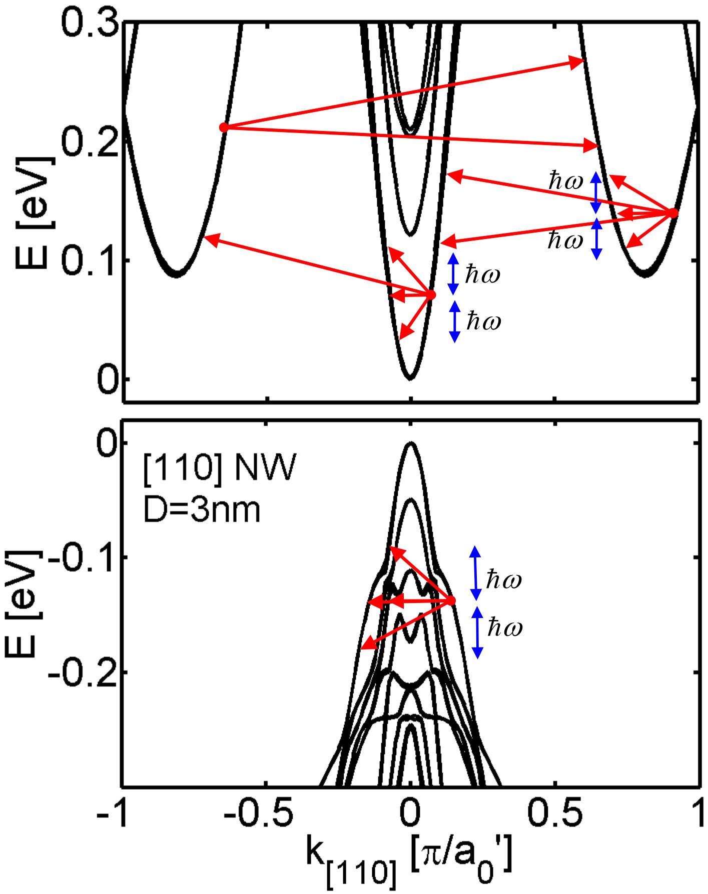
mass variation





NN, IEEE TED, 2008, Nano Lett., 2010

TB coupled to Linearized Boltzmann transport



$$\Xi(\varepsilon) = \sum_{\vec{k}} \vec{v}_{\vec{k}} \vec{v}_{\vec{k}} \tau_{\vec{k}} \delta\left(\varepsilon - \varepsilon(k)\right)$$

$$= g(\varepsilon) v(\varepsilon)^2 \tau(\varepsilon)$$

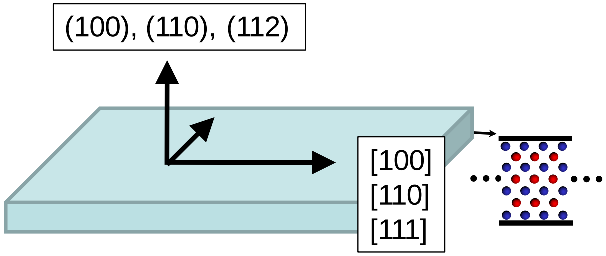
$$\underbrace{R^{(\alpha)} = q_0{}^2 \int_{E_0}^{\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \Xi(\varepsilon) \left(\frac{\varepsilon - \mu}{k_B T}\right)^{\alpha}}$$

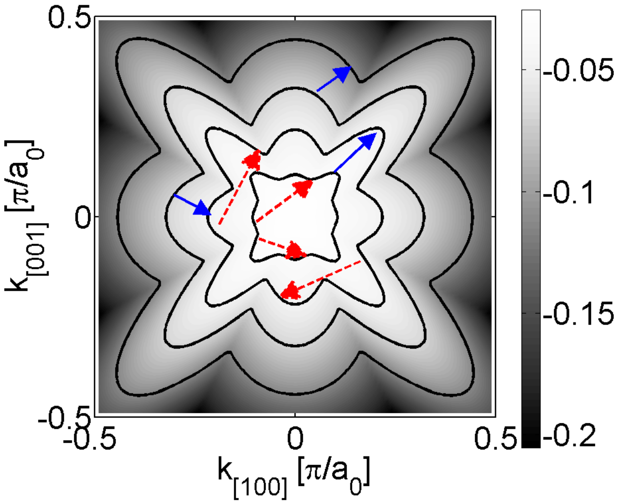
$$\boxed{\begin{gathered} \sigma = R^{(0)} \qquad S = \frac{k_B}{q_0} \frac{R^{(1)}}{R^{(0)}} \\ \kappa_e = \frac{k_B{}^2 T}{q_0{}^2} \left[R^{(2)} - \frac{\left[R^{(1)}\right]^2}{R^{(0)}} \right] \end{gathered}}$$

<u>At all κ-point, subbands:</u>

- velocity $$v_n(E) = \frac{1}{\hbar} \frac{\partial E_n}{\partial k_x}$$
- density of states $$g_{1D}^{n}(E) = \frac{1}{2\pi\hbar} \frac{1}{\left|v_n(E)\right|}$$

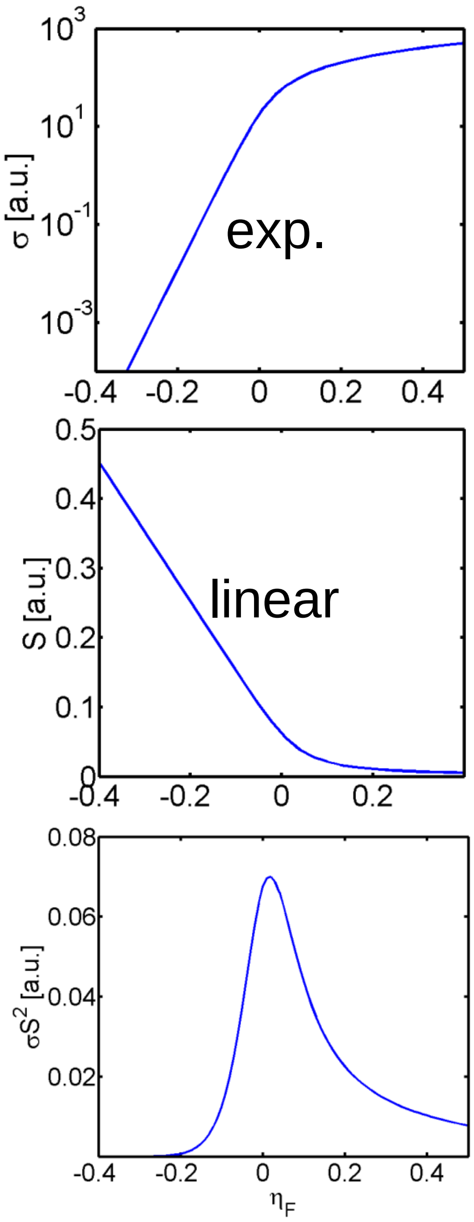
Linearized Boltzmann transport: 2D





- Relaxation times
(of every k-state, at every subband)
- phonon scattering (acoustic/optical)
- surface roughness scattering
- ionized impurity scattering

Basic features for TE coefficients – simple guidelines

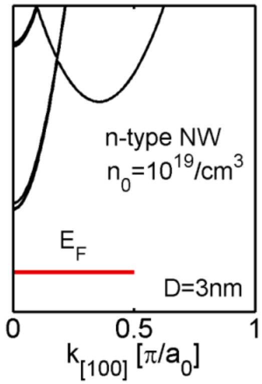


$$\sigma = q_0^{\;2}\int_{E_0}^{\infty} d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\Xi(\varepsilon)$$

$\sigma \sim 1/m_{eff} * \exp(-\eta_F)$

$$\eta_F = E_0 - E_F$$

$$S = \frac{k_B q_0}{\sigma}\int_{E_0}^{\infty} d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\Xi(\varepsilon)\left(\frac{\varepsilon - E_F}{k_B T}\right)$$

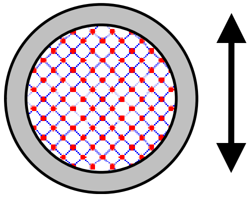


$S \sim \eta_F$

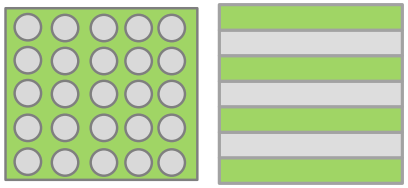
Power factor maximum around Ef

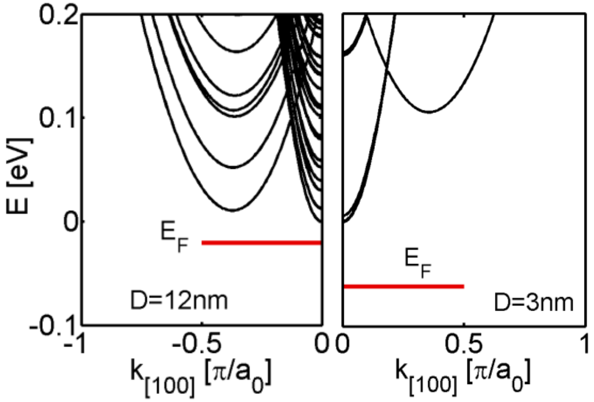
Design direction for σS^2 at low dimensions

Change geometry at the same charge density:



From:
3D to 1D





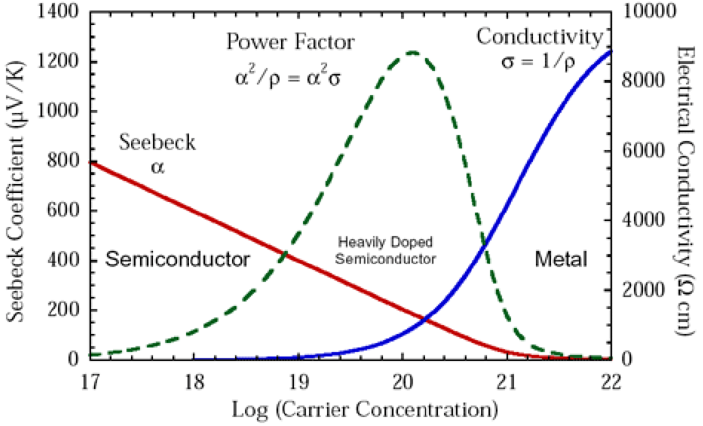
} $\eta_F = E_C - E_F$

Neophytou and Kosina, PRB, 83, 245305, 2011

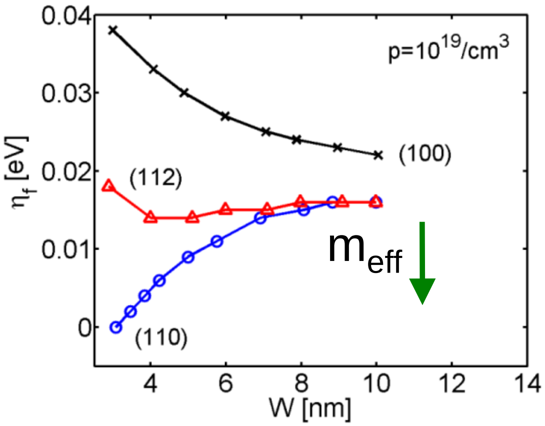
$\sigma \sim 1/m_{eff} * \exp(-\eta_F)$

$S \sim \eta_F$

σS^2

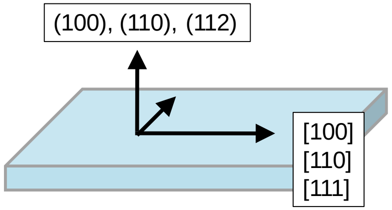


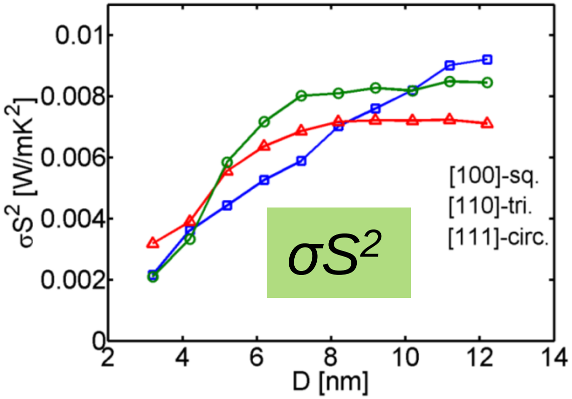
A thorough investigation for Si: σ determines σS^2

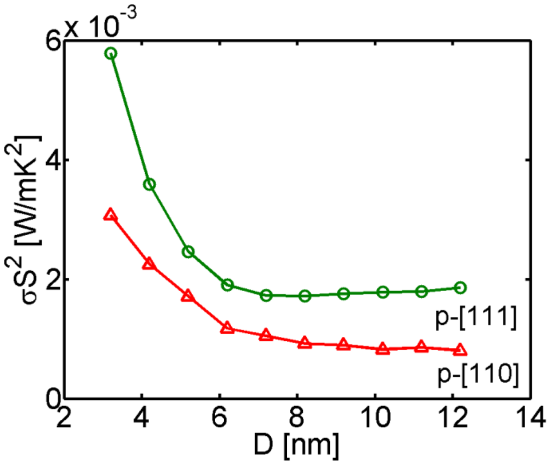


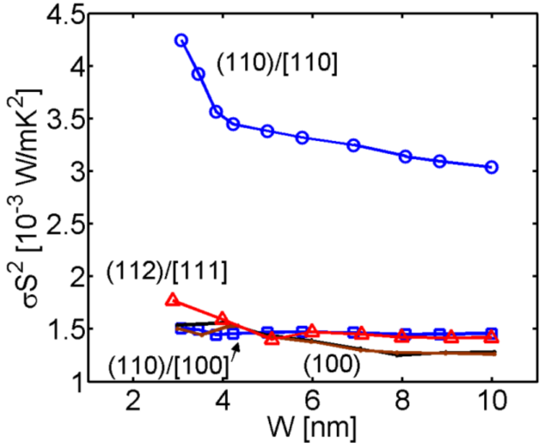
$\sigma \sim 1/m_{eff} * \exp(-\eta_F)$

$S \sim \eta_F$









S ↑ σ ↓↓

S σ ↑

S ↓ σ ↑↑↑

Neophytou and Kosina, PRB, 83, 245305, 2011

Neophytou and Kosina, J. Appl. Phys., 112, 024305, 2012

Outline

- Introduction – design at the nanoscale
    - Nanoscale thermoelectrics – design targets
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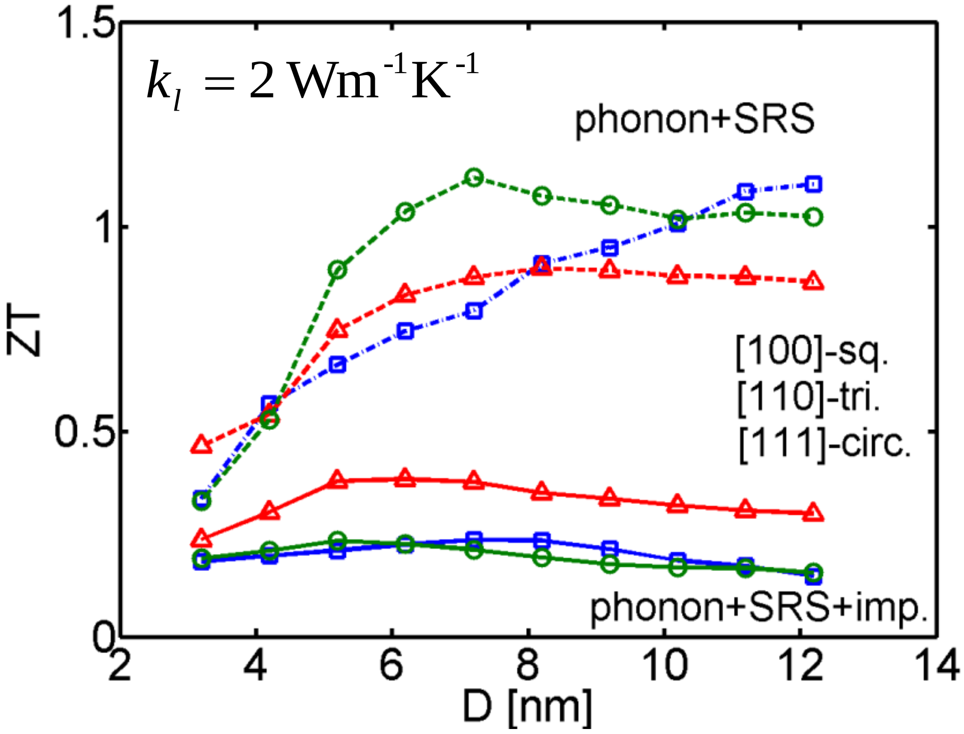
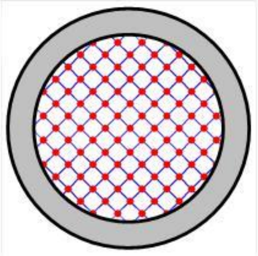
Transport: Impurity dominated



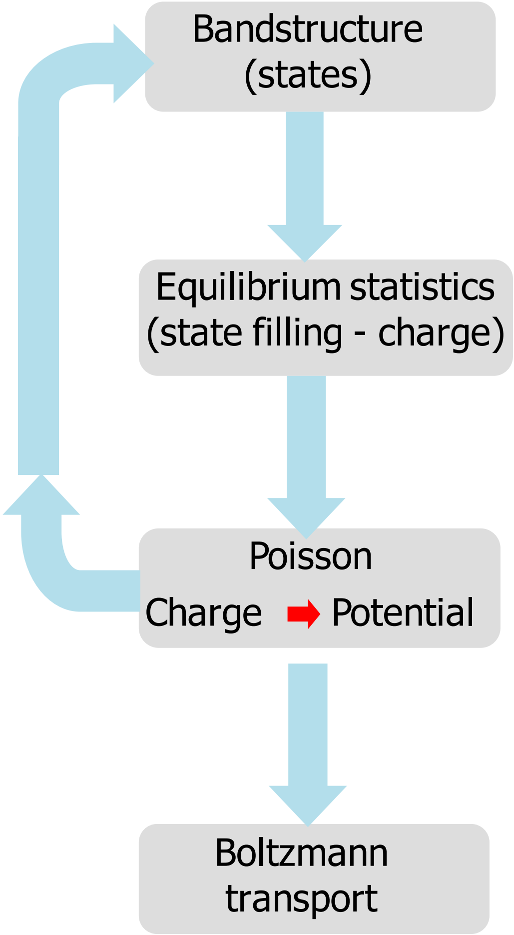
~2-4X reduction

gate all around (modulation doping)



Modulation doping?
Surface charge transfer?
Gating?

Self-consistent computational model

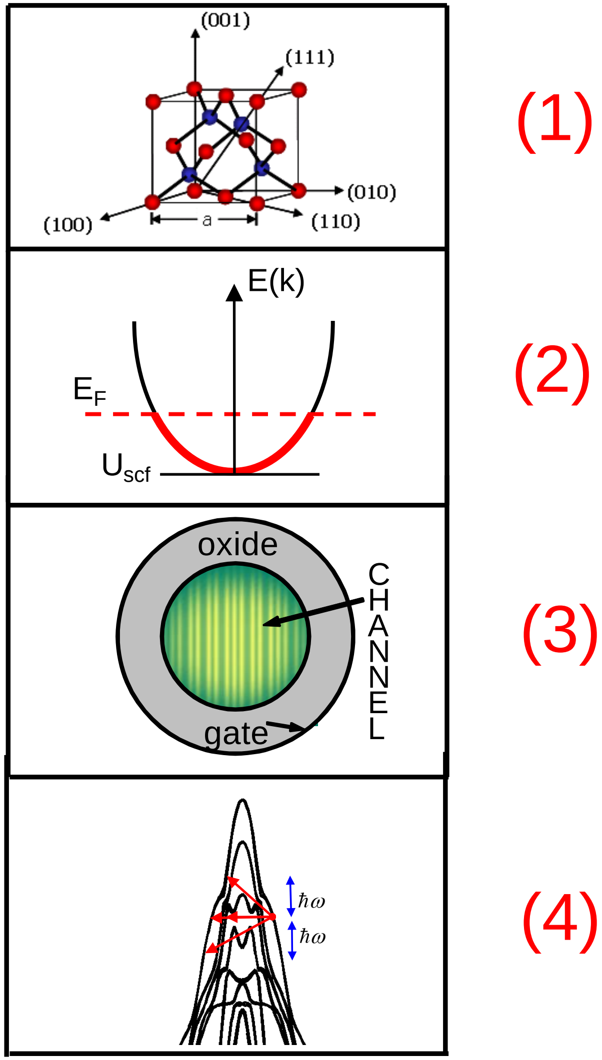


Bandstructure
(states)

Equilibrium statistics
(state filling - charge)

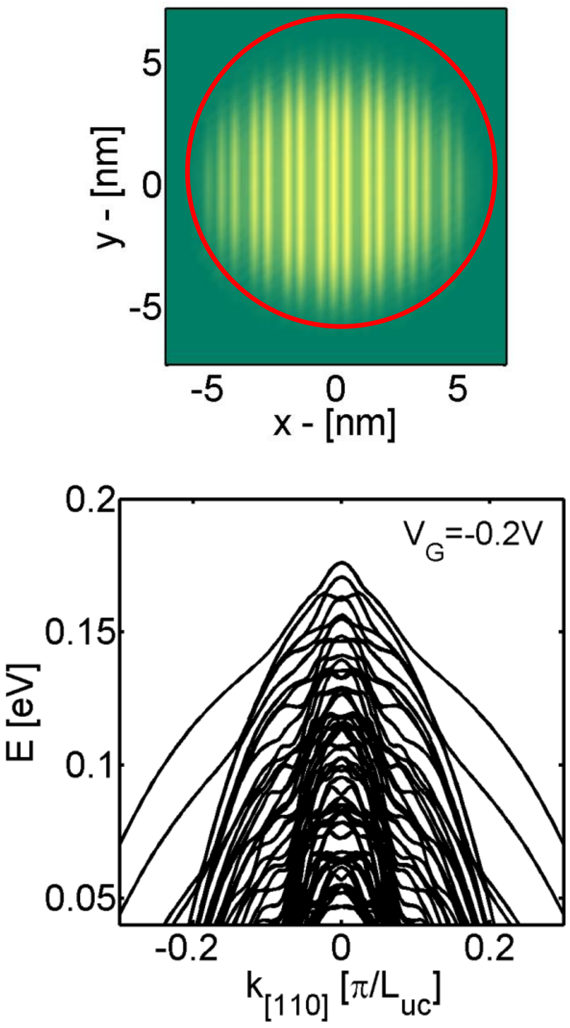
Poisson
Charge ➡ Potential

Boltzmann
transport

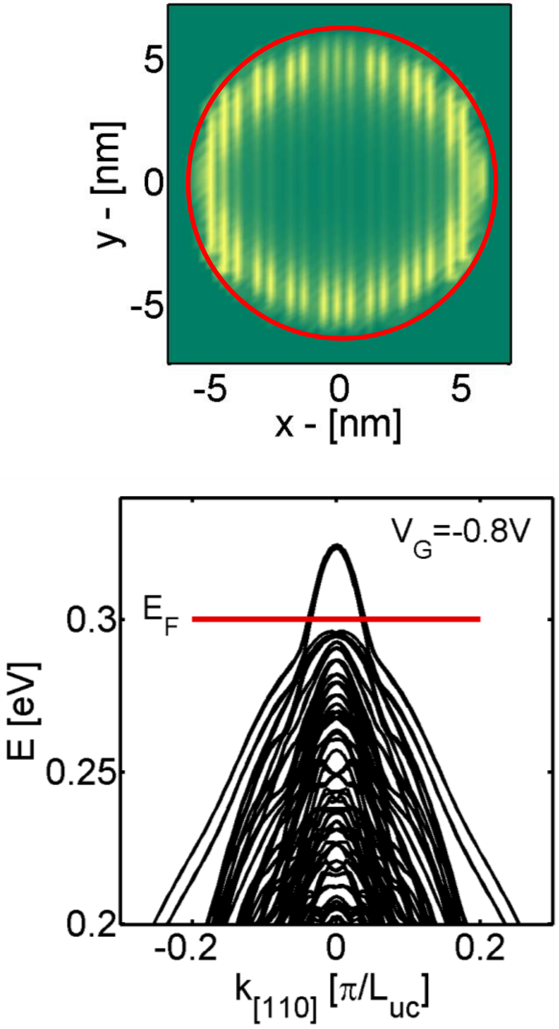


Hole dispersions under confinement

p-type
[110] NW
D=12nm

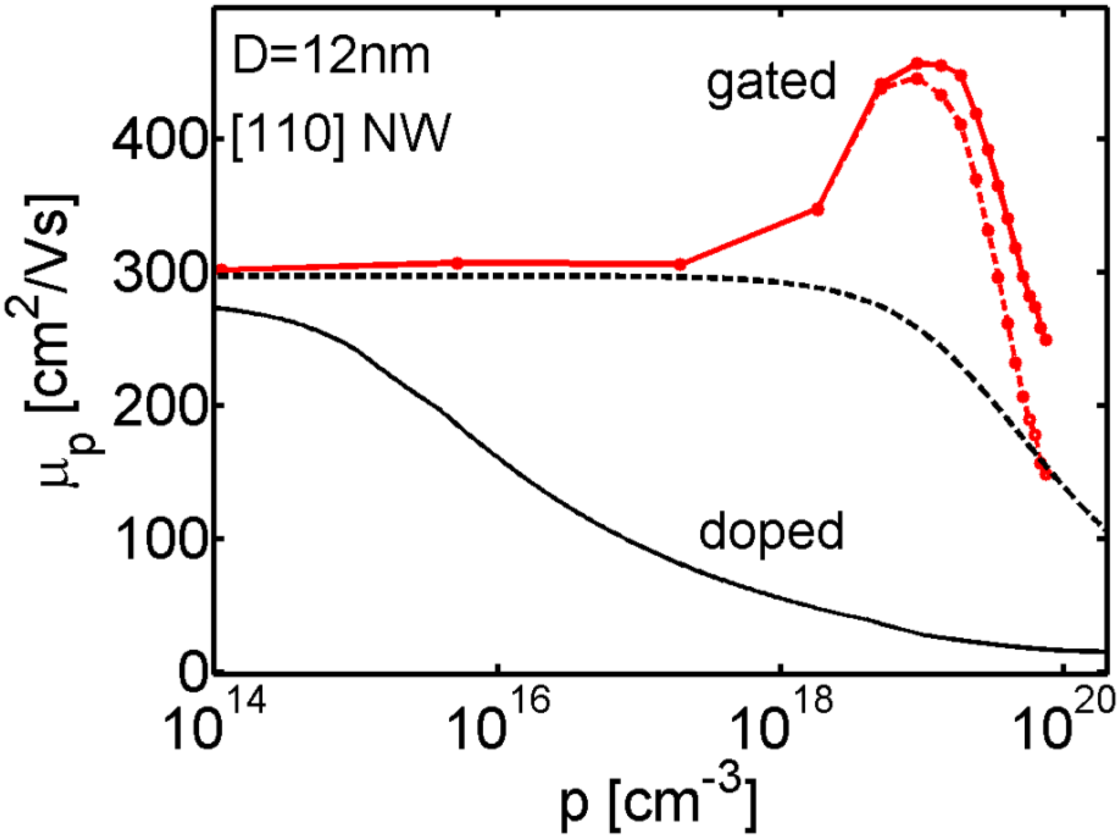


Low V_G



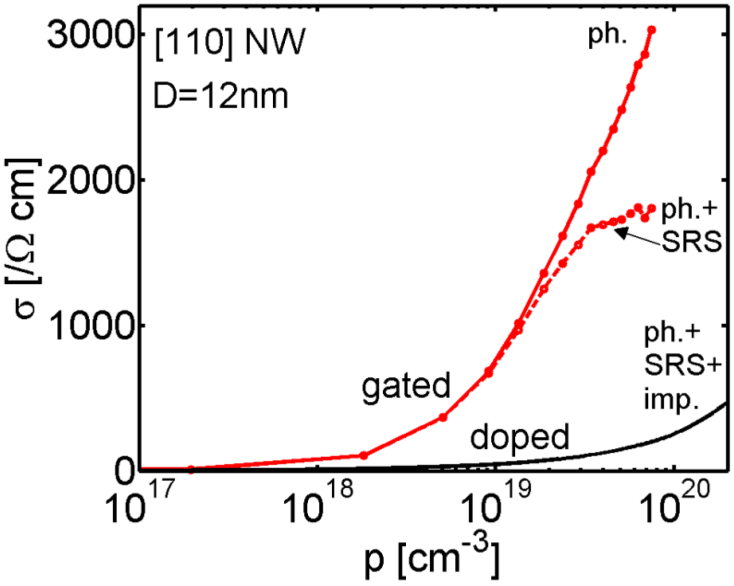
High V_G

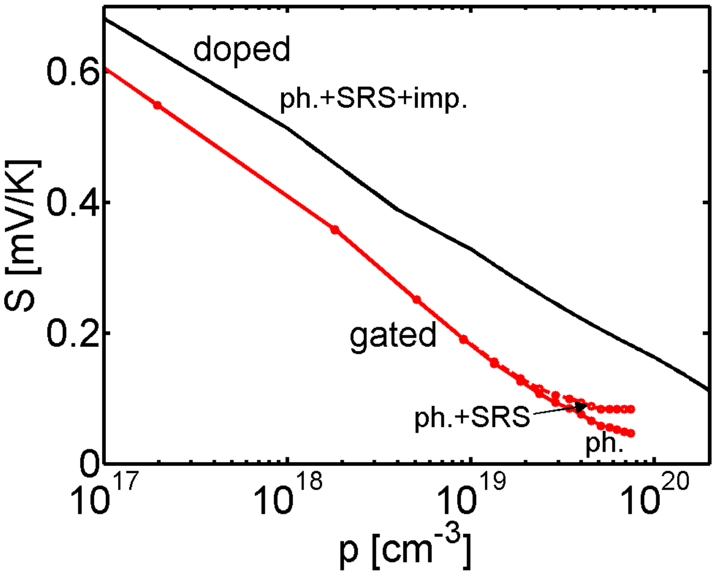
The effect of gating on NW mobility

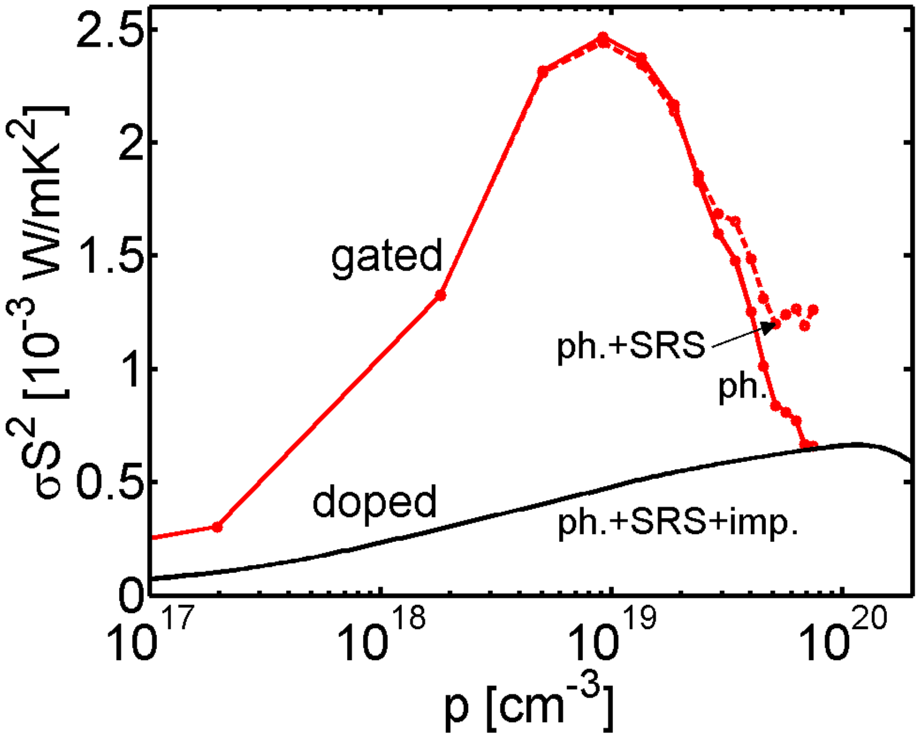


- Benefit from not using dopants
- Gating seems beneficial, even with surface roughness (accumulation is achieved with weaker fields)

Power factor improvement



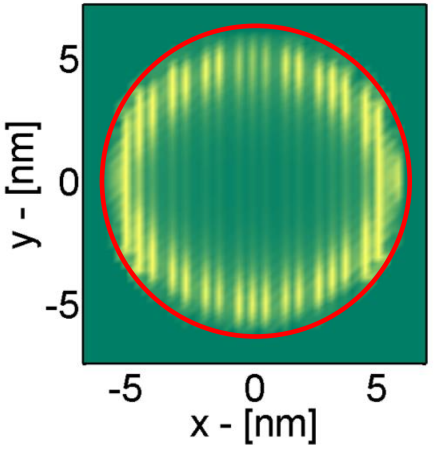


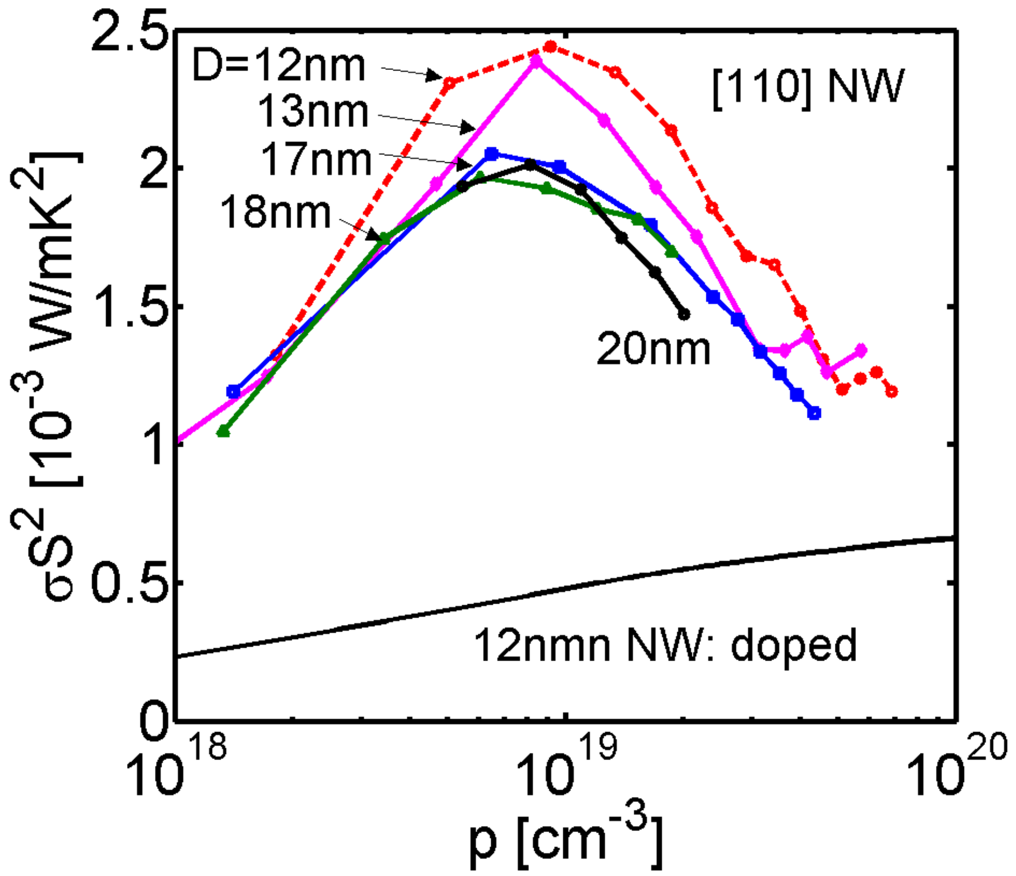


Power factor:

- Improved by ~5x

Power factor improvement versus diameter

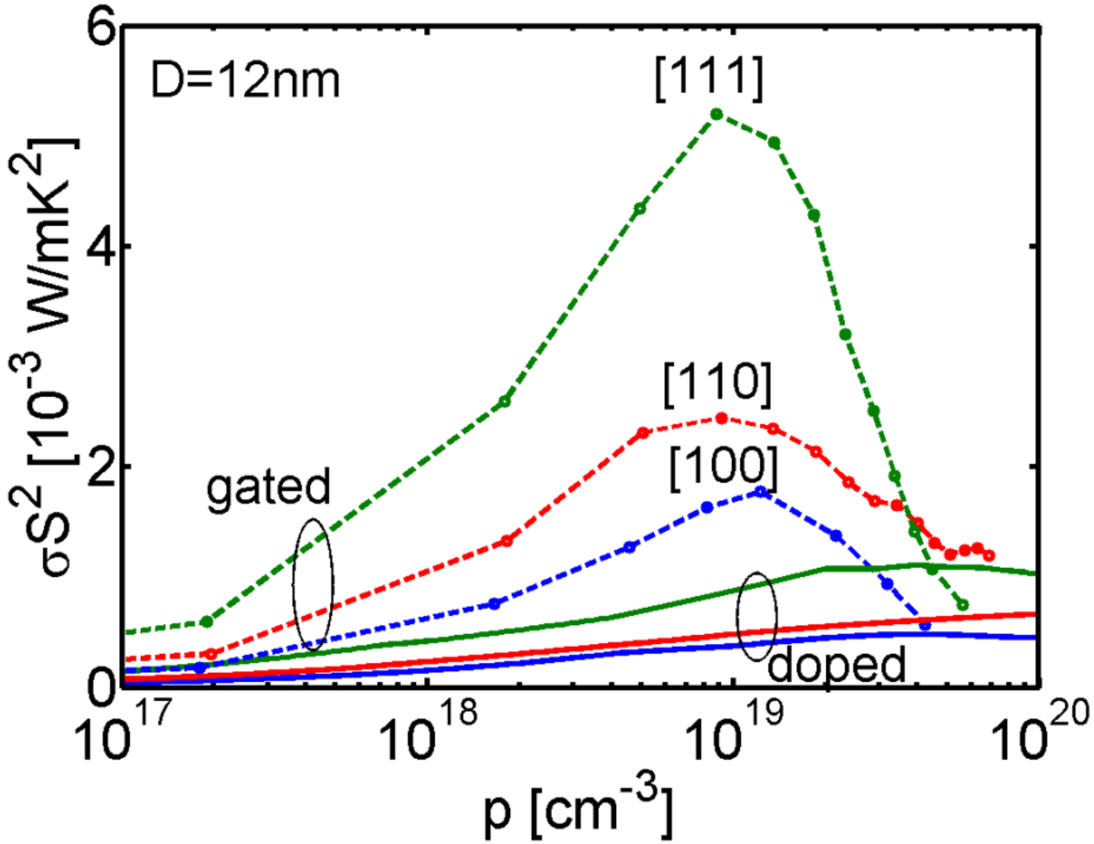




Power factor improvements:

- Still observed at *D*=20nm we were able to simulate
- Might be retained up to *D*~40nm

Power factor - anisotropy



Strong anisotropy:

- [111] NWs ~2x higher performance than [110]
  ~3x higher performance than [100]

Summary: Design strategies for low-D

1) Optimize the materials bandstructure:

- Best choice of geometry/confinement, η_F
- But in general, use of strain, alloying etc.

2) Avoid the most degrading scattering mechanisms:

- Remove dopant impurities by gate field
- But also modulation doping, would work

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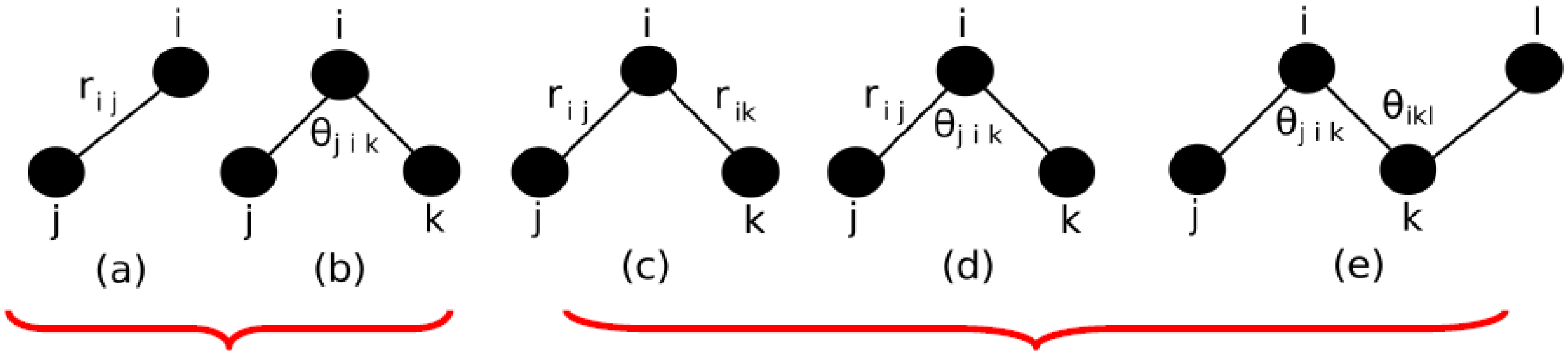
Modified Valence Force Field Method (MVFF)



Keating

Modified

$$U_{bs}^{ij} = \frac{3}{8}\alpha \frac{\left(r_{ij}^2 - d_{ij}^2\right)^2}{d_{ij}^2}$$

bond-stretching

$$U_{bb}^{jik} = \frac{3}{8}\beta \frac{\left(\Delta\theta_{jik}\right)^2}{d_{ij}d_{ik}}$$

bond-bending

$$U_{bs-bs}^{jik} = \frac{3}{8}\delta \frac{\left(r_{ij}^2 - d_{ij}^2\right)\left(r_{ik}^2 - d_{ik}^2\right)}{d_{ij}d_{ik}}$$

cross bond stretching

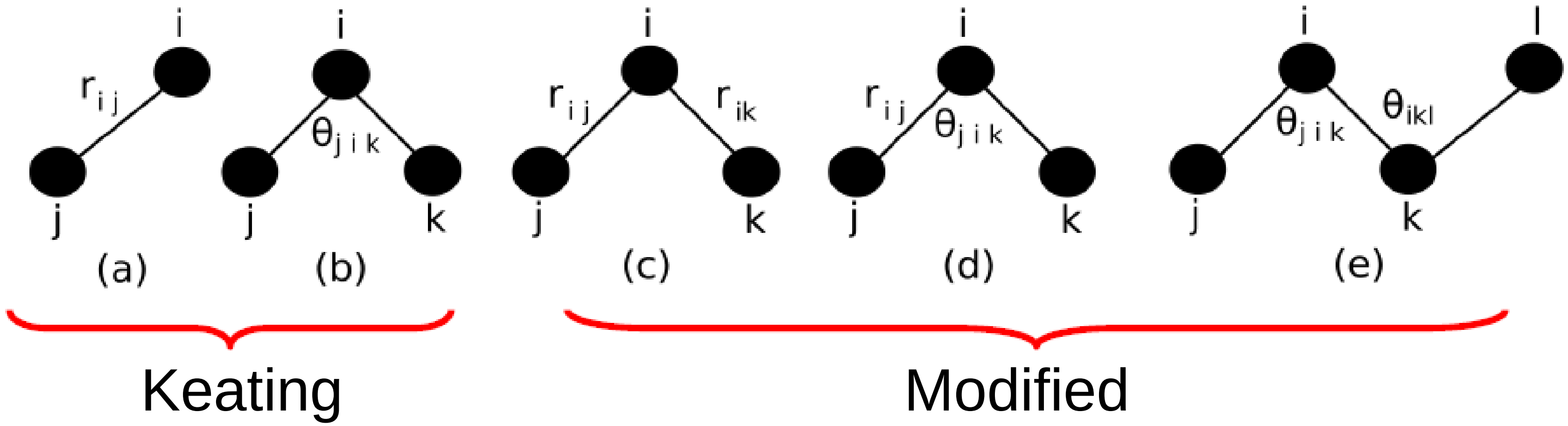
$$U_{bs-bb}^{jik} = \frac{3}{8}\gamma \frac{\left(r_{ij}^2 - d_{ij}^2\right)\left(\Delta\theta_{jik}\right)}{d_{ij}d_{ik}}$$

cross bond stretching/ bending

$$U_{bb-bb}^{jikl} = \frac{3}{8}\upsilon \frac{\left(\Delta\theta_{jik}\right)\left(\Delta\theta_{ikl}\right)}{\sqrt{d_{ij}d_{ik}^2 d_{kl}}}$$

coplanar bond bending

Modified Valence Force Field Method (MVFF)



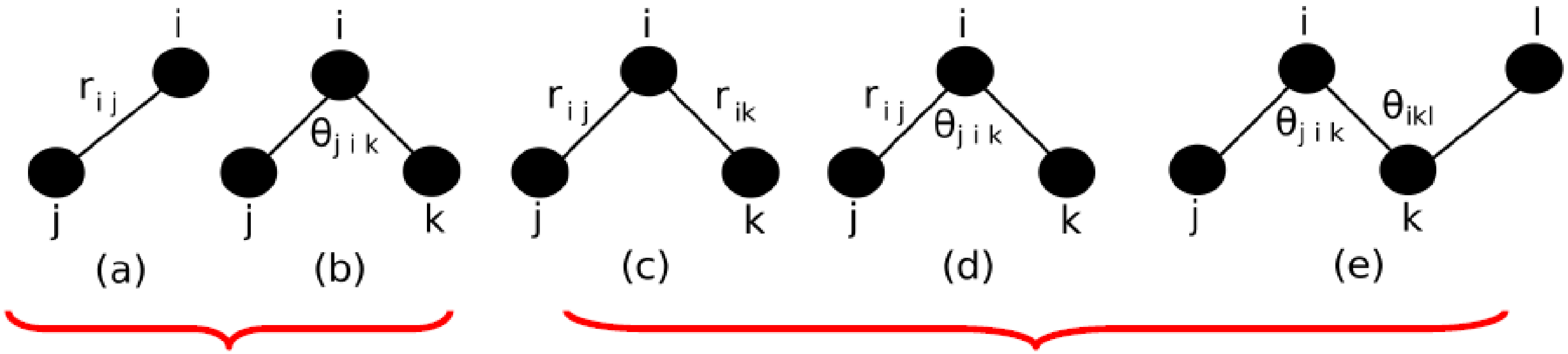
$$U \approx \frac{1}{2} \sum_{i \in N_A} \left[\sum_{j \in nn_i} U_{bs}^{ij} + \sum_{j,k \in nn_i}^{j \neq k} \left(U_{bb}^{jik} + U_{bs-bs}^{jik} + U_{bs-bb}^{jik} \right) + \sum_{j,k,l \in COP_i}^{j \neq k \neq l} U_{bb-bb}^{jikl} \right]$$

$$D_{mn}^{ij} = \frac{\partial^2 U_{mn}^{ij}}{\partial r_m^i \partial r_n^j}$$

$$D_{ij} = \begin{bmatrix} D_{xx}^{ij} & D_{xy}^{ij} & D_{xz}^{ij} \\ D_{yx}^{ij} & D_{yy}^{ij} & D_{yz}^{ij} \\ D_{zx}^{ij} & D_{zy}^{ij} & D_{zz}^{ij} \end{bmatrix}$$

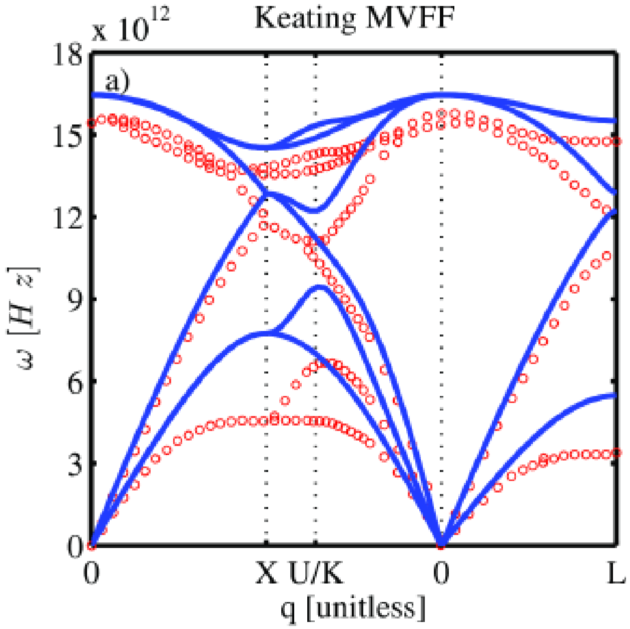
$$D + \sum_{l} D_l \exp\left(i\vec{q}.\vec{\Delta R}_l \right) - \omega^2 \left(q \right) I = 0$$

MVFF: Benchmarked to bulk Si

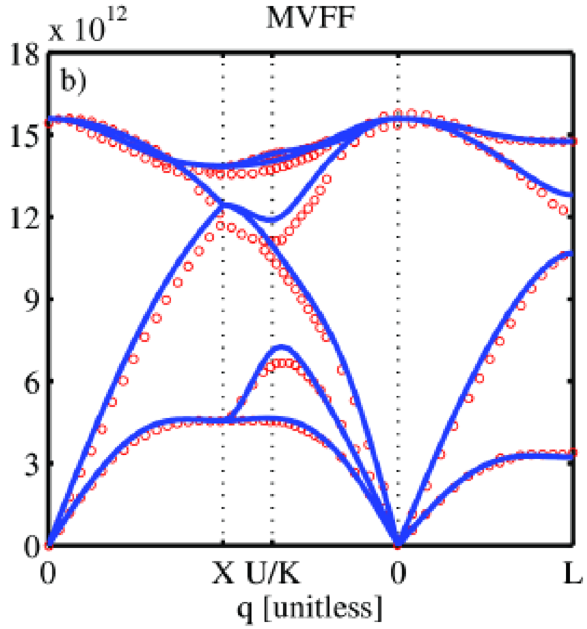


Keating

Modified

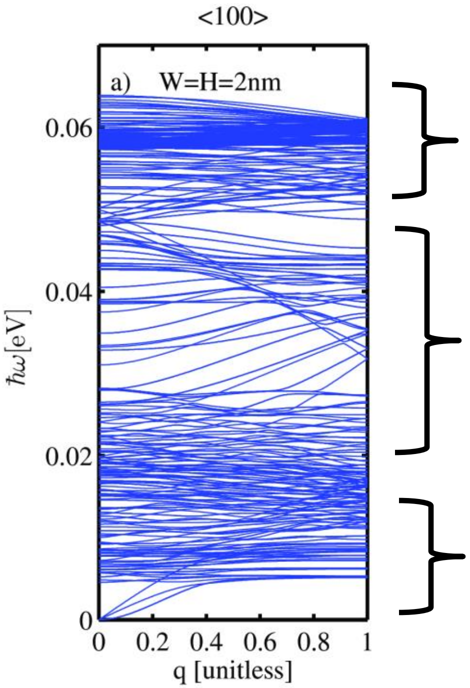


(f)



(g)

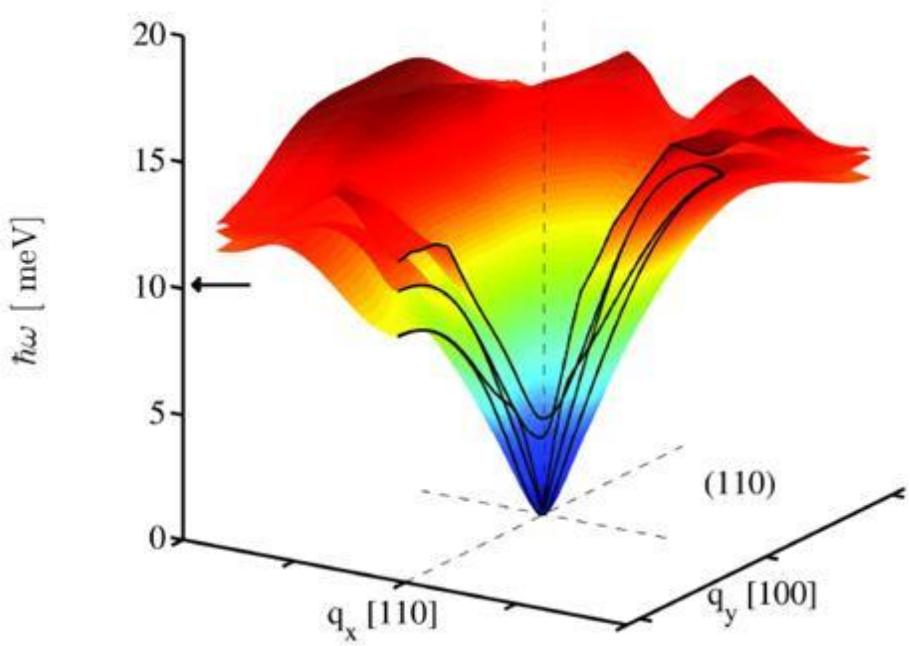
MVFF: Low-dimensional phonon spectrum



optical

quasi-
acoustic

acoustic



1D nanowire

2D ultra-thin layer

Phonon thermal conductivity (diffusive)

BTE for phonons (bulk formalism)

Umklapp scattering

$$\frac{1}{\tau_U} = B\omega_i(q)^2 T \exp(-\frac{C}{T})$$

Boundary scattering

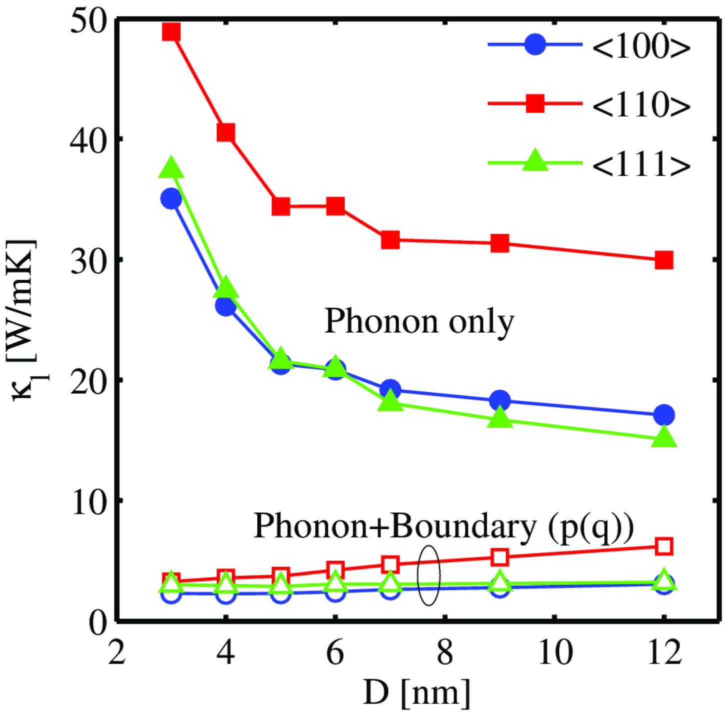
$$\frac{1}{\tau_{B,i}(q)} = \frac{1-p(q)}{1+p(q)} \frac{v_{g,i}(q)}{W}$$

$$p(q) = \exp(-4q^2\Delta_{rms}^2)$$

<u>*P*: specularity parameter</u>

P=1, fully specular

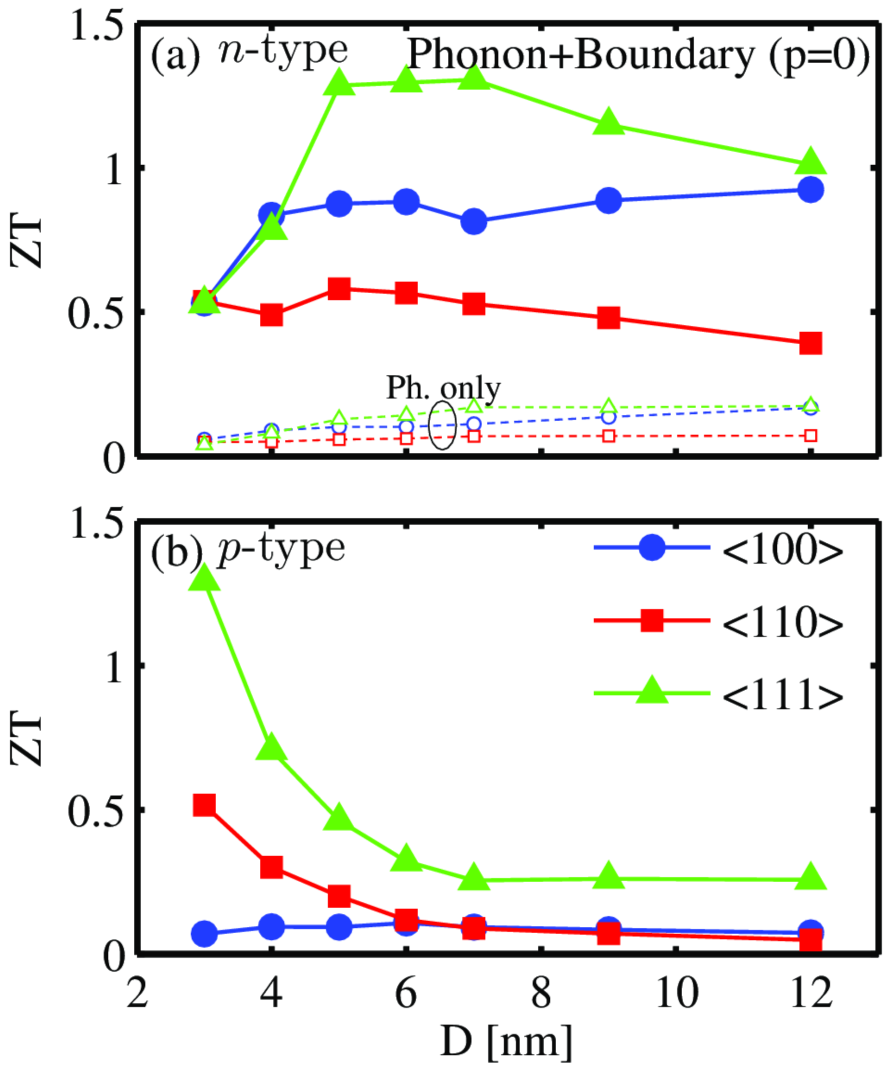
***P*=0, fully diffusive**



Higher order scattering

$$\frac{1}{\tau_{U2}} = A_0 T^2$$

ZT figure of merit



n-type NWs*:*
ZT~1.4 can be reached
(around 6-7nm)

p-type NWs*:*
ZT~1.4 can be reached
(around 3nm)

ZT is improved,
but still low !
(Bulk Si ZT is ~0.01)

Just low-D is not enough

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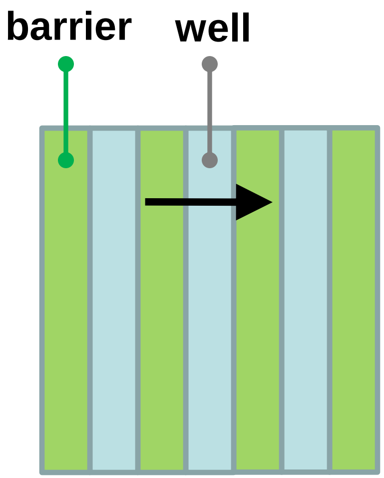
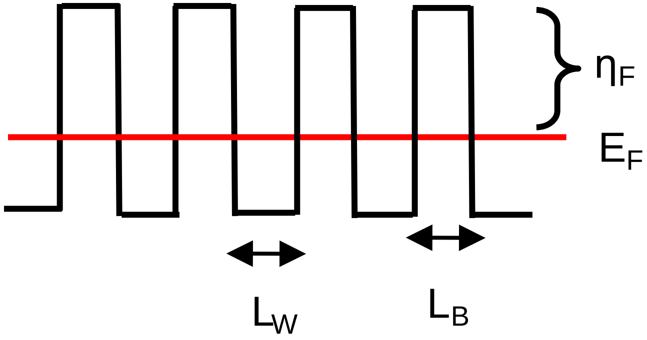
Nanocomposite channels for increased Seebeck

Make *S* and *σ* really independent?

How to increase both simultaneously?



superlattices
Si/SiGe

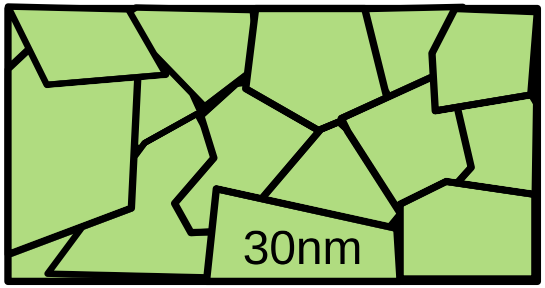


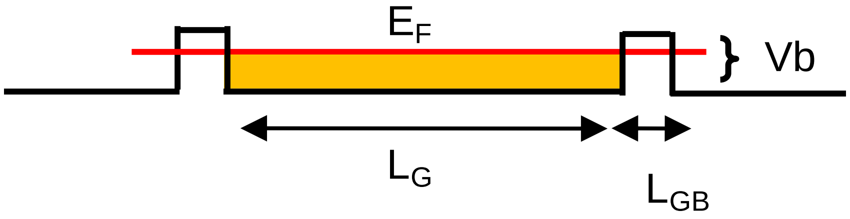
Barriers: $S \sim \eta_F$ ↑↑ $\sigma \sim \exp(-\eta_F)$ ↓

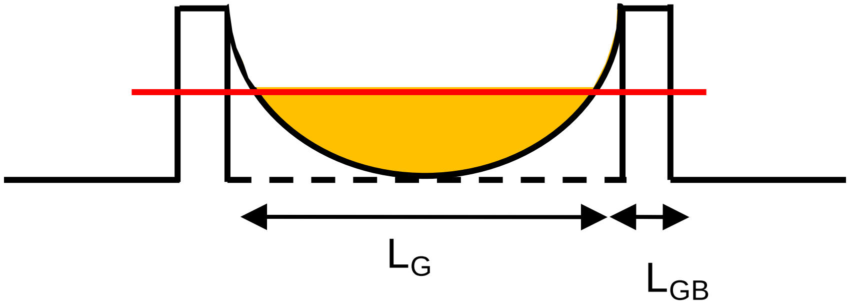
Wells: $S \sim \boldsymbol{E_F}$ ↓ $\sigma \sim \exp(-\boldsymbol{E_F})$ ↑↑

Nanocrystalline Si

Make *S* and *σ* really independent?
How to increase both simultaneously?







- Heavily boron doped
- Annealing steps
- Boron precipitates

(non-uniform distribution)

- charge decreases
- Vb increases
- W_D increases

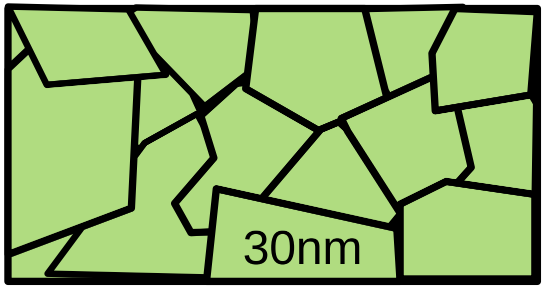
Neophytou *et* al., J. Electr. Mat., 2012, ICT 2012

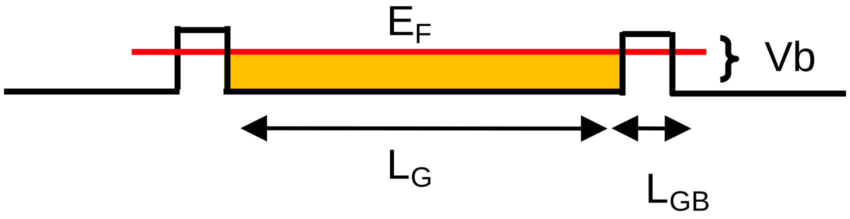
Collaboration: Prof. X. Zianni (Chalkida) and Prof. D. Narducci (Milano)

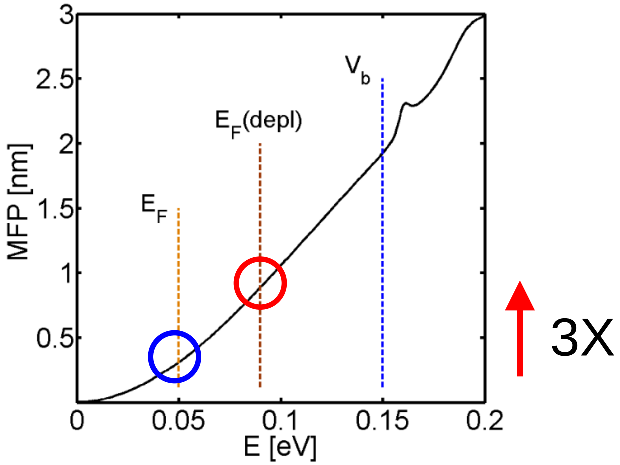
Nanocrystalline Si

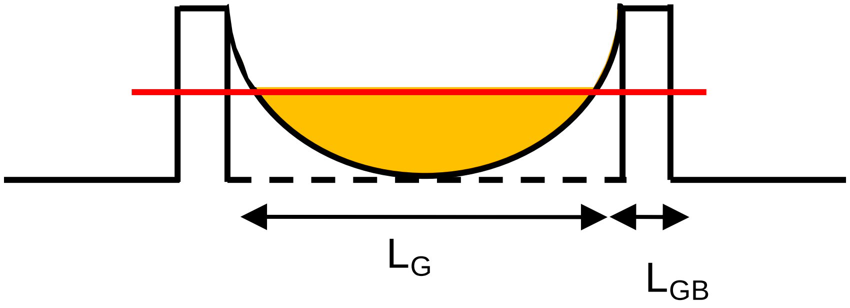
Make *S* and *σ* really independent?

How to increase both simultaneously?





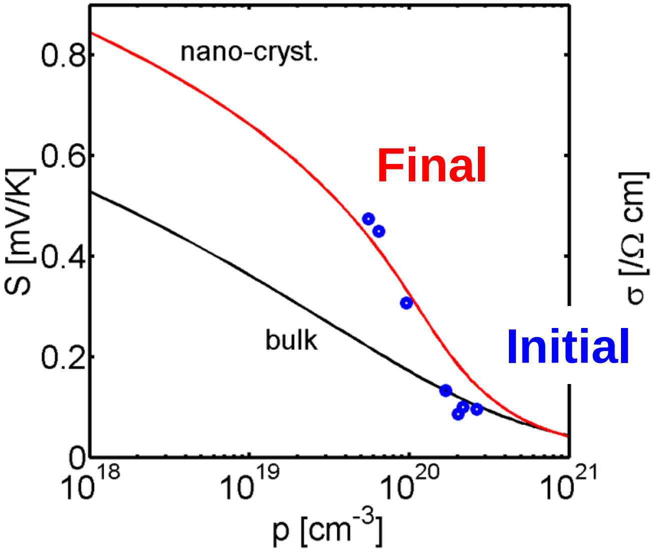


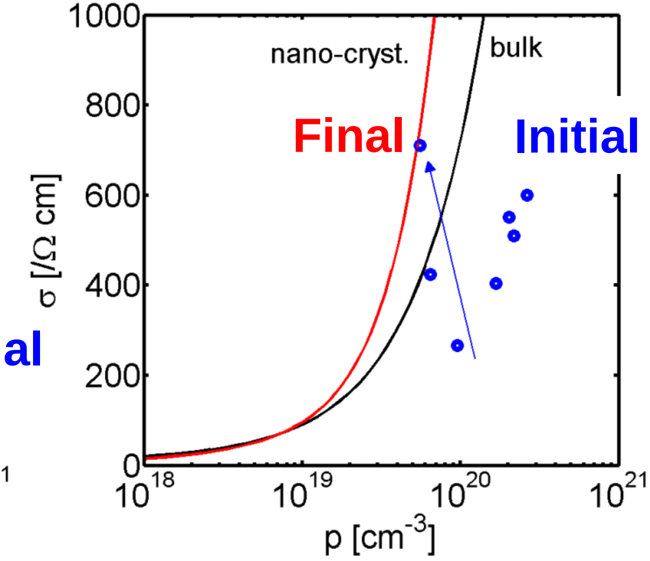


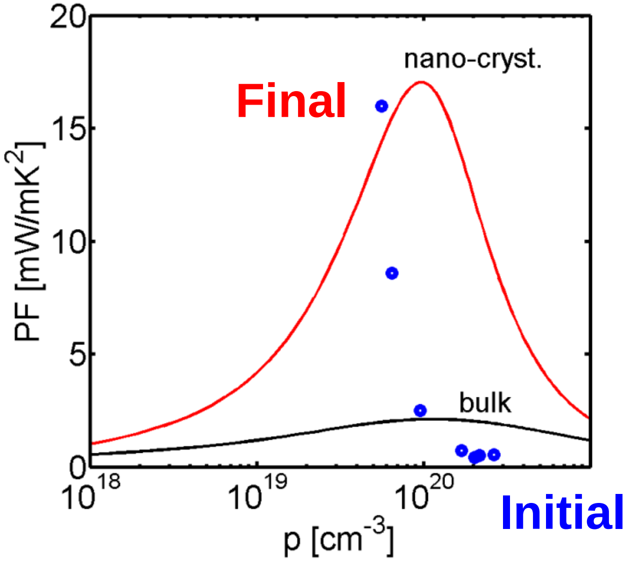
Neophytou *et* al., J. Electr. Mat., 2012, ICT 2012, nanotechnology, 2013

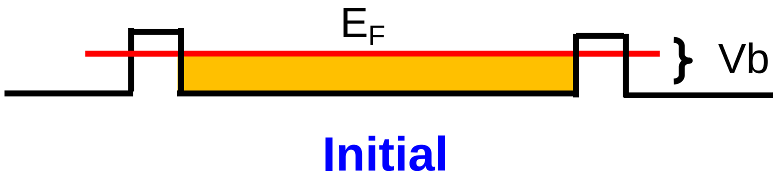
<u>Collaboration:</u> Prof. X. Zianni (Chalkida) and Prof. D. Narducci (Milano)

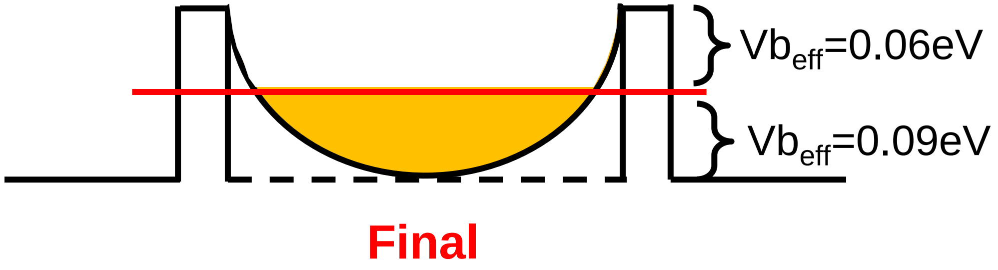
Nanocrystalline Si: Simulations vs. experiments











Simultaneous enhancement in *σ* and *S*

Neophytou *et* al., J. Electr. Mat., 2012, ICT 2012, nanotechnology, 2013

Collaboration: Prof. X. Zianni (Chalkida) and Prof. D. Narducci (Milano)

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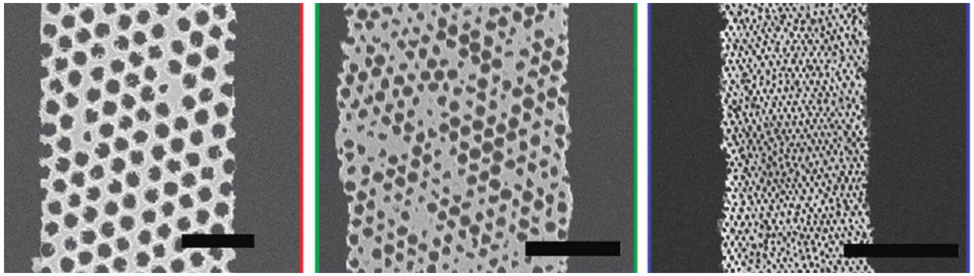
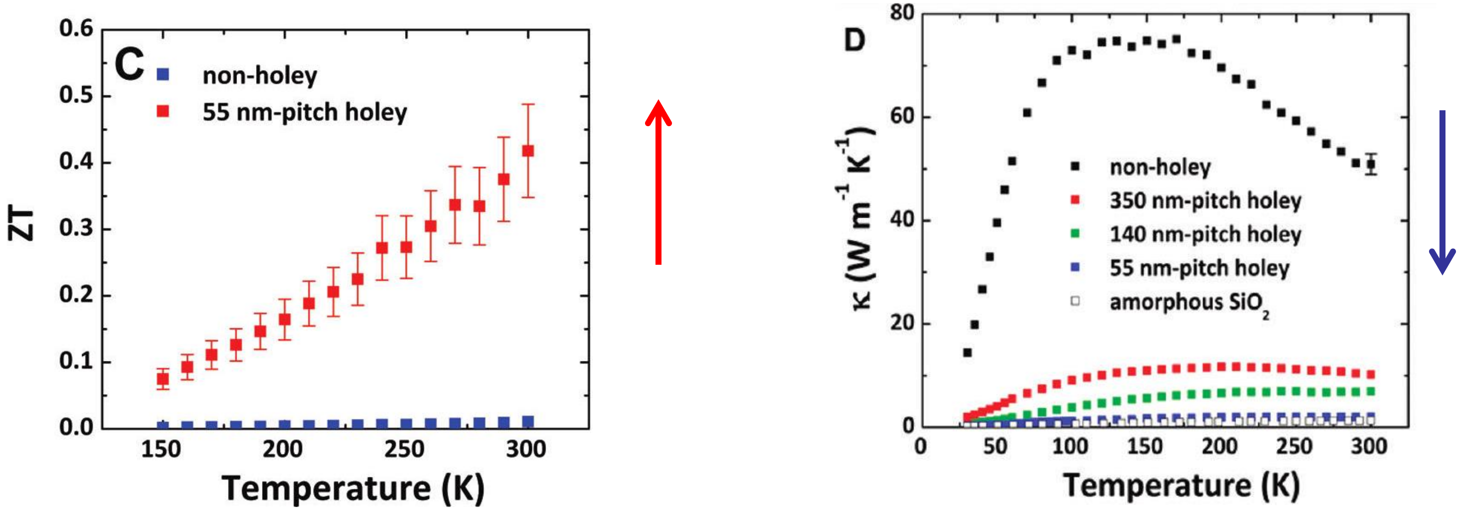
Si nanomeshes

Nanoporous membranes of single-crystalline Si (“holey” Si)

$$\uparrow\ ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l}\ \downarrow$$

$ZT \sim 0.4$





Tang et al, Nano Lett. 2010

Method: Solve BTE using Monte Carlo

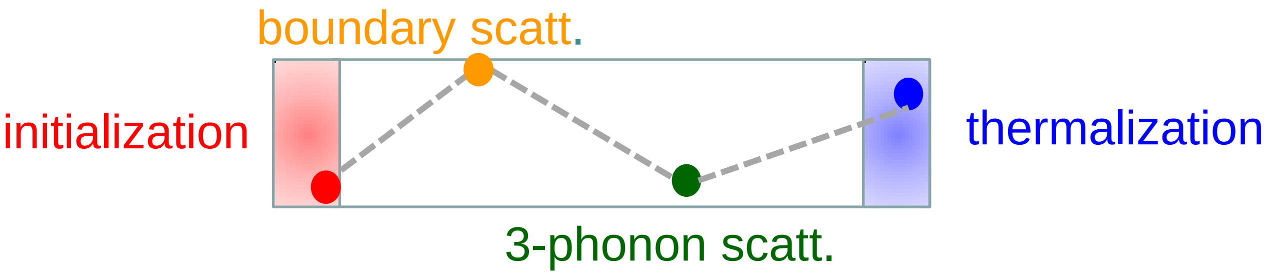
Boltzmann Transport Equation for phonon

$$\frac{\partial f}{\partial t} + v \cdot \nabla f = \left[\frac{\partial f}{\partial t}\right]_{scatt}$$

Relaxation time approximation

$$\left[\frac{\partial f}{\partial t}\right]_{scatt} = -\frac{f - f^0}{\tau}$$

Solve BTE using Monte-Carlo (MC)

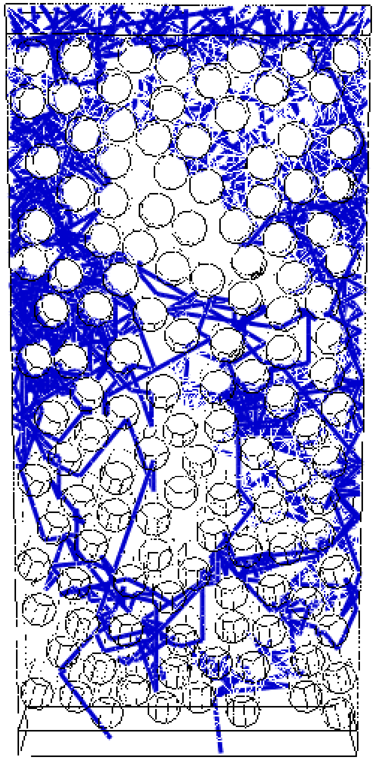


boundary scatt.

initialization

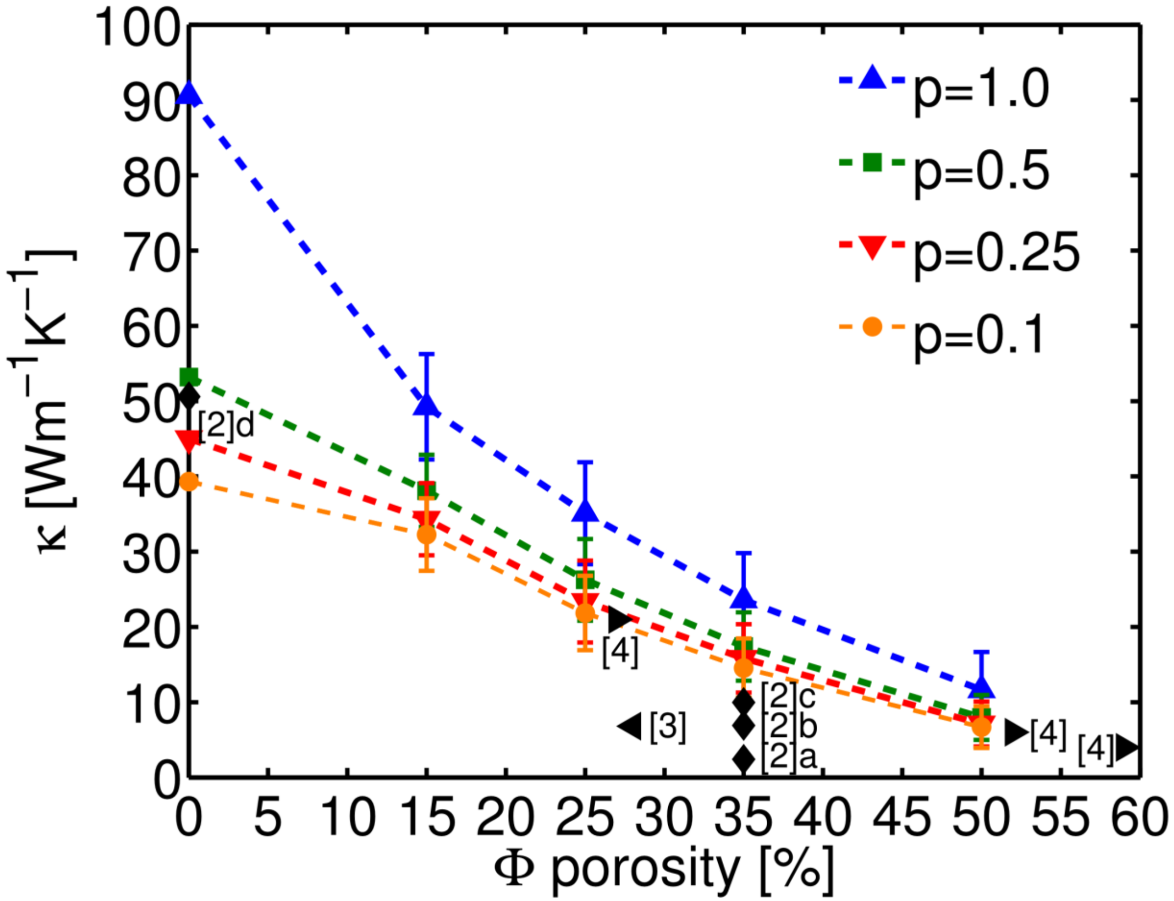
thermalization

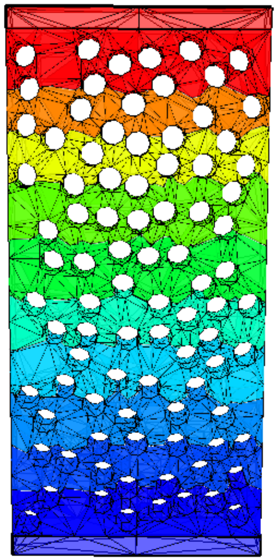
3-phonon scatt.



Wolf, Neophytou, and Kosina, JAP, 2014

Thermal conductivity vs porosity/roughness





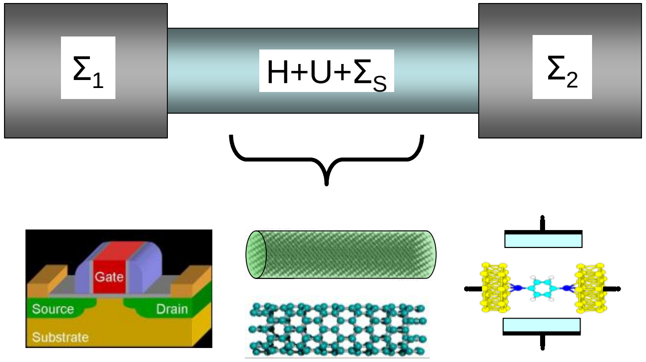
random pore arrangement

[4] Randomized pores

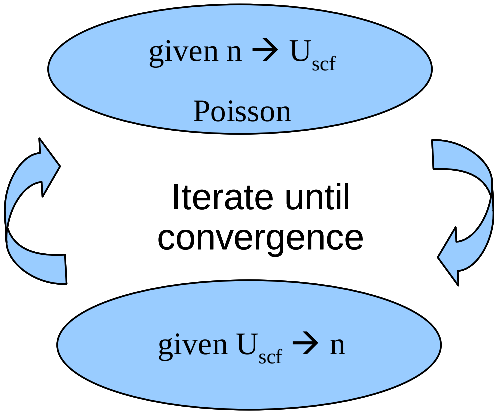
[2,3] Ordered arrays (rectangular/hexagonal)

Phonon coherent effects are present !

Non-Equilibrium Green’s Function (NEGF)



ELECTROSTATICS



given n → U_{scf}

Poisson

Iterate until convergence

given U_{scf} → n

TRANSPORT

(NEGF)

- Device Green’s function:

$$G(E) = [(E + i0^+)I - H - \Sigma_1 - \Sigma_2]^{-1}$$

- Density of states:

$$D(E) = \frac{1}{2\pi} Trace(G\Gamma G^+),$$

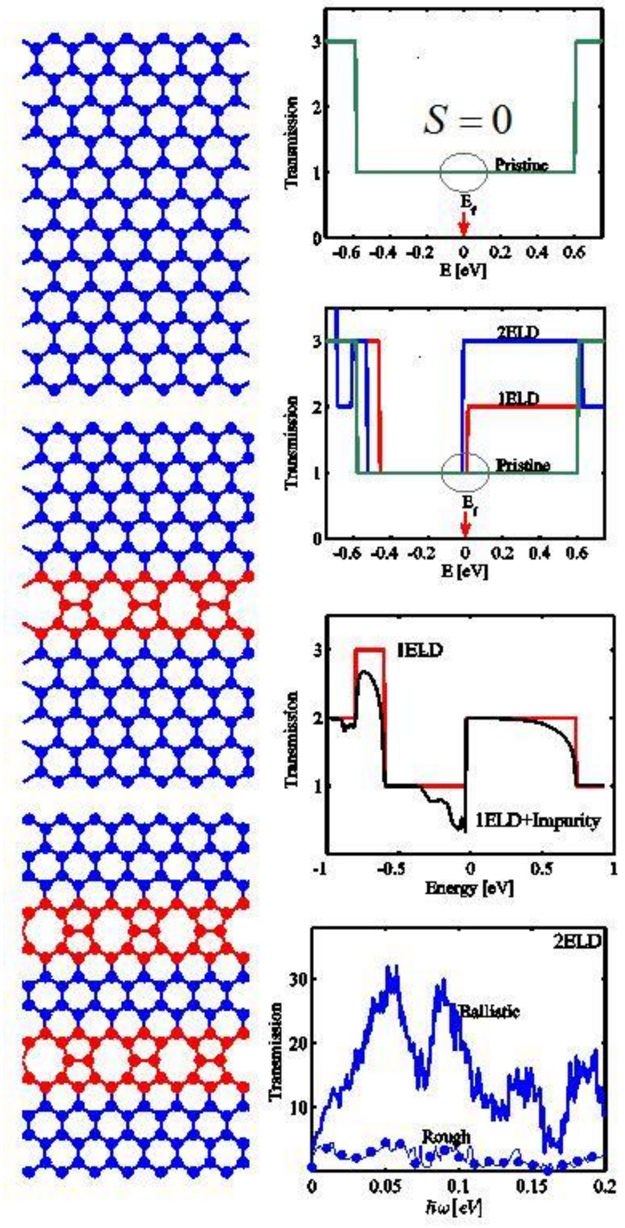
$$where \quad \Gamma = i(\Sigma - \Sigma^+)$$

- Transmission:

$$T(E) = Trace(\Gamma_1 G \Gamma_2 G^+)$$

- ➢ Very powerful approach
- ➢ Can include scattering (decoherence)
- ➢ Can be computationally very expensive
- ➢ For both electrons (Hamiltonian) and phonons (dynamic matrix)

Graphene nano-ribbon thermoelectrics



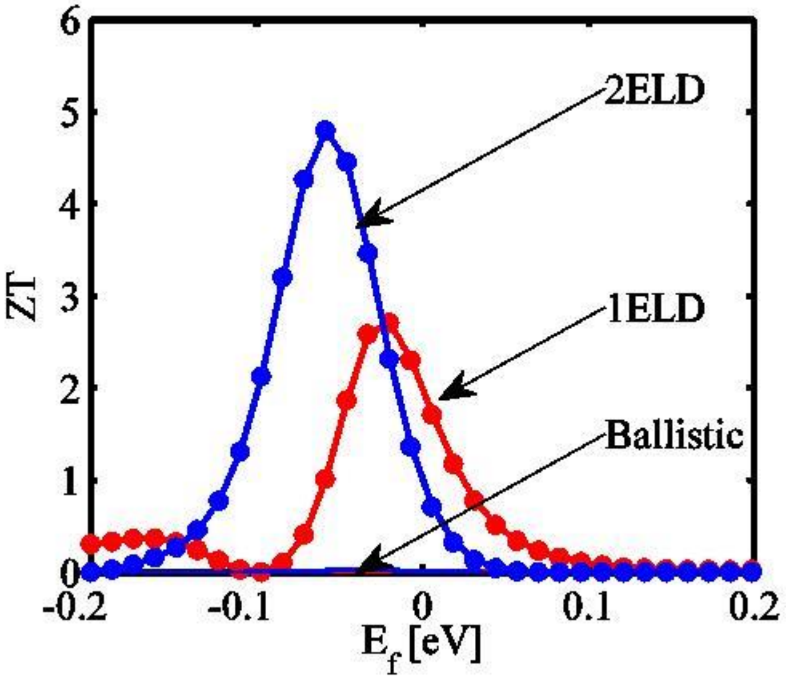
ZT=0

$$S \sim \frac{d}{dE} DOS(E)$$

(1)

(2)

(3)



Karamitaheri, Neophytou, Kosina, *et* al., JAP 111, 054501, 2012.

Outline

- Introduction – design at the nanoscale
    - Nanoscale thermoelectrics – design targets

- Low-dimensional TEs (atomistic tight-binding + BTE)

- Gated thermoelectrics

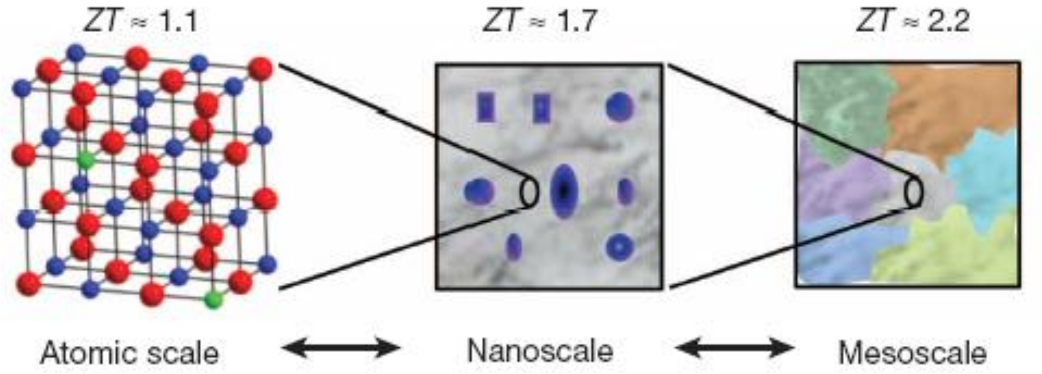
- Phonons transport for low-D (Modified Valence Force Field)
    - *ZT* figure of merit for low-D channel

- Nanostructured thermoelectrics

- Other studies: Nanomeshes (MC), Graphene (NEGF)

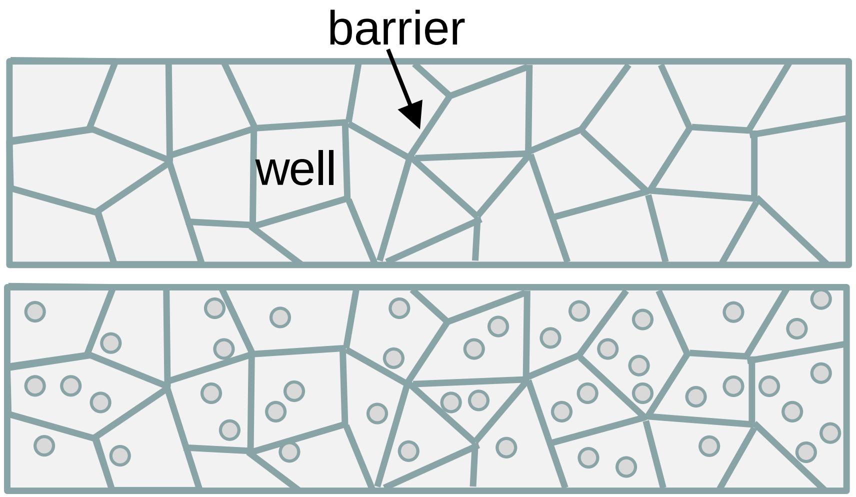
- Future directions and conclusions

Hierarchy in geometry



Hierarchical scattering of phonons
Biswas et al. (Kanatzidis group)

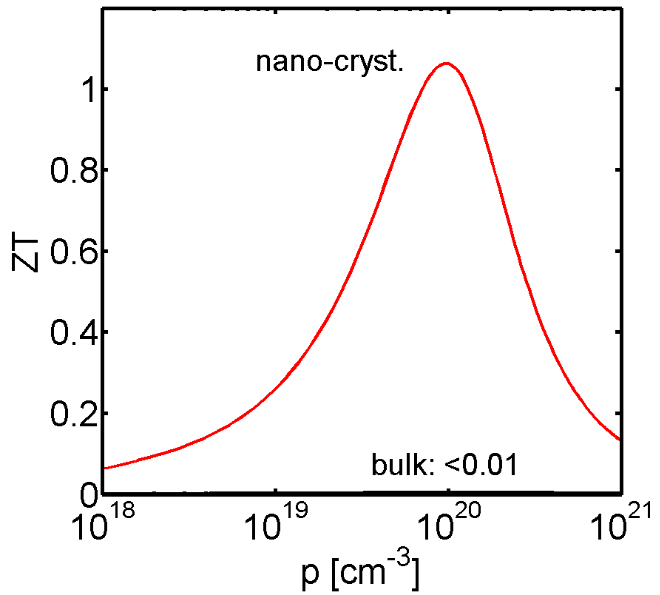
Very low κ_l



<u>Very high PF:</u>
2-phase materials: 15 mW/K^2m^{-1}
3-phase materials: 22 mW/K^2m^{-1}
(~7x compared to bulk)
larger S with 3rd phase

Neophytou, Narducci, *et* al.,
Nanotechnology 2013,
J. Electronic Materials 2014

ZT figure of merit



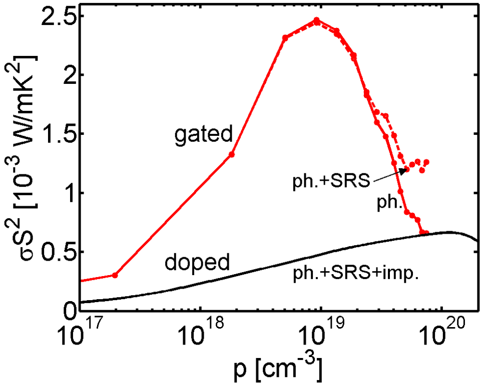
$$ZT = \frac{\sigma S^2 T}{\kappa_l}$$

5X

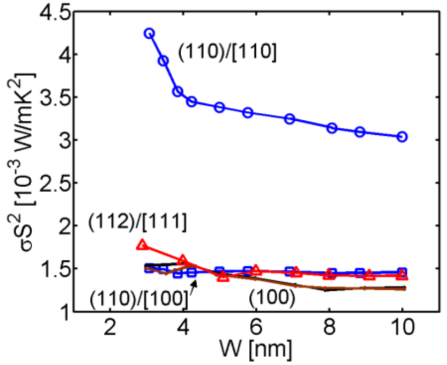
15X

κ_l=140 W/mK (bulk)

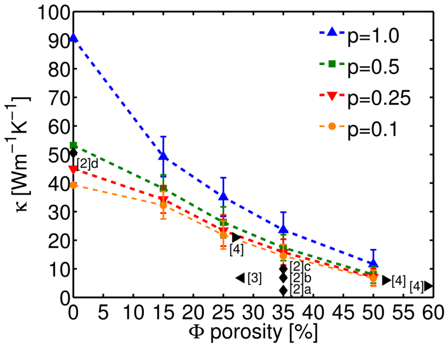
κ_l=8 W/mK (our nano-grains, calculations)



placement of dopants



bandstructure engineering



Reduce κ_l

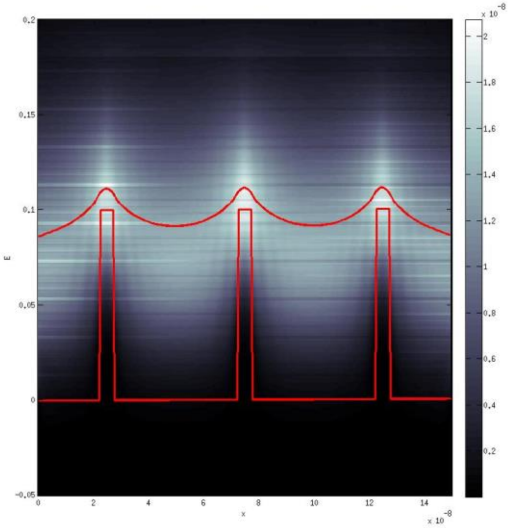
κ_l=1-2 W/mK (as in NWs)

Put all together:

- *ZT~4 ?*

Transport in multi-phase materials using NEGF

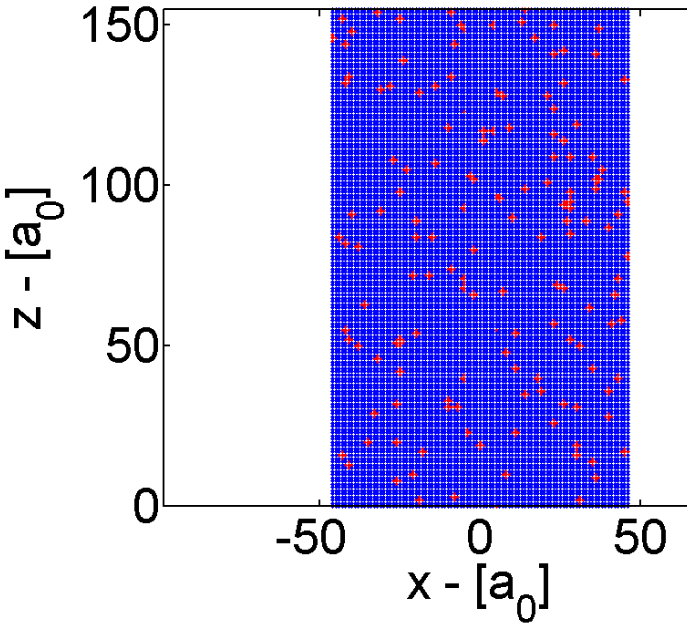
- We start with 1D
- Then extend to 2D



Transport through wells and barriers:

- Include acoustic and optical phonons
- Energy relaxation as current flows
- Include quantum effects.
- Can retrieve ballistic and diffusive regimes

Red spots: defects
(here they are barriers of Vb=0.3eV)
Blue region: channel



Conclusions

- Nanostructures offer the additional length scale degree of freedom in design

- Thermoelectric properties can be largely improved.
  - Very low thermal conductivities can be achieved
  - Very high power factors can be achieved

- Advanced simulation techniques are required
  - Atomistic models for electronic and phonon bandstructure
  - Linearized BTE, Monte Carlo, NEGF methods for transport

- Future work
  - Use all appropriate design guidelines to target TE performance of nanocomposites (bandstructure, doping, κ_l)
  - Collaborate with experimentalists and material scientists to establish technologies