Strategies Towards Efficient Thermoelectric Performance in Silicon

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Why silicon?

HERIOT WATT UNIVERSITY

Si

- Abundant
- Low-cost
- Non-toxic
- Technical know-how
- Mass manufacture

Bi_2Te_3 / Sb_2Te_3 / PbTe

- Scarce (Te)
- Expensive
- Toxic (Pb)
- Less technically mature
- Not manufactured at scale

Focus on devices manufactured from single-crystal wafer feedstock

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Why not silicon?

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

Si power factor similar to Bi_2Te_3 (3-4 mW m^{-1} K^{-2}) (@300 K)

Z is figure-of-merit,
T is absolute temp,
σ is electrical conductivity,
S is Seebeck coefficient,
κ is thermal conductivity

Si comparable to Bi_2Te_3 in terms of *S* and σ

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Why not silicon?

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

Si thermal conductivity is ~150 W m^{-1} K^{-1} (@300 K)

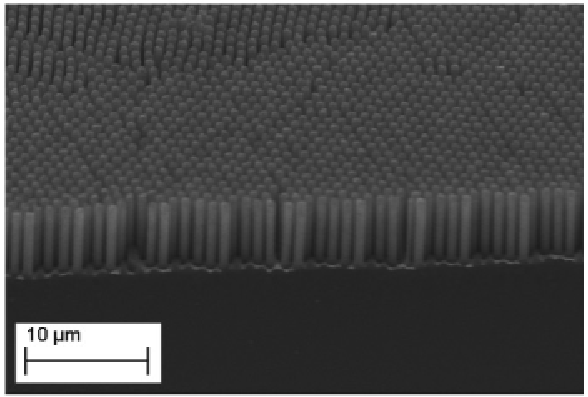
Z is figure-of-merit,
T is absolute temp,
σ is electrical conductivity,
S is Seebeck coefficient,
κ is thermal conductivity

Si comparable to Bi_2Te_3 in terms of *S* and σ
but... κ is 100x larger

$\Rightarrow$ *ZT* 100x smaller

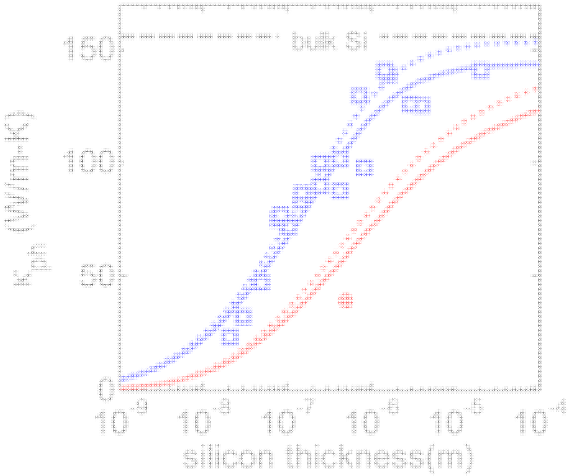
How to reduce κ?

Nanowires



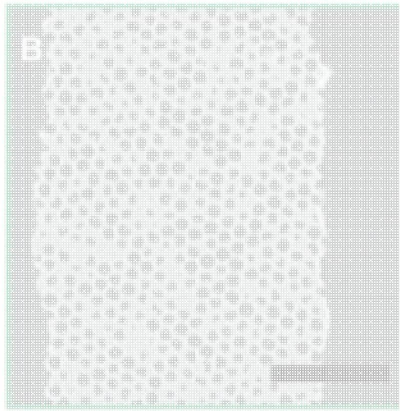
Boukai *et al*., Nature 451 (2008) 168
Hochbaum *et al*., Nature 451 (2008) 163

Nanofilms



Jeong *et al*., J. Appl. Phys. 111 (2012) 093708

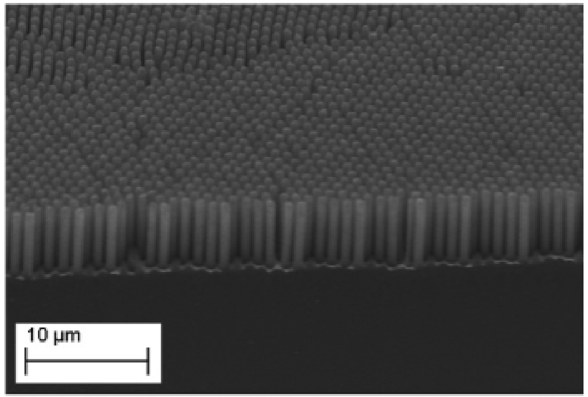
Nano pores



Tang *et al*., Nano Lett. 10 (2010) 4279

How to reduce κ?

Nanowires



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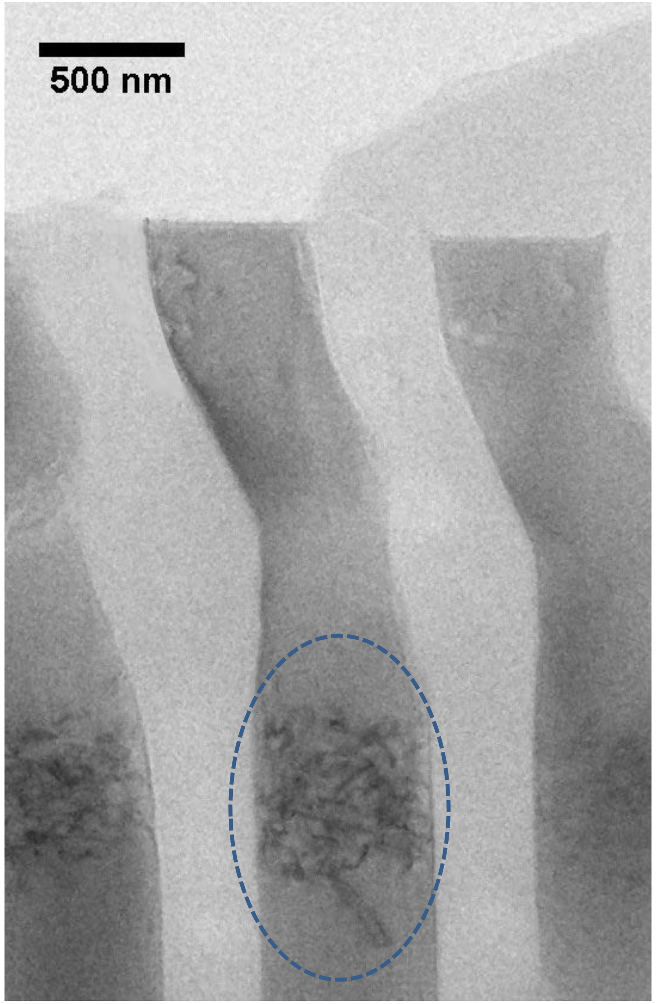
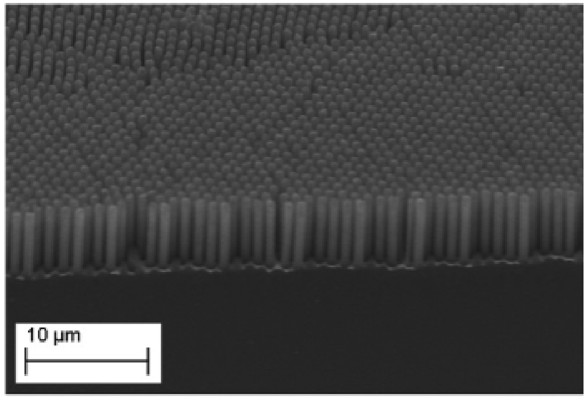


Bennett *et al.*, Appl. Phys. Lett. 107 (2015) 013903

(We have shown recently that SiNWs containing dislocations have enhanced Seebeck coefficient)

How to reduce κ?

Nanowires



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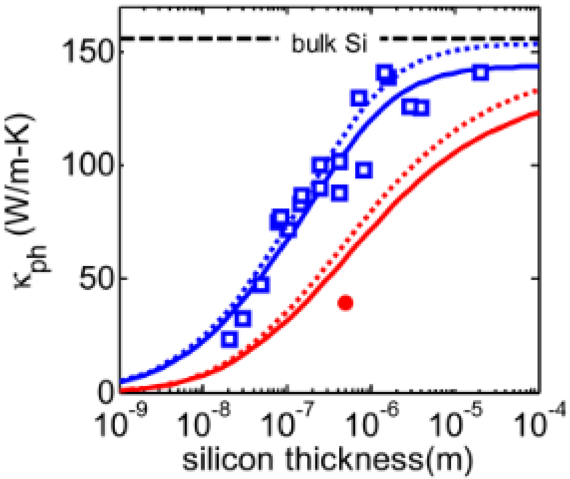

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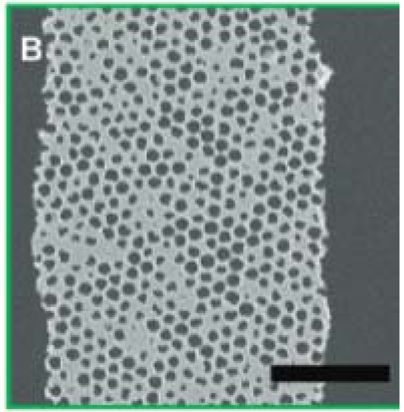
Nano pores



Tang *et al*., Nano Lett. 10 (2010) 4279

Interesting physics, but how do we make devices?

Why vacancy defects?

Numerous molecular dynamics studies have predicted that high vacancy (*V*) concentrations in Si can reduce κ

$$1.5\%\ V \Rightarrow 95\% \text{ reduction in } \kappa$$

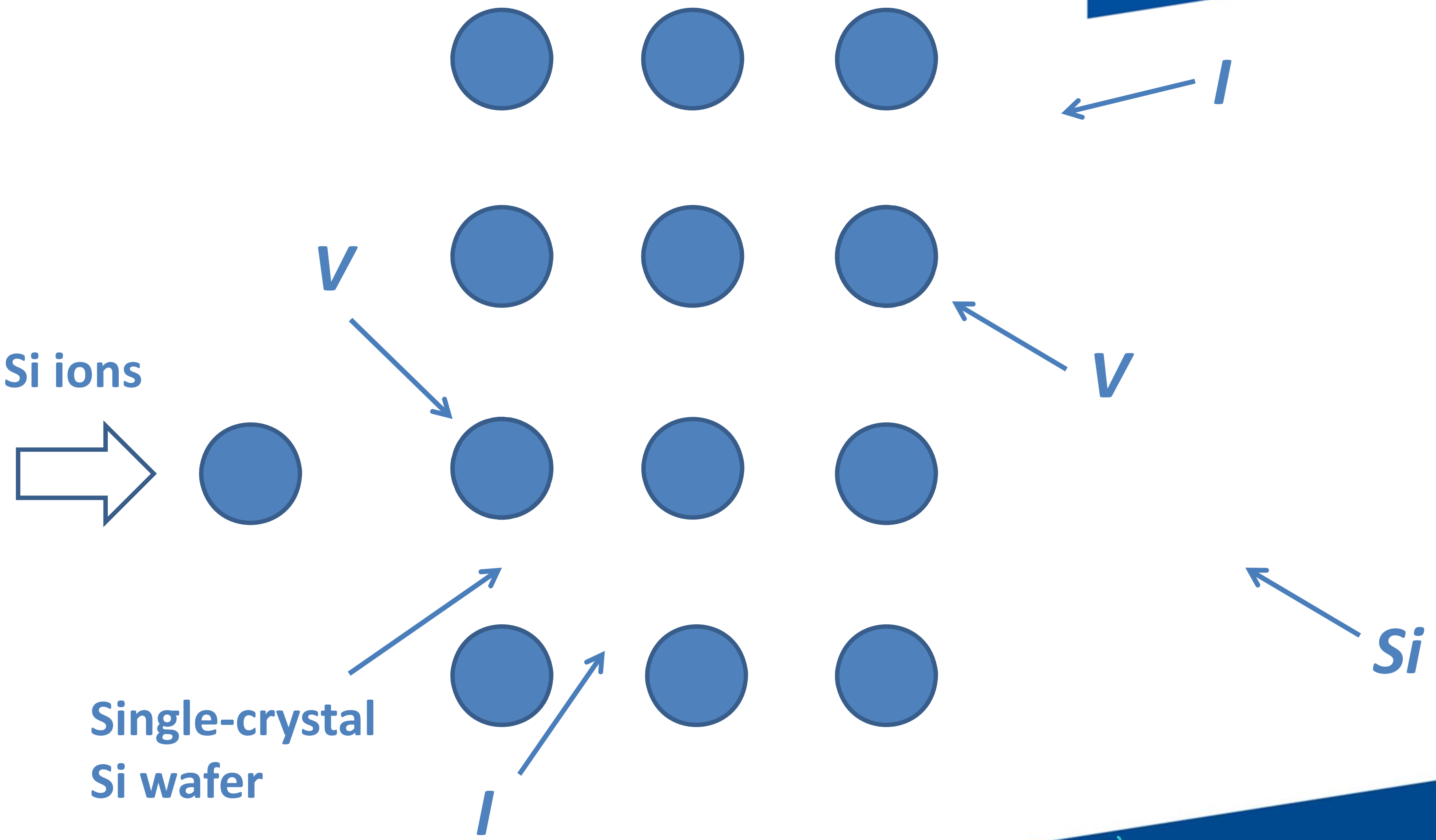
Lee *et al*., Phys. Rev. B 83 (2011) 125202

Huang *et al*., Scientific World Journal (2014) 863404

Wang *et al*., Modelling Simul. Mater. Sci. Eng. 22 (2014) 035011

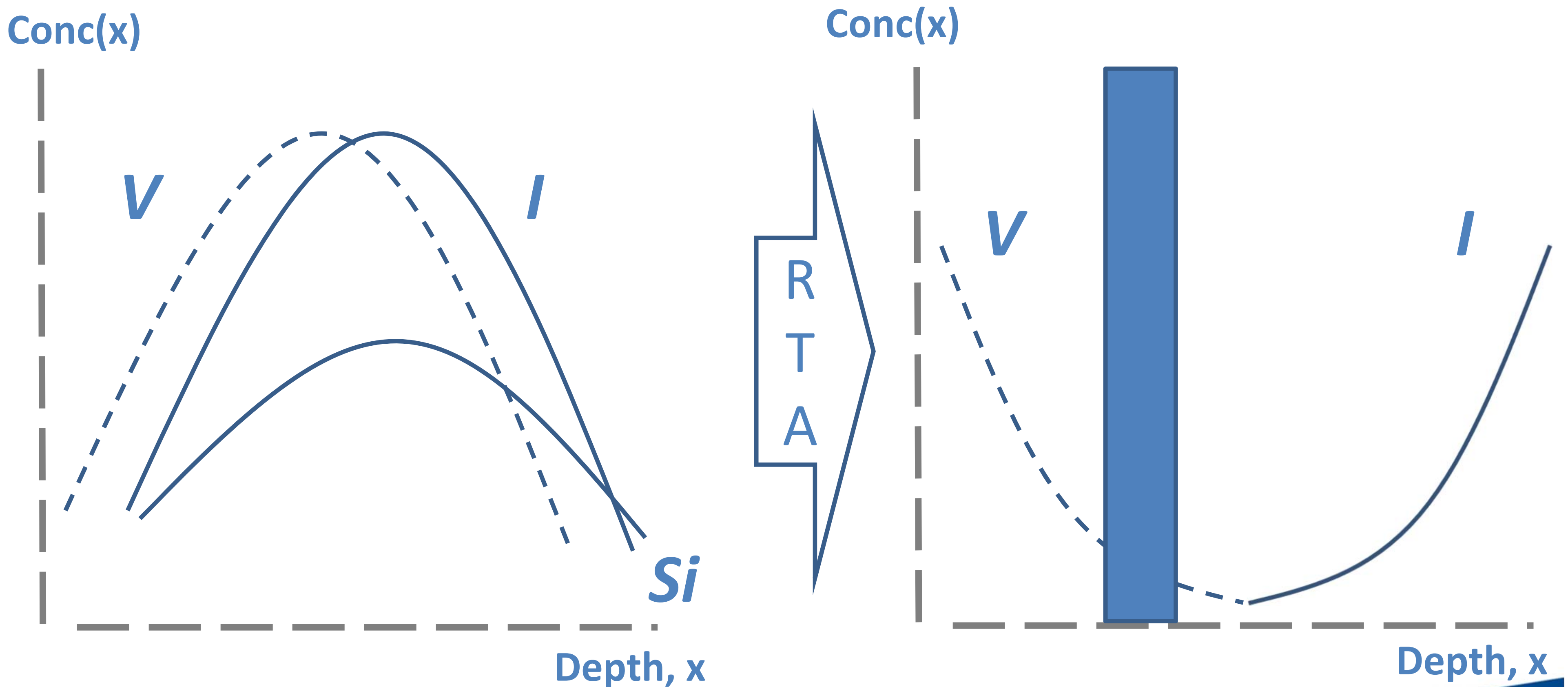
Shahraki *et al*., J. Phys. Chem. Sol. 85 (2015) 233

Vacancy engineering



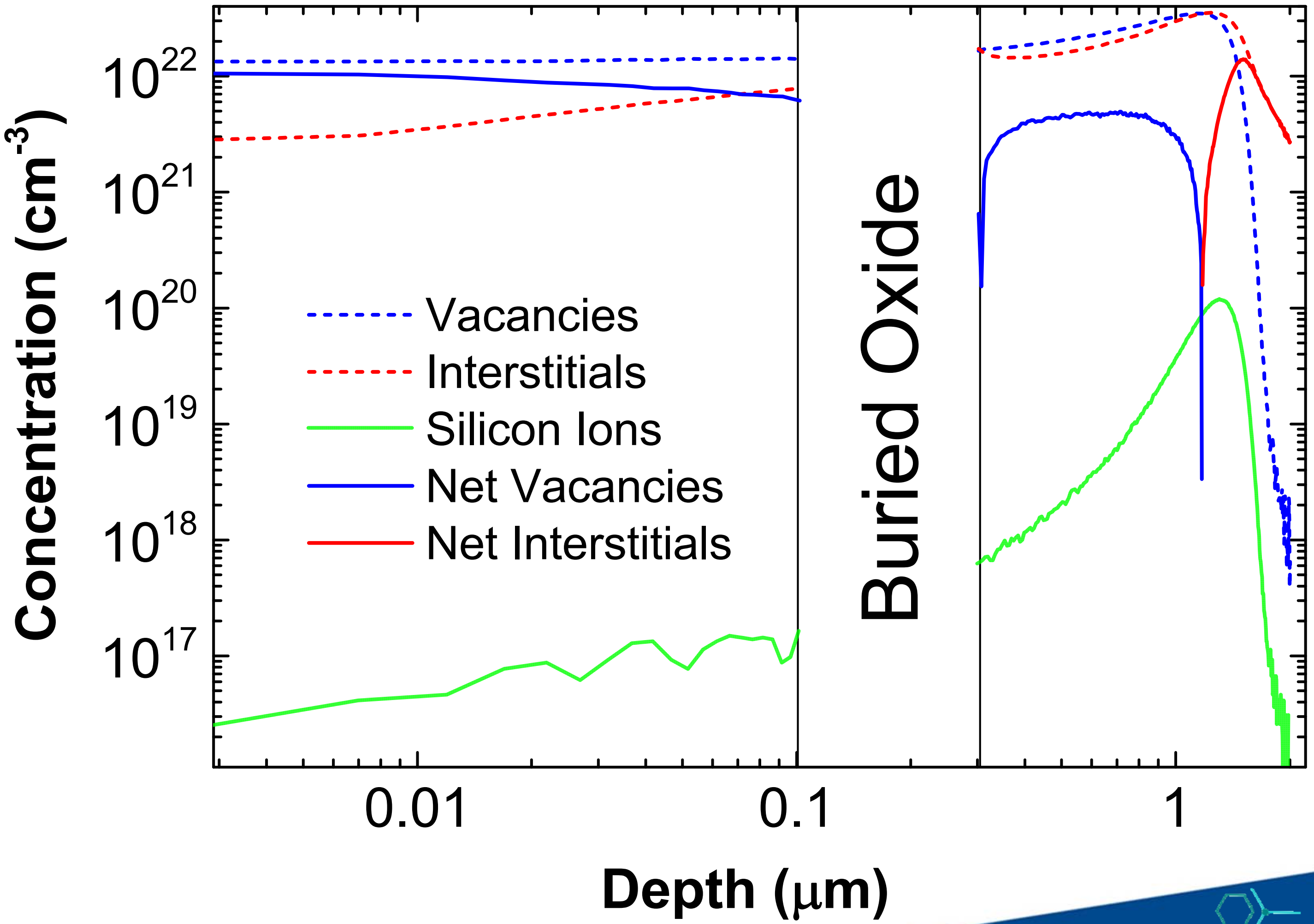
Vacancy engineering

$$Conc(x) = Si(x) + I(x) - V(x)$$



RTA is rapid thermal annealing

TCAD simulation



Energy:
1MeV

Si fluence:
$4.5 \times 10^{15} cm^{-2}$

Temp: 300K

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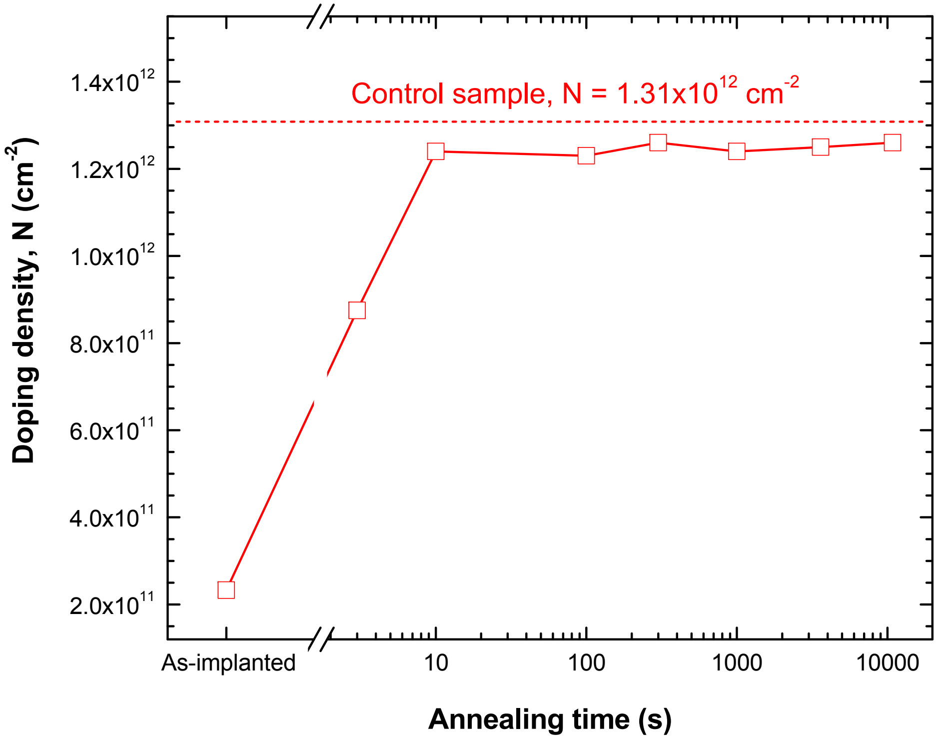
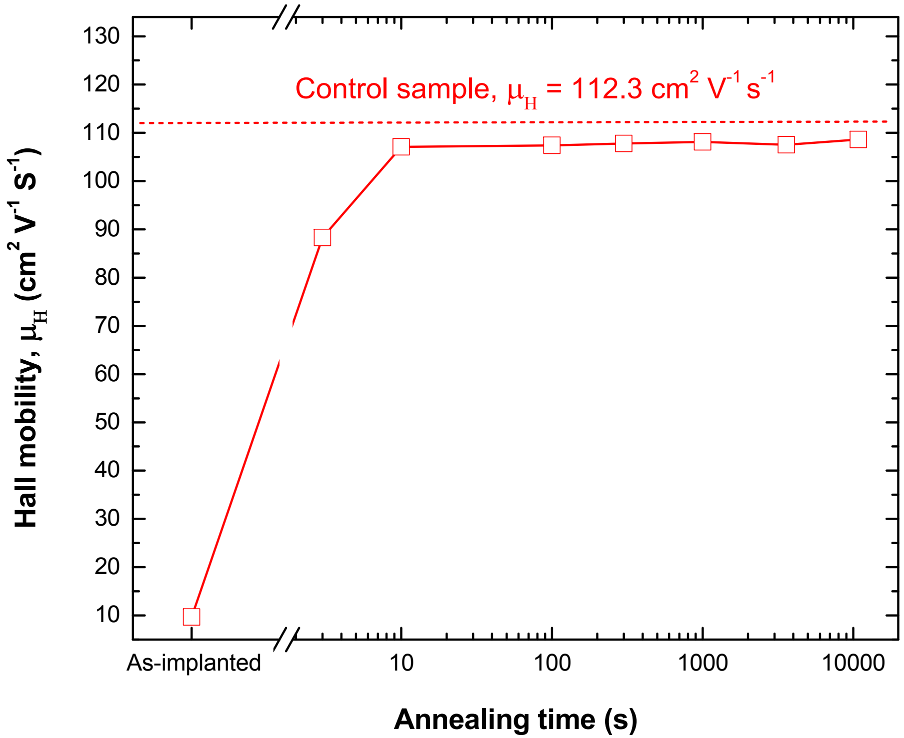
Electrical properties (300K)



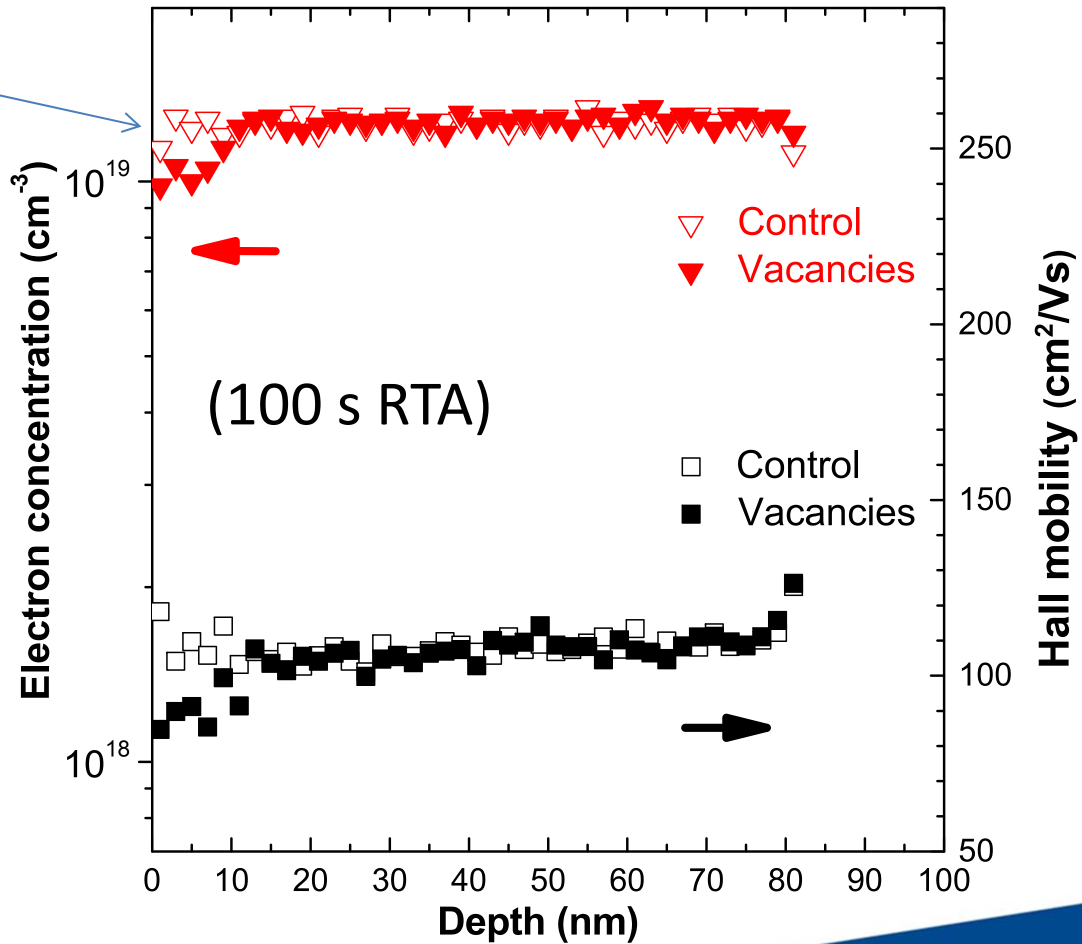


Phosphorus-doped, $\sigma = 200$ S cm^{-1}

$N = 10^{12}$ $cm^{-2} \equiv 10^{19}$ cm^{-3}

Electrical properties (300K)

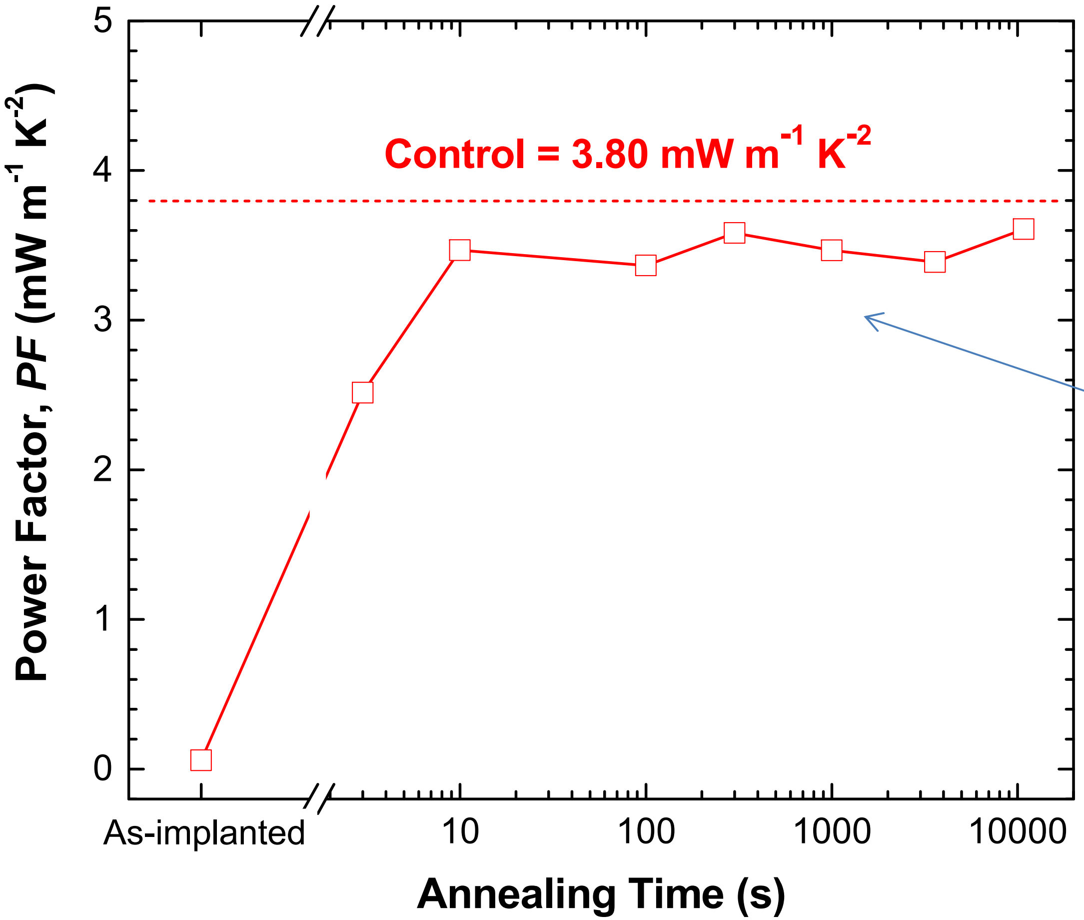
Post-RTA differences in electrical properties only exist at the near-surface region where *V* concentration is highest



(Measured via differential Hall profiling)

Bennett & Cowern, Appl. Phys. Lett. 100 (2012) 172106

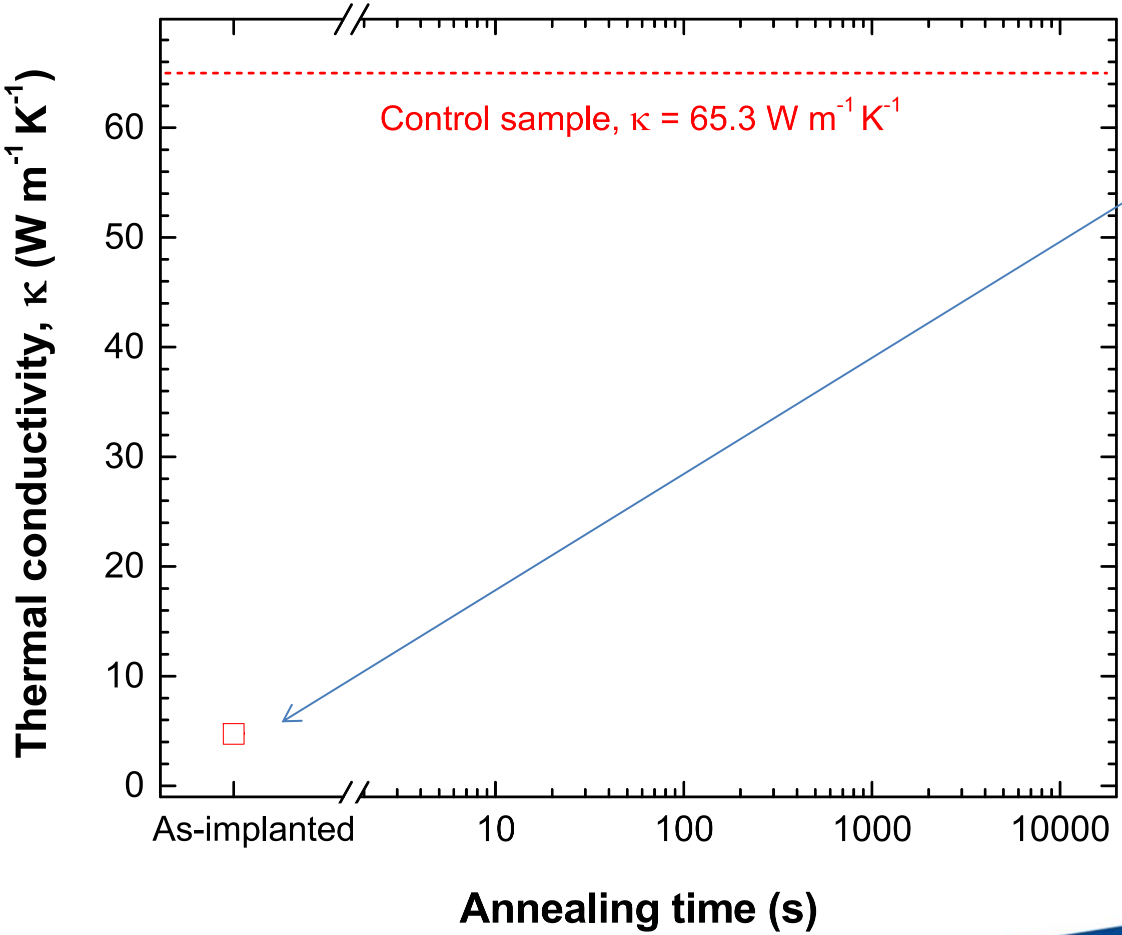
Power factor (300K)



When we also consider Seebeck coefficient…

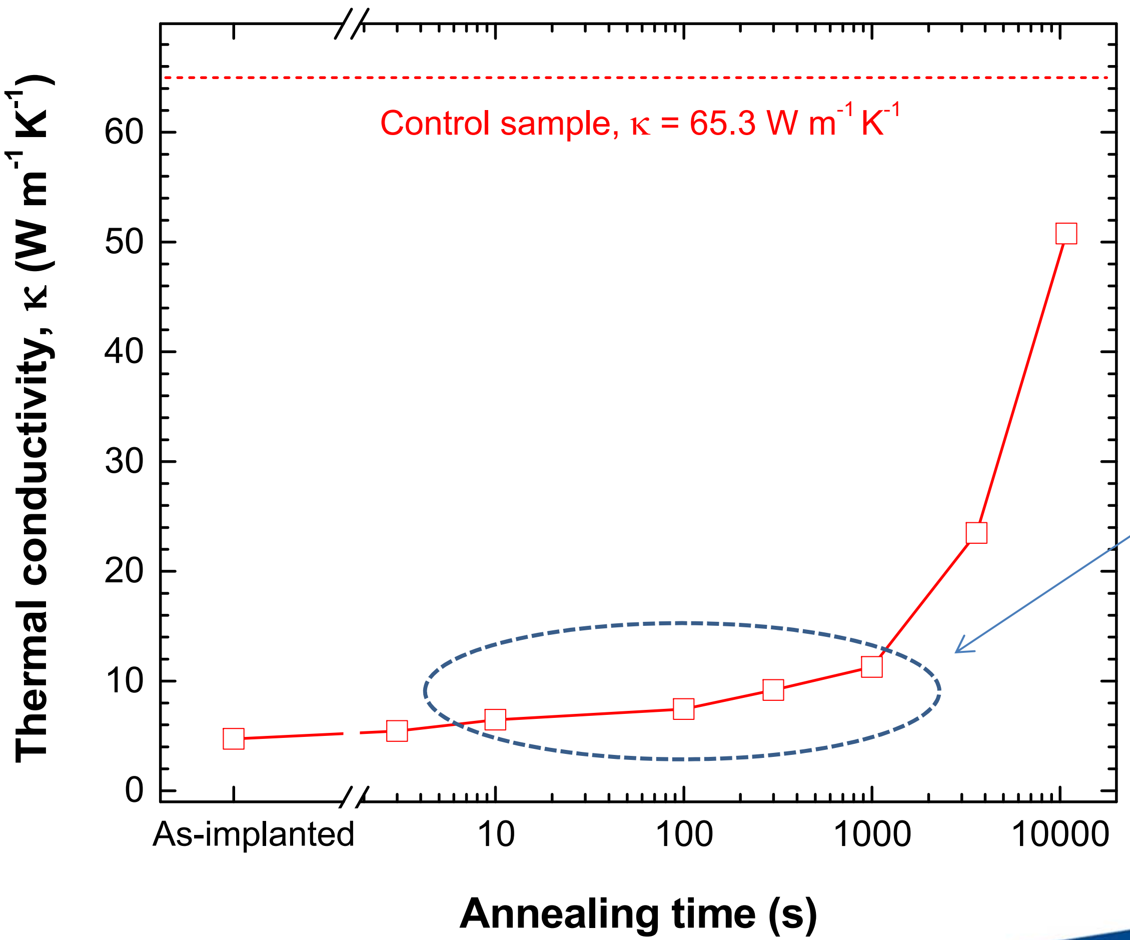
PF restored almost in line with control samples

Thermal conductivity (300K)



κ is significantly reduced by implantation

Thermal conductivity (300K)



κ is significantly reduced by implantation

After RTA, κ remains low due to the excess of *V*s

Thermal transport significantly affected by *V*

Figure of merit

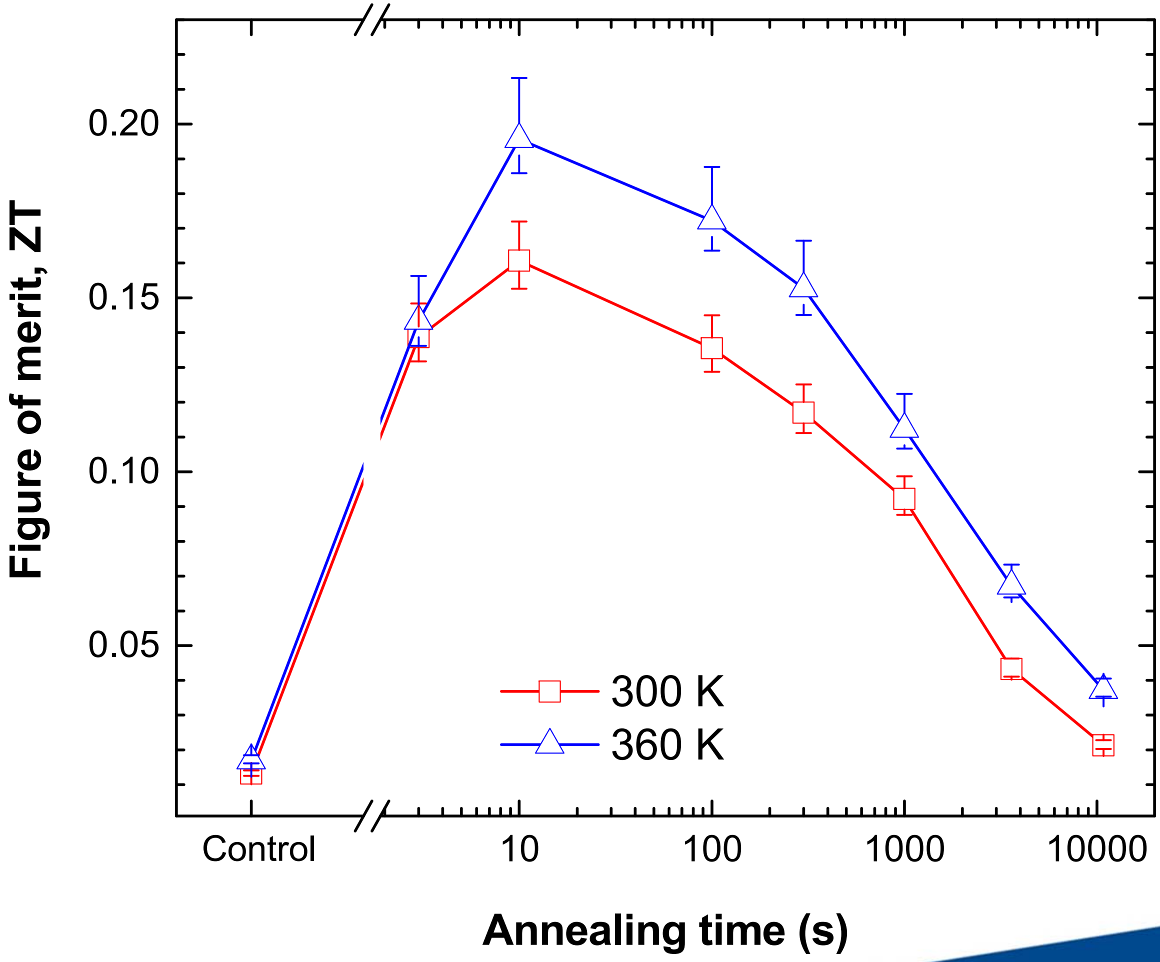
ZT raised by x20 compared to control samples

Performance competitive with nano-structuring approaches

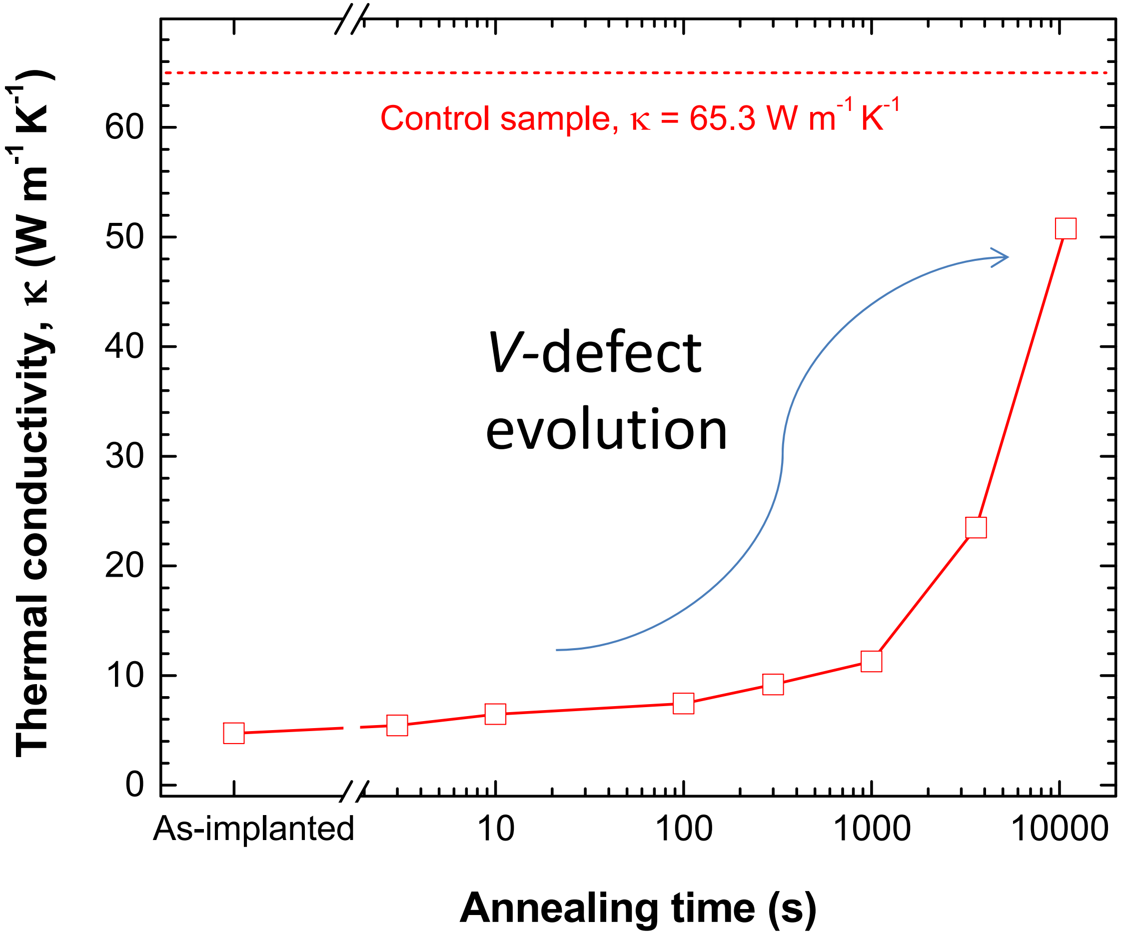
Much more simple to implement

Material more robust

Bennett *et al.*, Nano Energy 16 (2015) 350



Challenge (1): Stability?

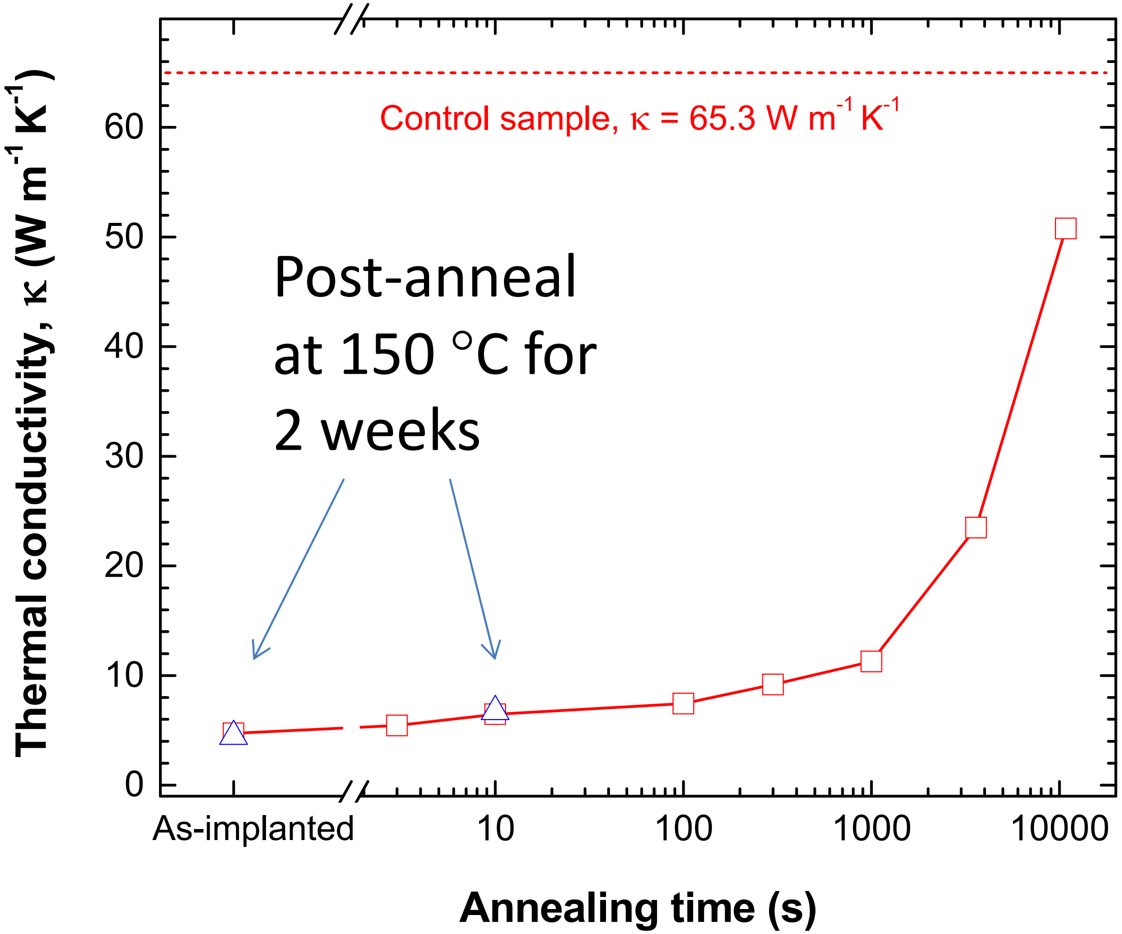


κ rises after long (high-temp) anneal

V clustering and/or removal when exposed to increased thermal budget

Larger clusters and/or less *V* $\Rightarrow$ higher κ [Lee *et al.*, Phys. Rev. B 83 (2011) 125202]

Challenge (1): Stability?

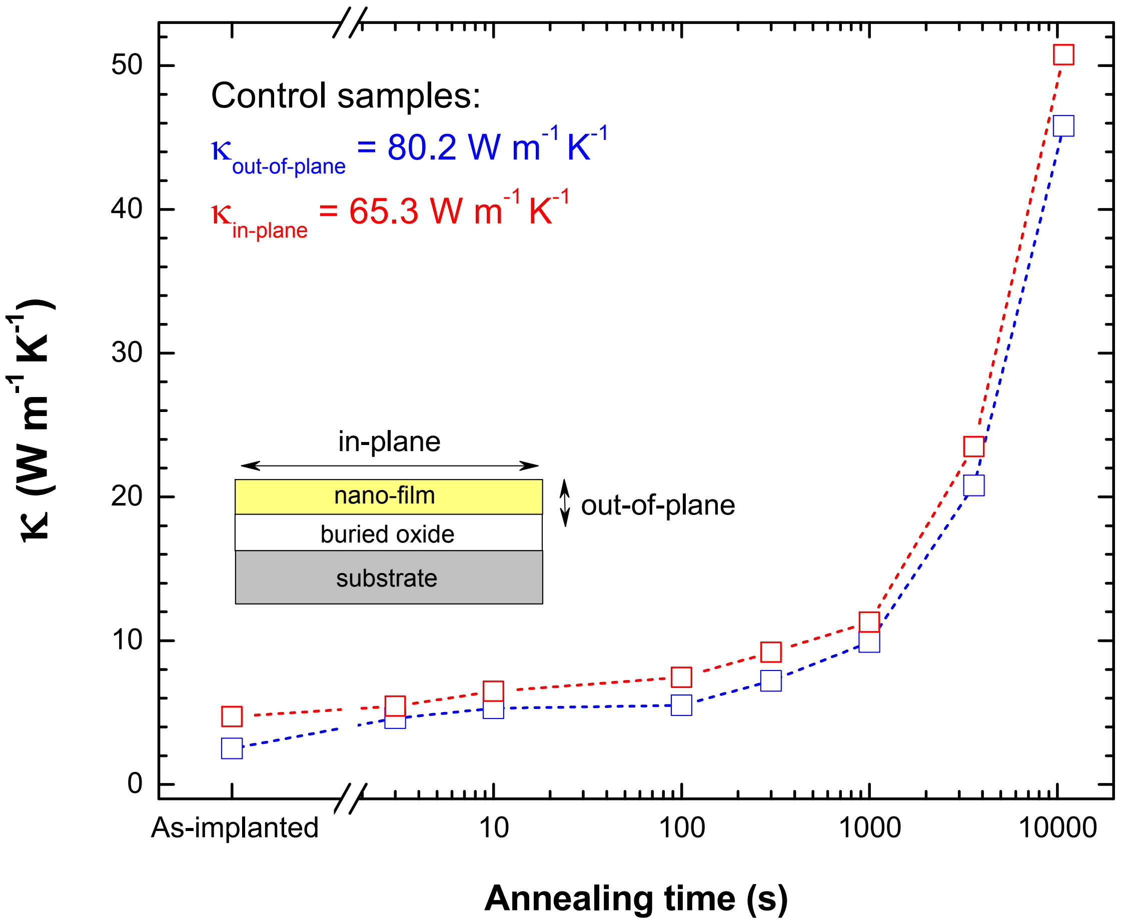


TEGs must be exposed to high temp in order to work!

For low device operating temps this appears to be ok

i.e. <300°C, κ does not increase

Challenge (2): Architecture?

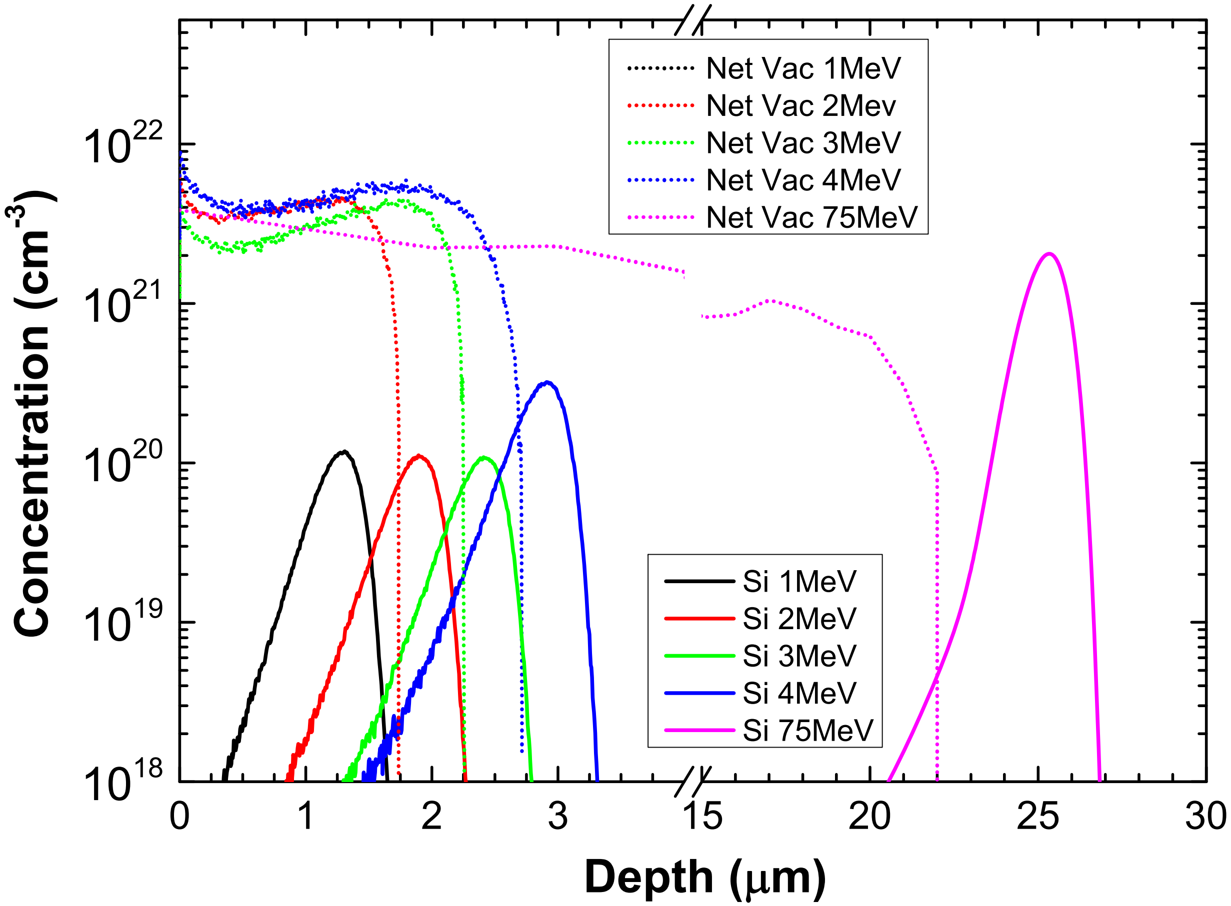


All properties measured in the in-plane direction

Devices likely to be formed out-of-plane

In the out-of-plane direction κ is still reduced (by a little more)

Issue (3): Scalability?



Increasing implant energy allows depth of *V*-rich region to be extended

Can be combined with increased fluence (blue) to maintain *V* concentration

Scalable for thin-films

Wight & Bennett, Solid State Phenomena 242 (2016) 344

Conclusions

- Many good reasons why Si should be used for TEs

  … also some good reasons why not!
- Vacancy engineering – a novel concept to introduce high *V* concentrations in Si
- Significantly reduces κ without degrading σ or *S* (much)
- *ZT* raised from 0.01 to 0.2
- κ stable for low temperature post-exposure (<300°C)
- *V*-concentrations will be optimized further
- Scalable approach for thin-film thermoelectrics

  … (maybe bulk?)

Acknowledgements

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Thank you for your attention

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