Phonon Filtering by Nanovoids In Silicon: a Computational and Experimental Analysis

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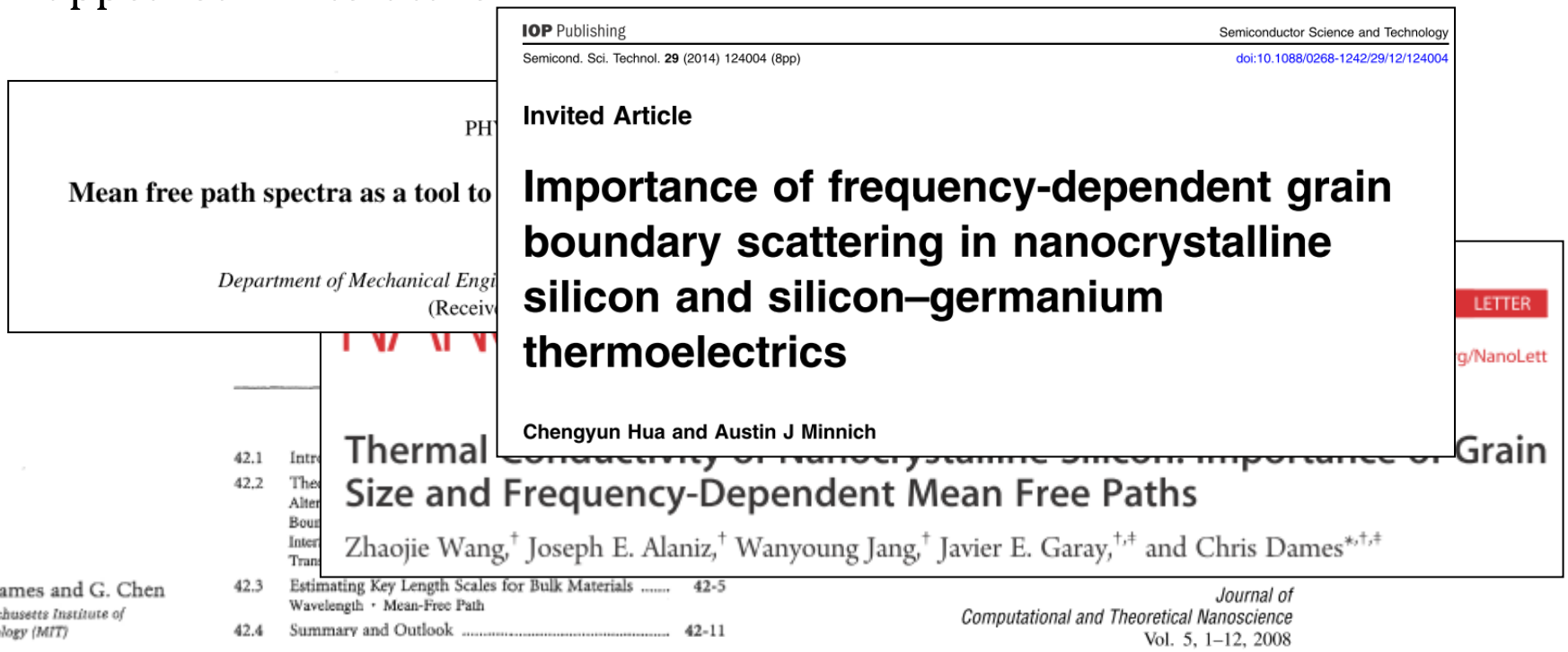
Background

The role played by morphological defects (md's) on thermal conductivity and phonon MFPs has been the subject of a wealth of papers recently appeared in literature.



Mean free path spectra as a tool to

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IOP Publishing Semiconductor Science and Technology

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Invited Article

Importance of frequency-dependent grain boundary scattering in nanocrystalline silicon and silicon–germanium thermoelectrics

Chengyun Hua and Austin J Minnich

LETTER

g/NanoLett

Thermal Grain Size and Frequency-Dependent Mean Free Paths

Zhaojie Wang,† Joseph E. Alaniz,† Wanyoung Jang,† Javier E. Garay,†,‡ and Chris Dames*,†,‡

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42.3 Estimating Key Length Scales for Bulk Materials 42-5

Wavelength · Mean-Free Path

42.4 Summary and Outlook 42-11

C. Dames and G. Chen

Massachusetts Institute of Technology (MIT)

Journal of Computational and Theoretical Nanoscience
Vol. 5, 1–12, 2008

Spectral Phonon Transport Properties of Silicon Based on Molecular Dynamics Simulations and Lattice Dynamics

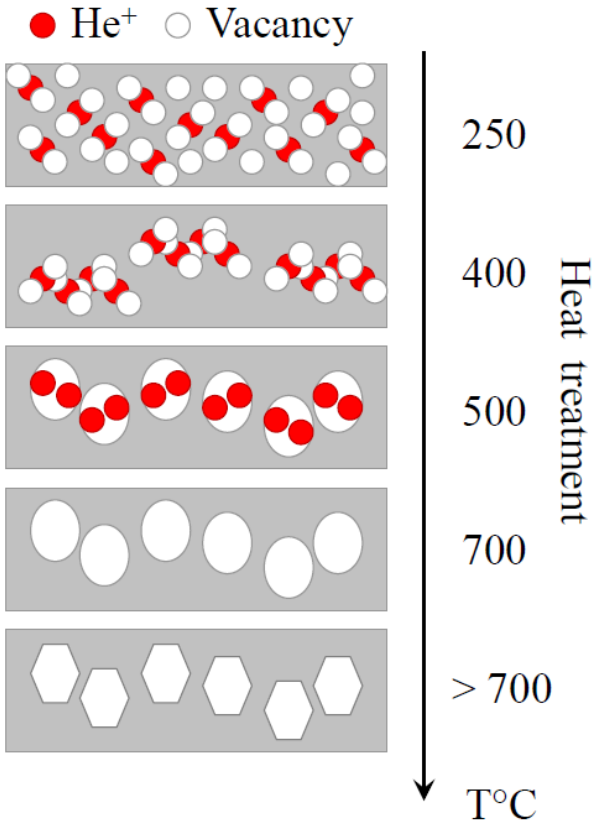
Asegun S. Henry[1,*] and Gang Chen[2]

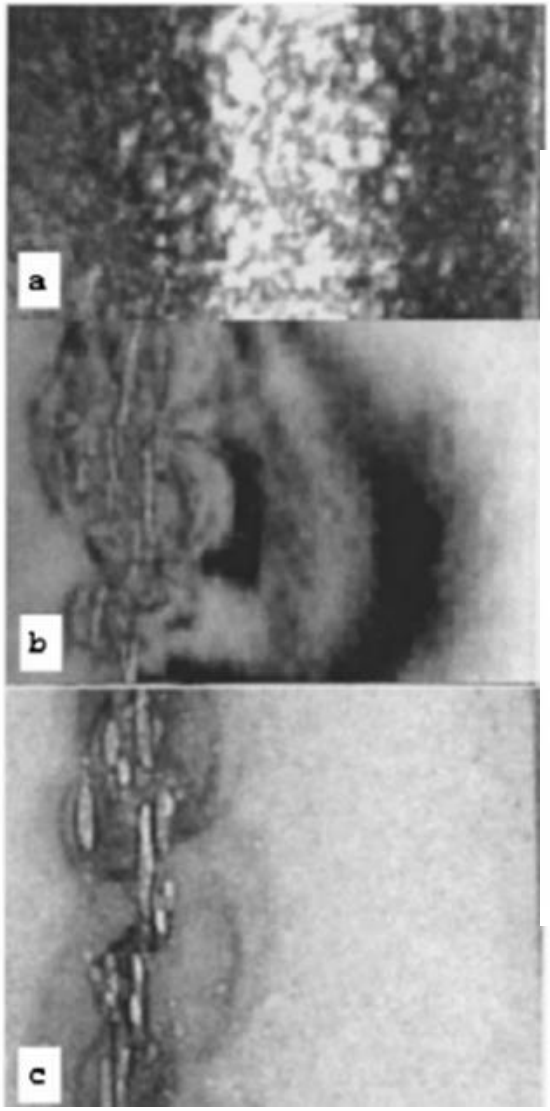
Aim of this work

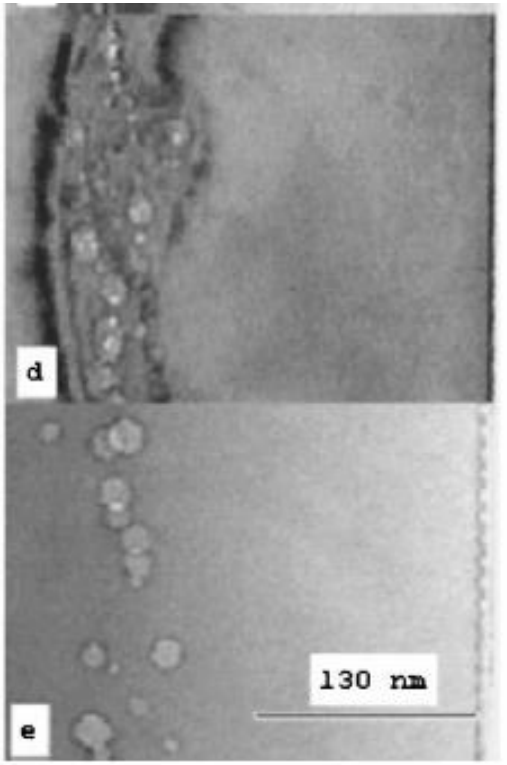
- Investigate the interplay among md size and density
- Compare thermal conductivity trends when fixed-size md's are also present

- Reference system is silicon, both single- and nano-crystalline
- Fixed-size md's are grain boundaries (GBs)
- Variable-size md's are nanovoids (NVs)

Helium implantation







Nanovoids generated by He-implantation in scSi

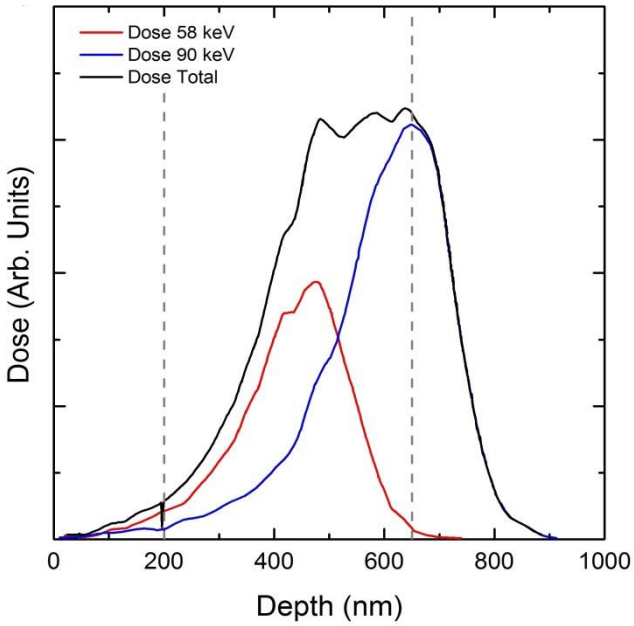
G. F. Cerofolini et al., Mater. Sci. Eng., R; 27 (2000) 1-52

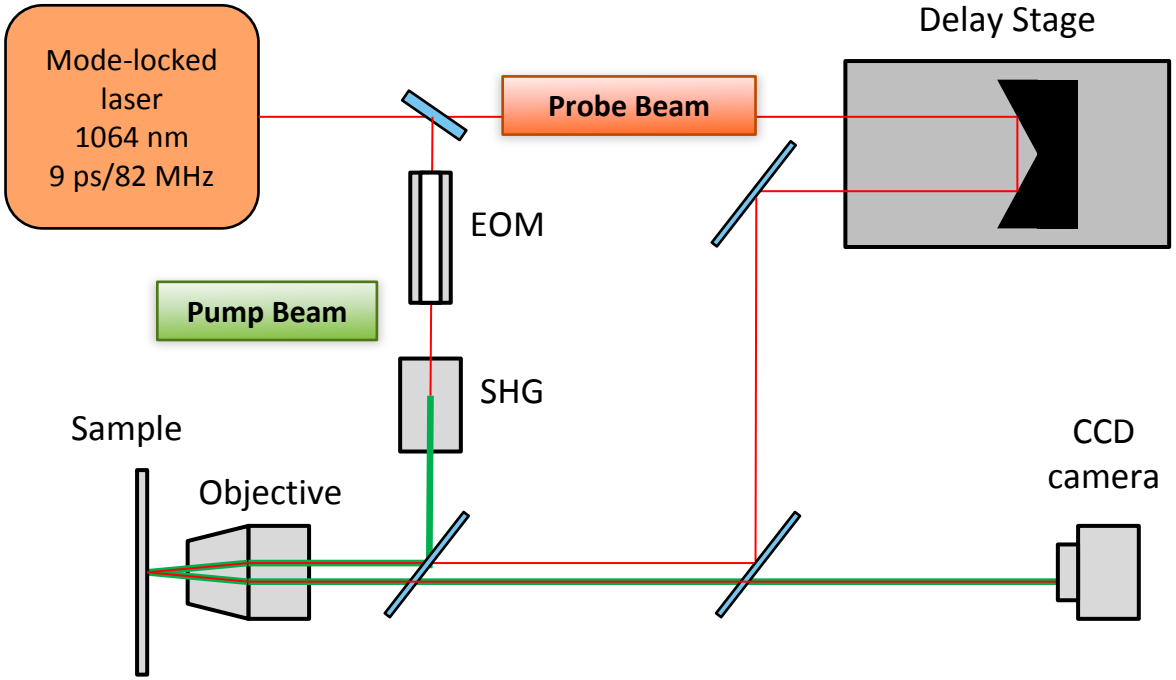
Sample preparation & TDTR

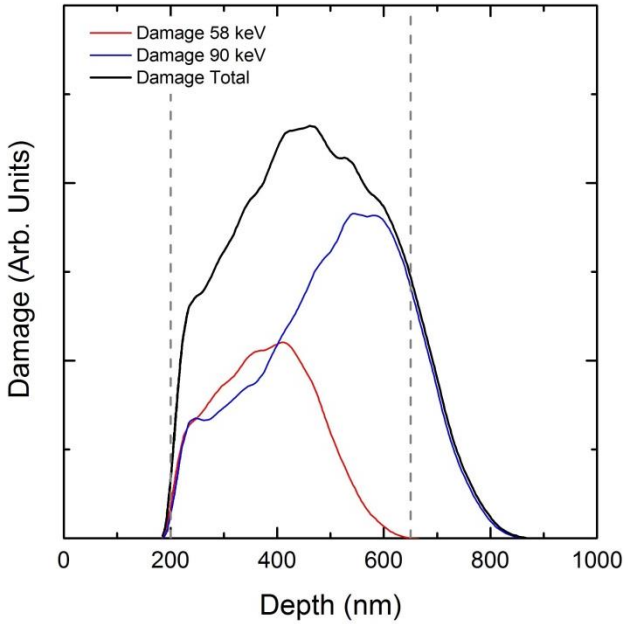
Double I^2 on 450-nm thick nanocrystalline Si films grown by CVD on oxidized Si

1. 90 keV, 4×10^{16} cm^{-2}
2. 58 keV, 1.5×10^{16} cm^{-2}

Six-step annealing	**One-step annealing**
500 – 1000 °C	1000 °C
B6S1, B6S2, B6S3, B6S4, B6S5, B6S6	B1S1

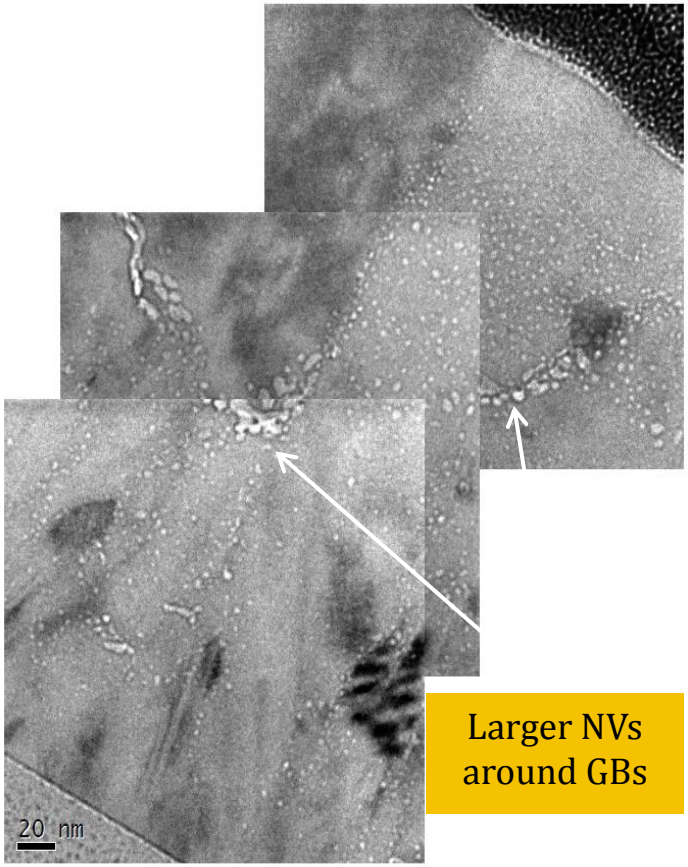






NV Shape and Distribution

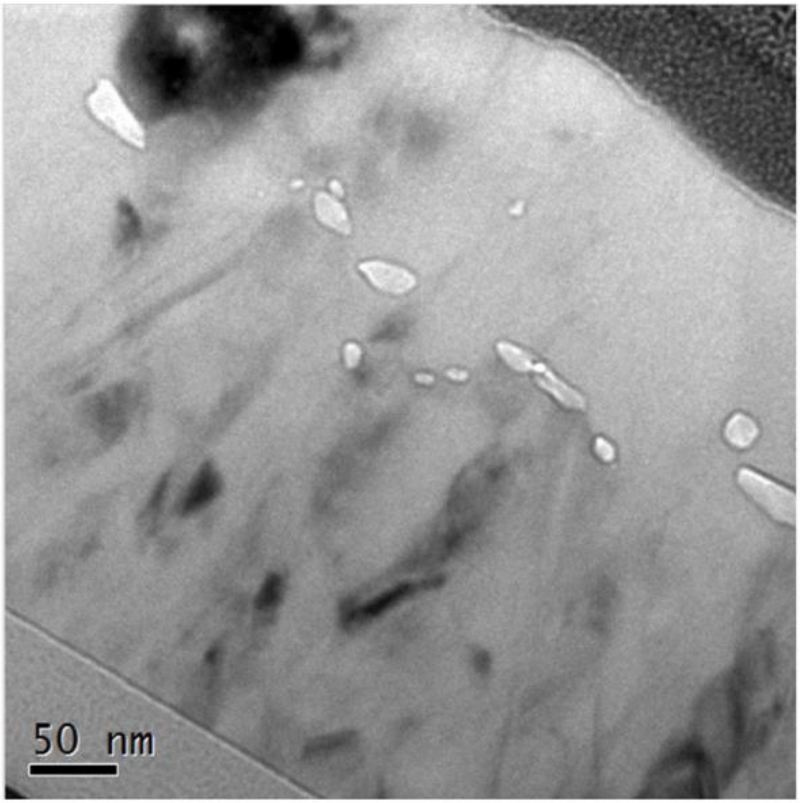
Sample B6S1: Annealed at 500°C



Larger NVs around GBs

WITHIN THE GRAINS:
Void diameter $d_p \approx 2$ - 4 nm
Void density $\approx 3 \times 10^{17}$ cm^{-3}
Void spacing $d_s \approx 11$ nm

Sample B6S6: After the whole cycle



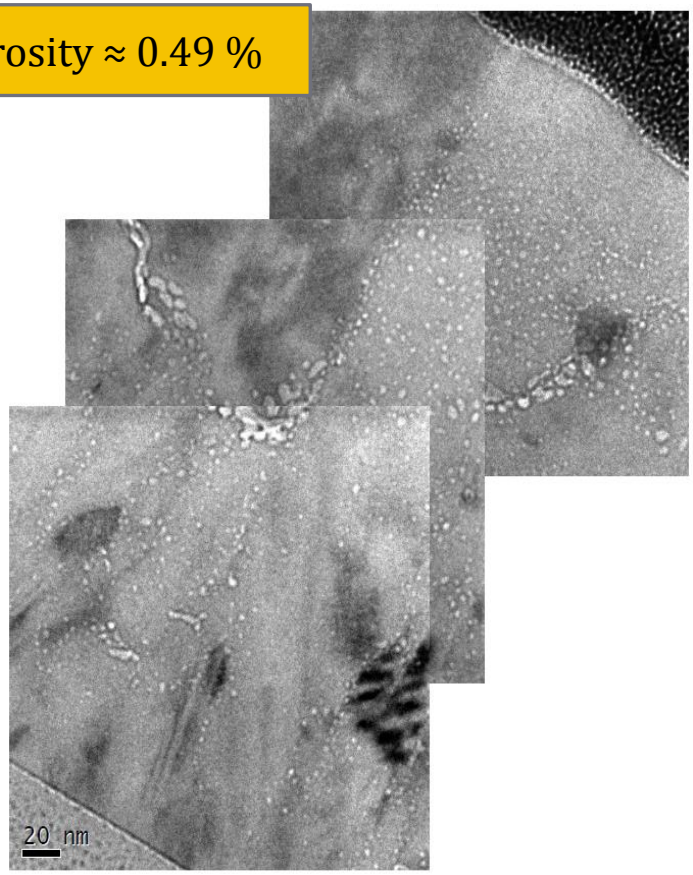
Coalescence of voids as in the single-crystal case

B. Lorenzi, et al.; J. Electron. Mater., 43 (2014) 3852-3856

NV Shape and Distribution

Sample B6S1: Annealed at 500°C

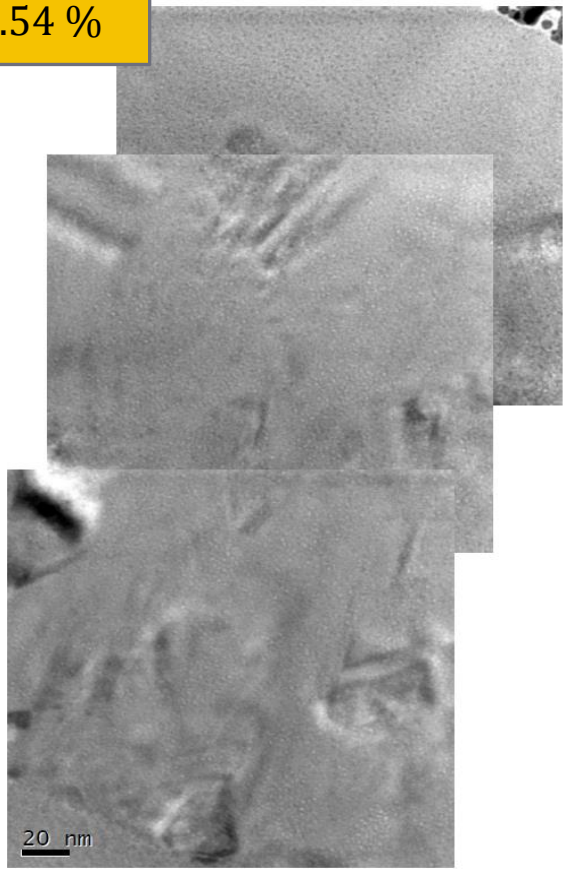
Porosity ≈ 0.49 %



WITHIN THE GRAINS:
Void diameter $d_p \approx 2$ - 4 nm
Void density ≈ 3 x 10^{17} cm^{-3}
Void spacing $d_s \approx 11$ nm

Sample B1S1: Annealed at 1000°C

Porosity ≈ 0.54 %



Void diameter $d_p \approx 1$ - 2 nm
Void density ≈ 2 x 10^{18} cm^{-3}
Void spacing $d_s \approx 6$ - 9 nm

B. Lorenzi, et al.; J. Electron. Mater., 43 (2014) 3852-3856

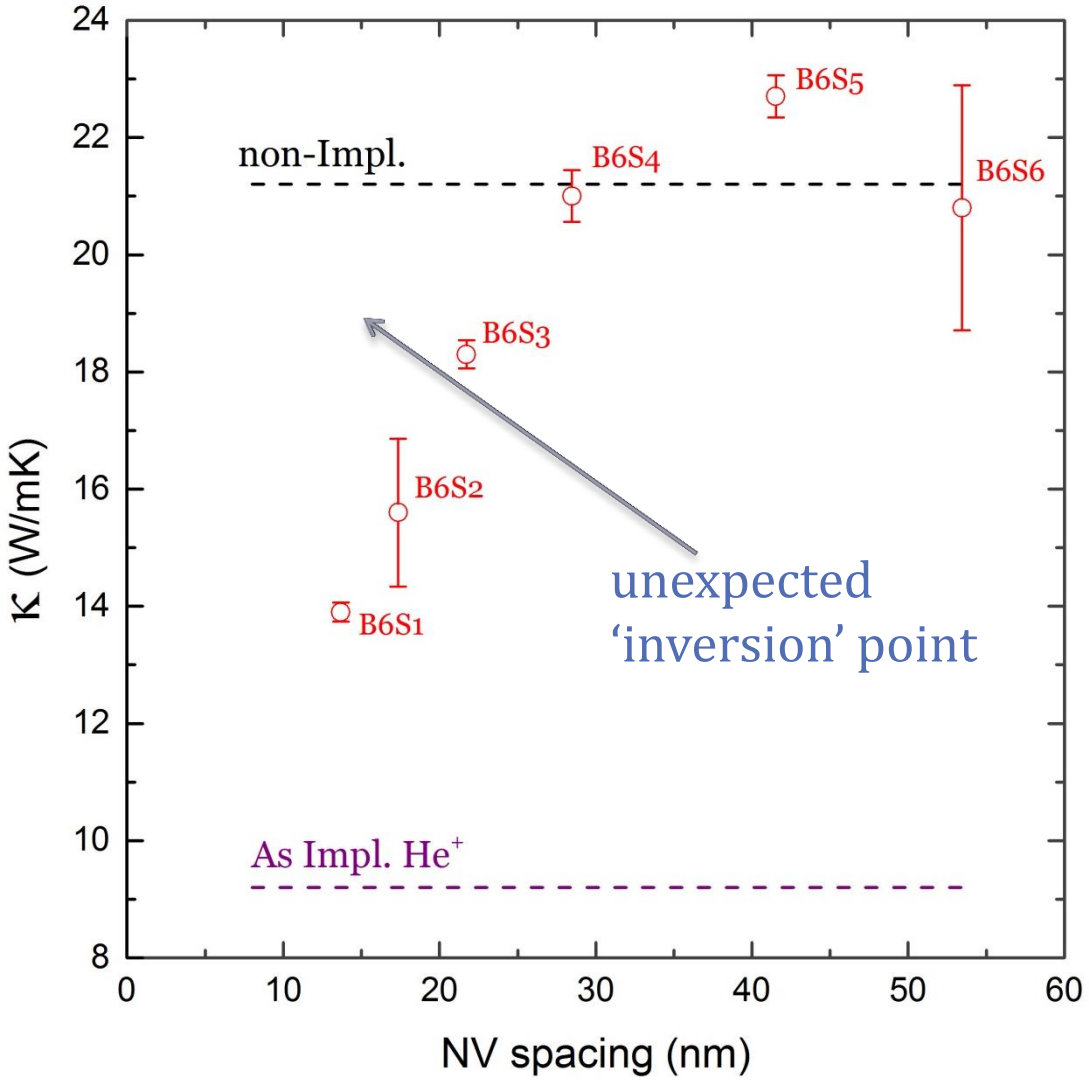
κ vs. d_s, d_p

Eucken model not valid

$$\kappa_{\text{eff}}(\varphi) = \kappa_{\text{bulk}} \frac{1-\varphi}{1+\frac{\varphi}{2}}$$

(φ constant)

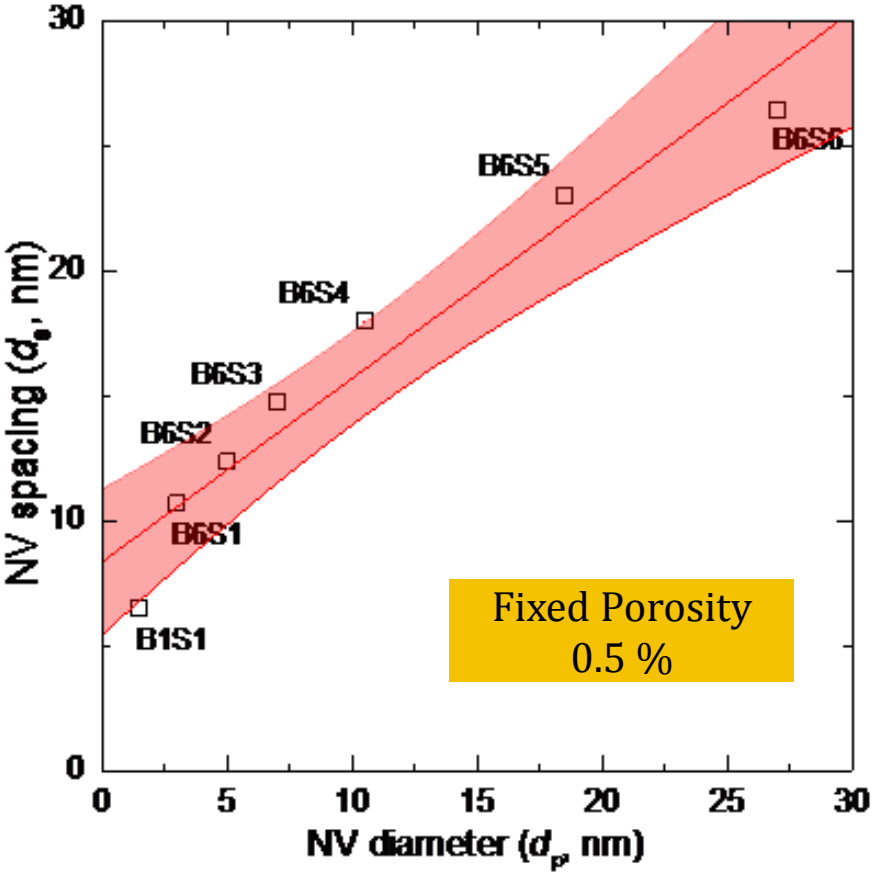
κ tunable with thermal processing

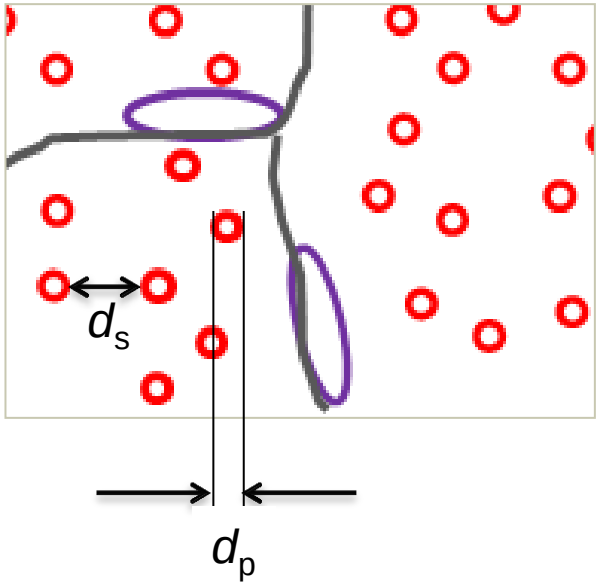


A. S. Henry & G. Chen, J. Comput. Theor. Nanosci. 5 (2008) 1–12.
A. Eucken, Ceram. Abstr. 11 (1932) 576
J. Tang et al., Nano Lett., 10 (2010) 4279–4283

A possible explanation

$$\varphi \equiv \frac{V_p}{V_{tot}} = \frac{4\pi}{3} \frac{(d_p/2)^3}{\beta (d_s - d_p)^3}$$



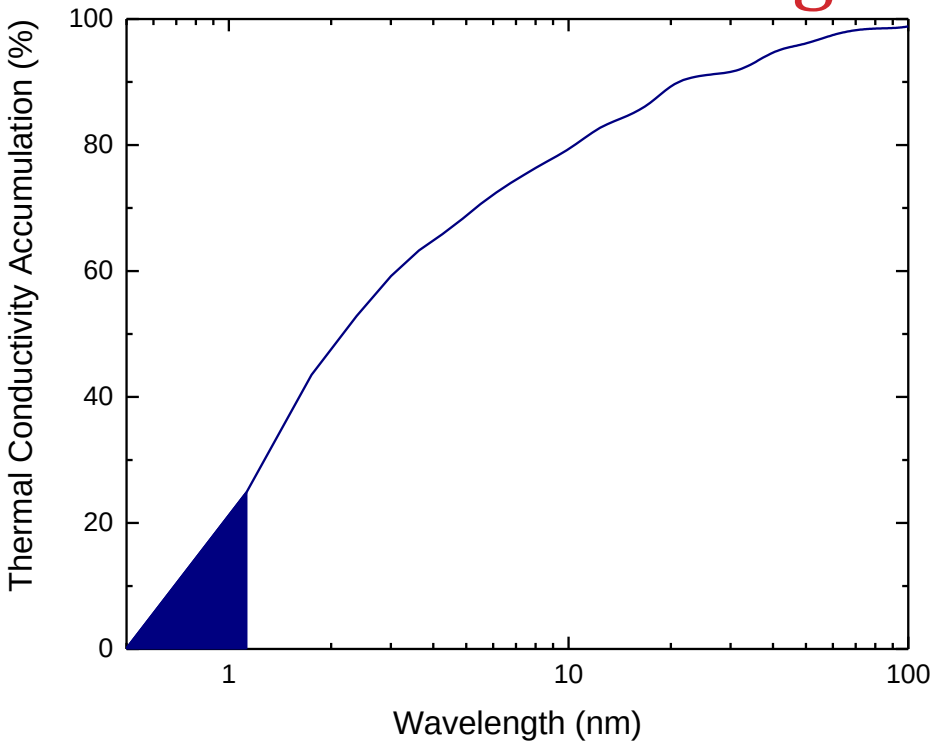


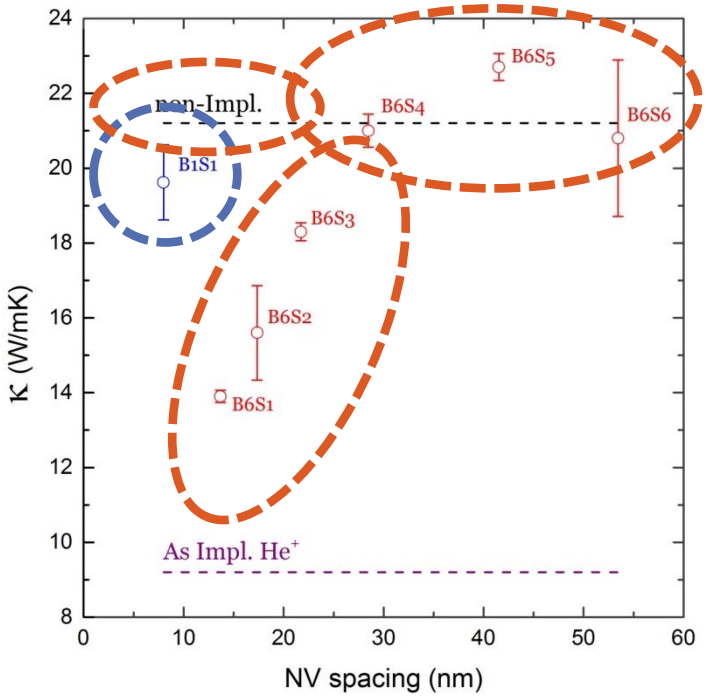
If porosity φ is constant, $d_s \propto d_p$

Thus, the spacing d_s between scattering centers scale with the *roughness* d_p of the scattering surface.

- d_s sets the MFP of scattered phonons
- d_p sets the wavelength range of scattered phonons

Concurrent scattering at NVs and GBs





- With no NV, MFP is limited by GB only, affecting phonons with $\lambda < d_{GB}$=50 nm
- For large d_s, d_p ($\approx d_{GB}$) NVs have little effect as they scatter phonons already scattered by GBs (B6S6 and B6S5)
- The more d_s and d_p decrease, the more the MFP of phonons with $\lambda < d_p$ decreases (MFP $\approx d_s$) (B6S3, B6S2 and B6S1), i.e. NVs decrease the MFP of phonons with $\lambda < d_p$ to $\approx d_s$
- For very small d_s and d_p (B1S1) NVs scatter phonons of very low λ ($< d_p \approx 1$ nm), that however marginally contribute to κ. Thus they are ineffective on κ, that gets back to its NV-free value

Computational framework

Method: Approach-to-Equilibrium Molecular Dynamics

- AEMD solution of heat-transport equation under PBC for an initial step-like initial temperature profile

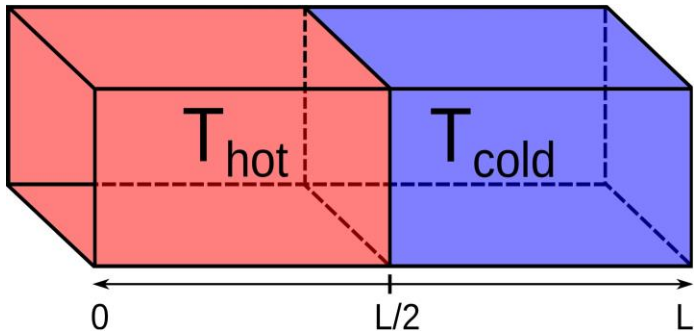
C. Melis et al., Eur. Phys. J. B. 87, 96 (2014)

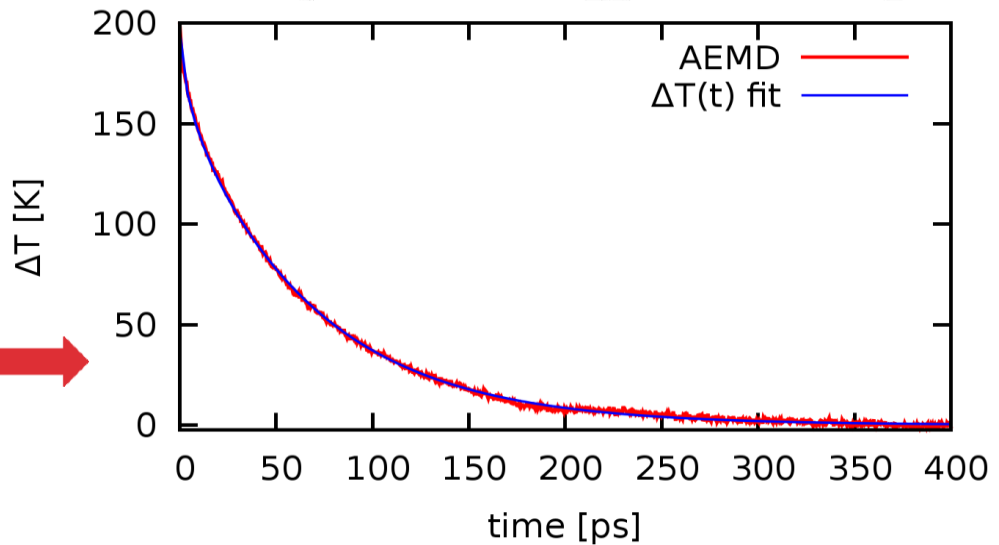
- Time-dependent temperature difference between the two regions

$$\Delta T(t) = \sum_{n=1}^{\infty} C_n e^{-\alpha_n^2 \left(\frac{\kappa}{\rho c_V}\right) t}$$

where:
κ is the thermal conductivity
ρ and c_V density and specific heat
$\alpha_n = 2\pi n / L_z$
$C_n = 8(T_{hot} - T_{cold})[\cos(\alpha_n L_z/2) - 1]^2/(\alpha_n L)$

- ΔT is fitted to obtain κ





Computational framework

Investigated systems:

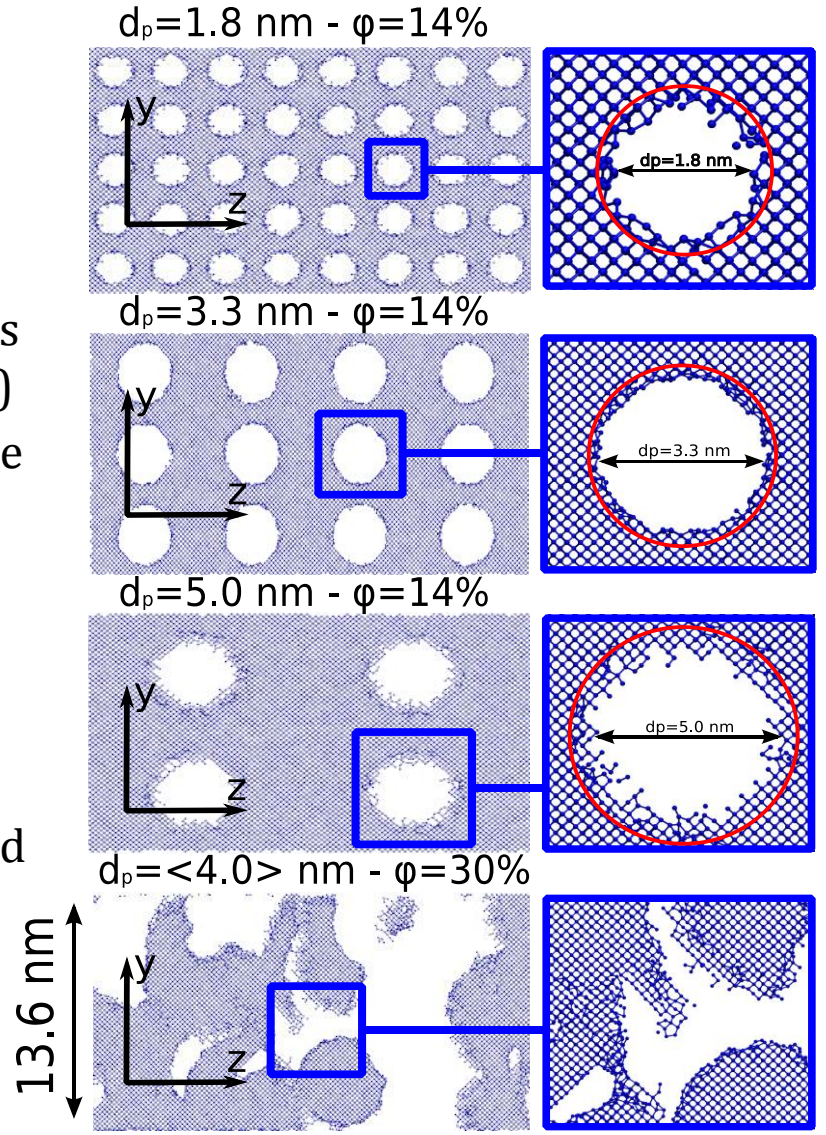
- Ordered porous sc-Si (OPscSi)
- Random porous sc-Si (RPscSi)
- Quasi-random porous nc-Si (RPncSi)

In OPscSi the porosity $\varphi=\varphi(N_p, d_p)$ actually depends on the number of NVs (N_p) and on NV diameter (d_p)

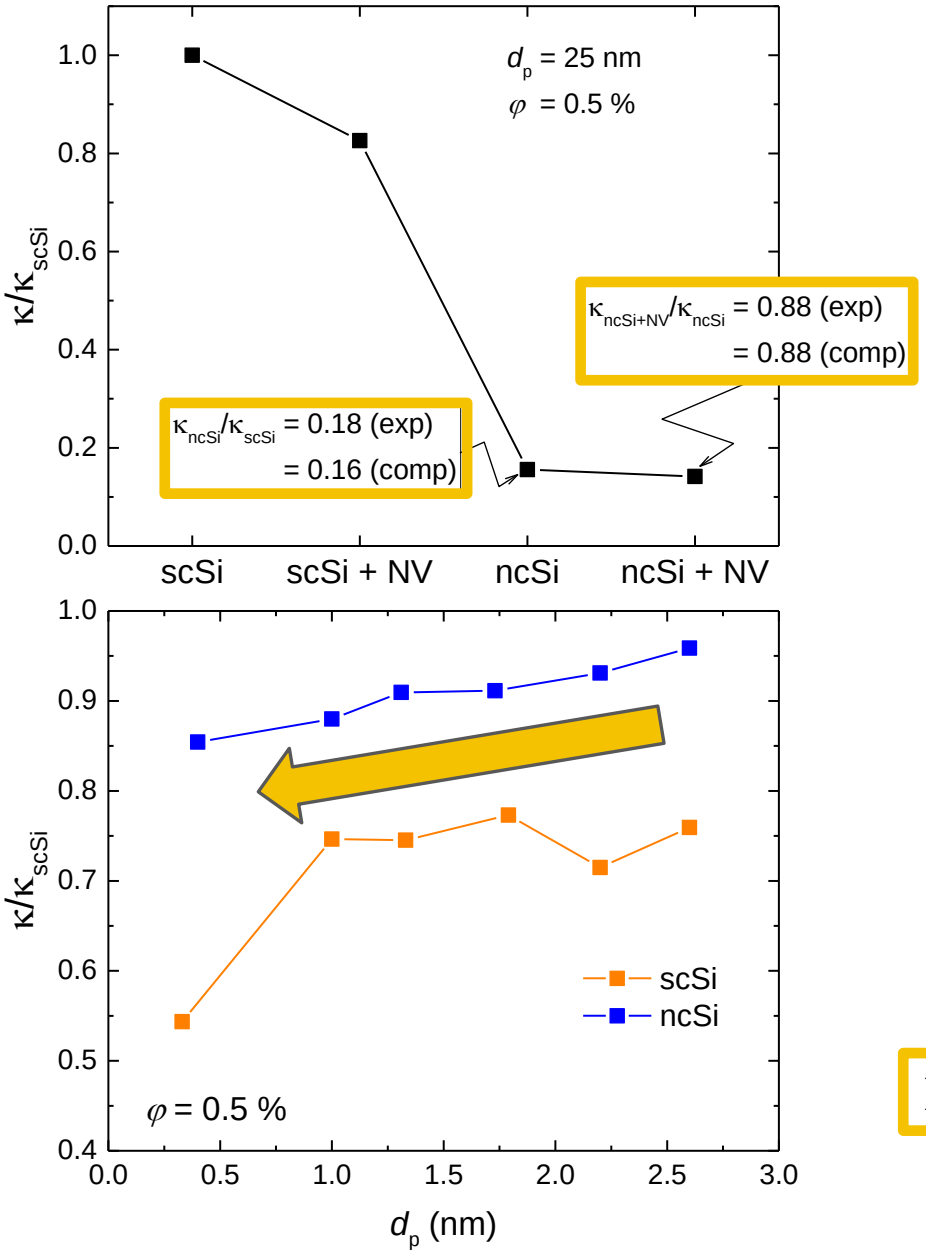
In RPscSi a uniform φ is generated along the sample

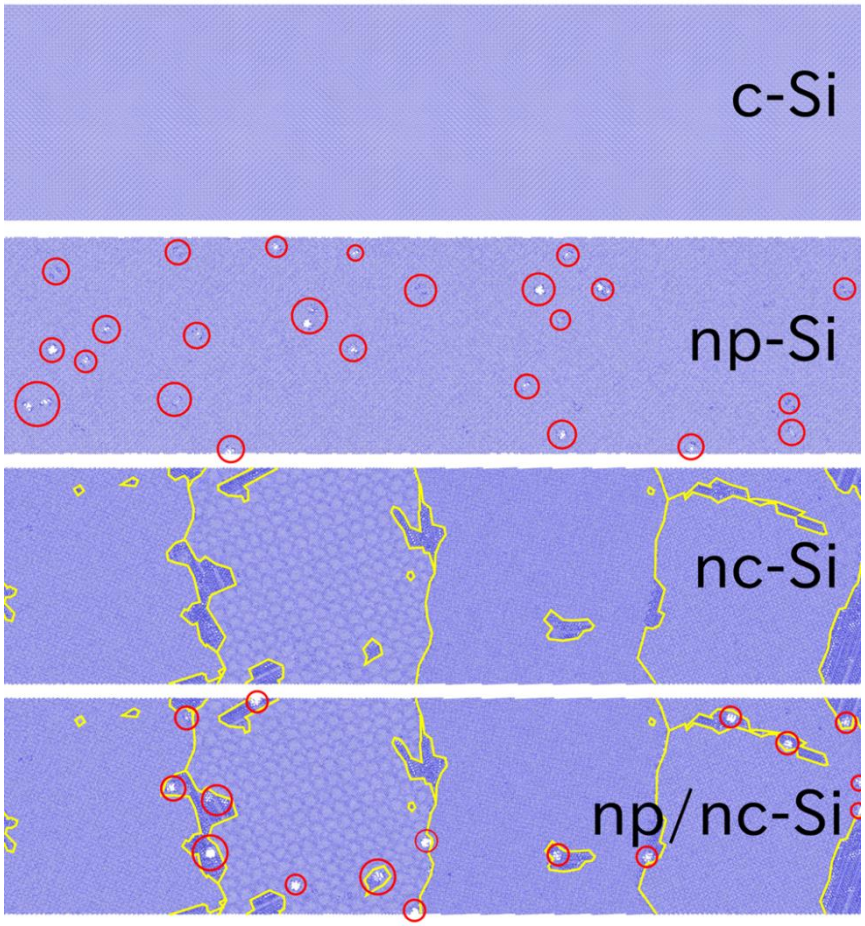
Simulation protocol:

1. high-temperature simulated annealing
2. careful equilibration at room temperature
3. inner surfaces fully relaxed to a highly-defected structure
4. used EDIP potential [Justo et al., PRB 58 (1998) 2539]



Trends in ncSi





However, no 'inversion point' was found

Possible reasons for the discrepancy

- NV distribution in the simulation is not uniform, NV segregating close to the GBs (thus, $d_s \not\propto d_p$)
- NVs may not be fully described by their size, i.e. termination of inner surfaces by e.g. H may make ultrasmall NVs qualitatively different from standard NVs

  E. Romano et al., *Surf. Interf. Anal.*, **42** (2010) 1307; E. Romano et al., *Surf. Interf. Anal.*, **42** (2010) 1321; G.F. Cerofolini et al., *Surf. Sci.*, **604** (2010) 1215

- Other ideas?

Summary and Conclusions

- Ion implantation demonstrated a suitable technique to introduce controlled porosity in silicon
- NVs were found to modulate κ depending on their spacing and size
- Euken model of thermal conductivity was falsified
- AEMD simulation quantitatively confirmed the effect of NV in ncSi on κ
- Gray model of thermal conductivity confirmed inadequate to explain the physics of the system

- A question remains open about why ultrasmall NVs do not impact on κ

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