Recent developments in understanding and modeling of defects in Czochralski germanium

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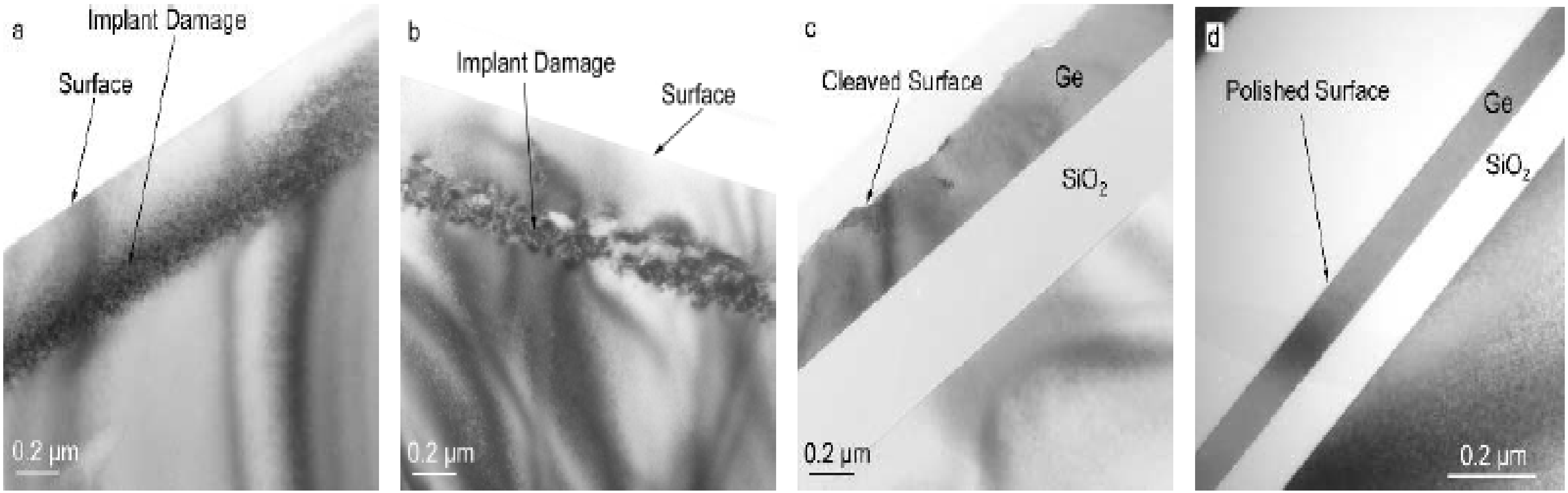
- COP's on polished Ge wafer surfaces
- Intrinsic point defects properties: experimental
- Calculation of intrinsic point defect properties
- Simulation of void formation in Cz germanium
- Conclusions

Introduction

- Today main application of Ge substrates for GaAs epitaxy: highly doped, 100 mm diameter. Also for optical components (mirrors, lenses) and HR Ge for detectors.
- Renewed interest to use Ge in nano-electronics due to high carrier mobility.
- Limited reserves, high cost → GeOI.
- Development of electronics grade Cz Ge “donor” wafers:
  - grown-in lattice defects
  - metallic impurities
  - geometry.

Bonded GeOI wafer



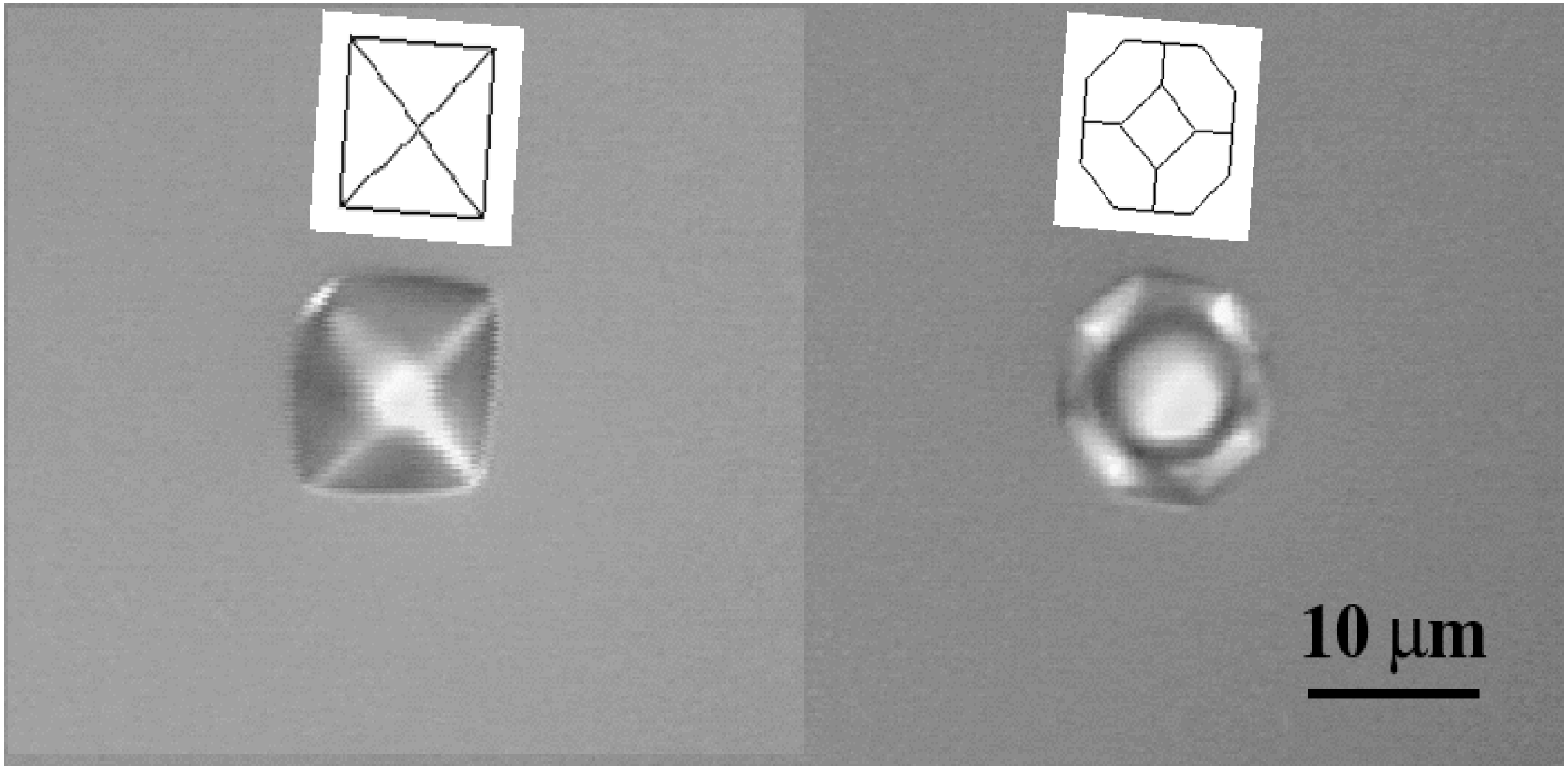
- XTEM of implanted Ge (a); after thermal treatment (b); after bonding and cleaving (c) and after CMP (d).

C.J. Tracy et al. Journ. Electron. Mater. **33**, 887 (2004)

Cz germanium for nano-electronics

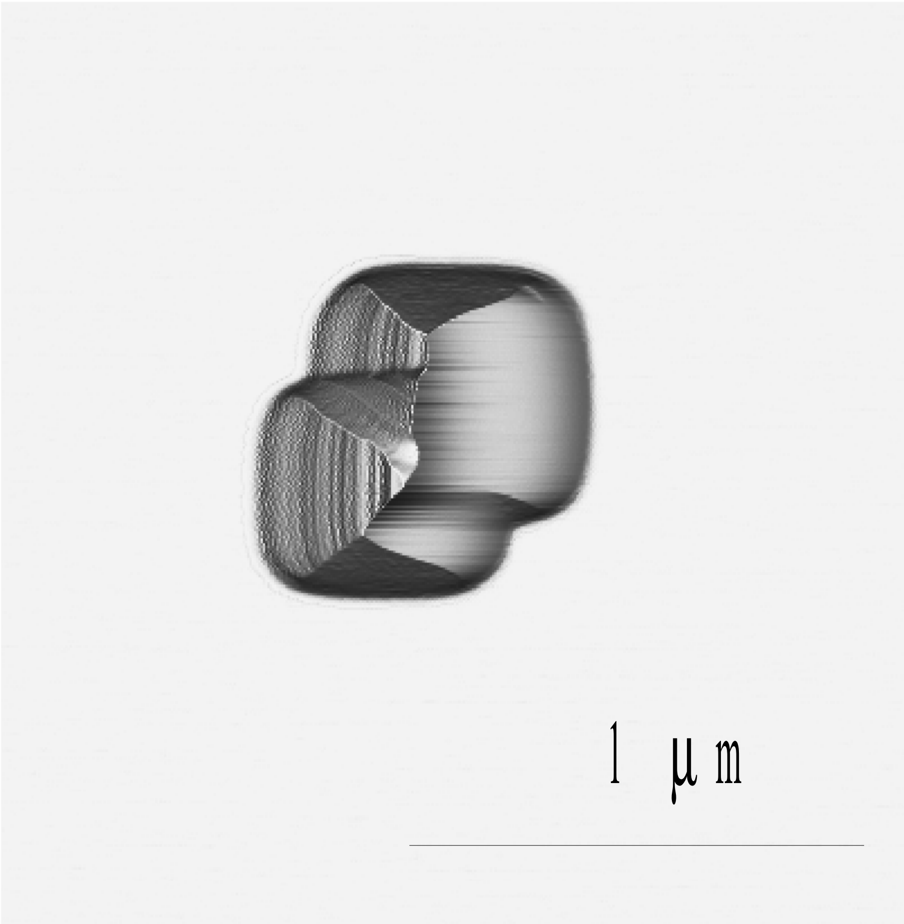
- 200 mm Ge wafers commercially available.
- Ge wafers fulfilling 300 mm wafer geometry specs demonstrated.
- Dislocation free; metals below detection limit.

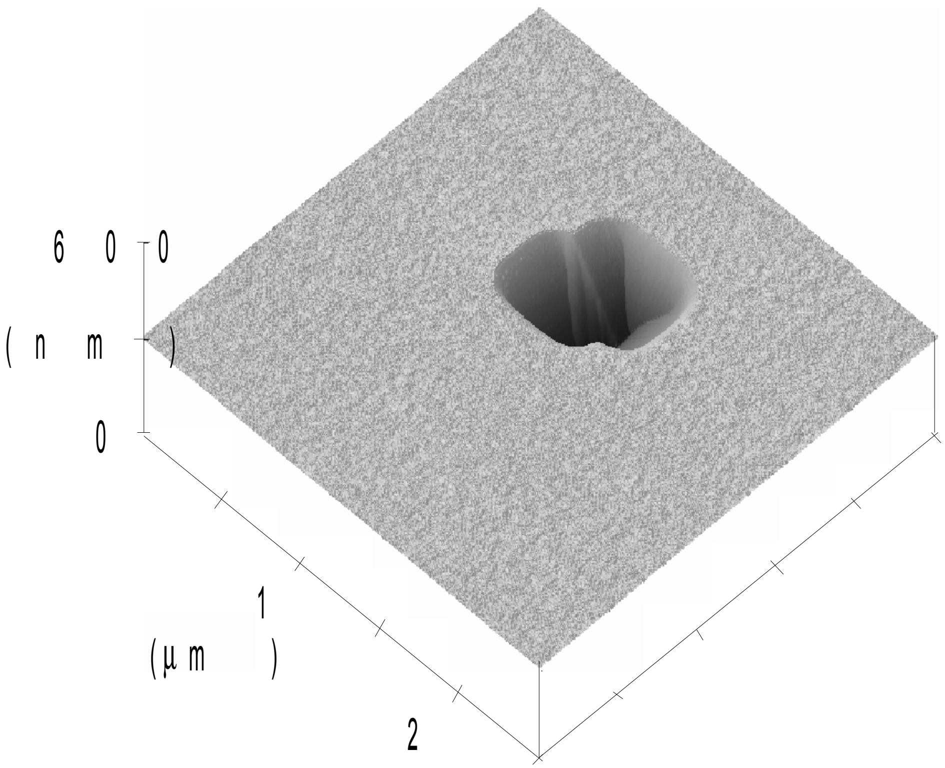
Surface pits on Cz germanium wafers



- Optical micrographs showing surface pits occasionally observed with the naked eye on Cz Ge wafer surfaces.

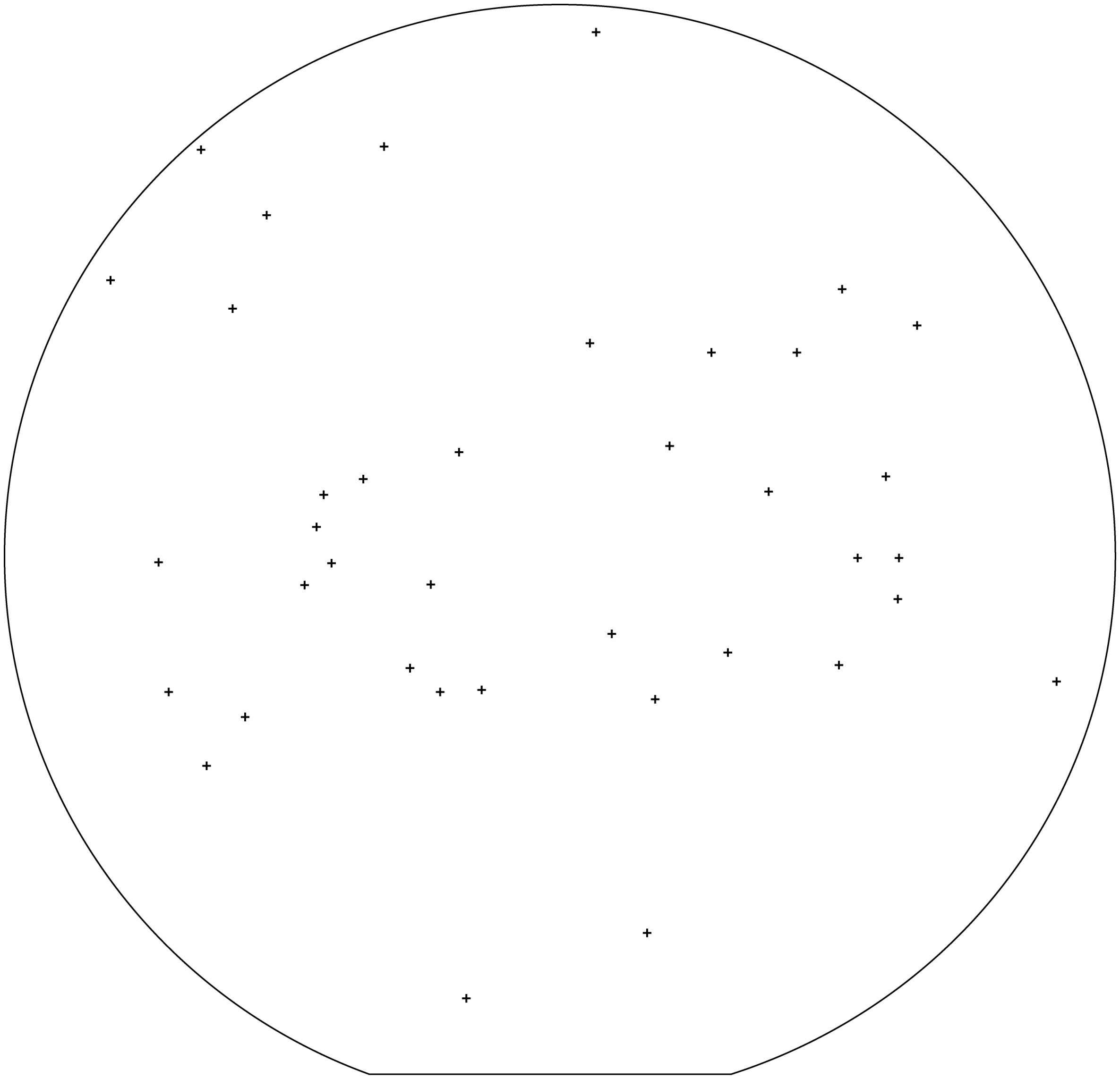
COP'S on Cz silicon wafers





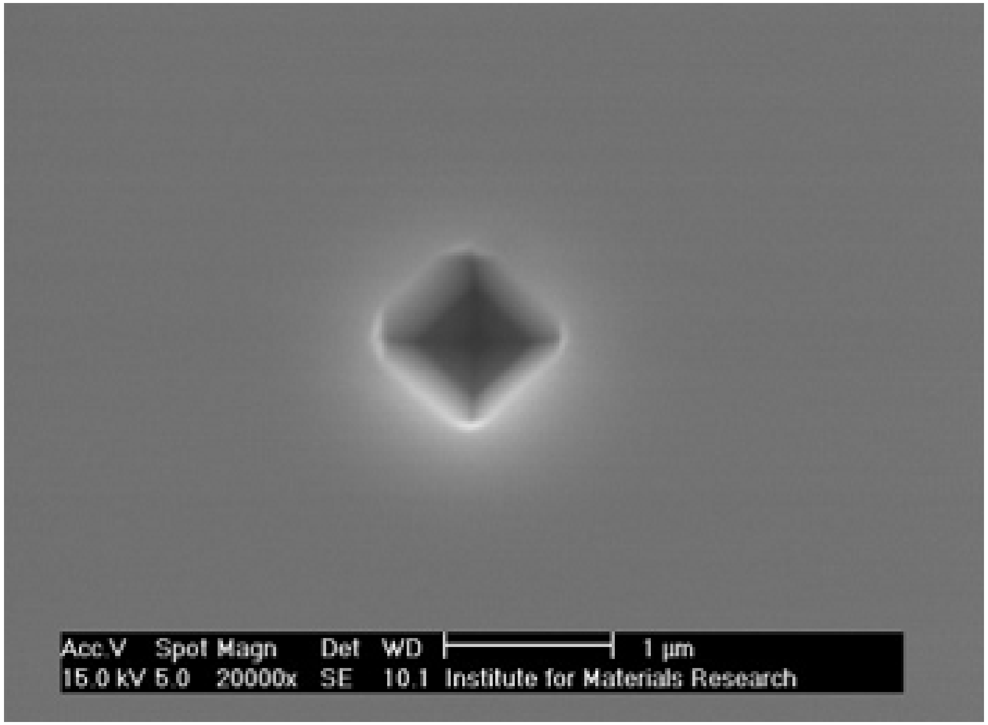
- AFM images of a typical double COP after 4h SC1 delineation. Left: top view. Right: 3D-view.

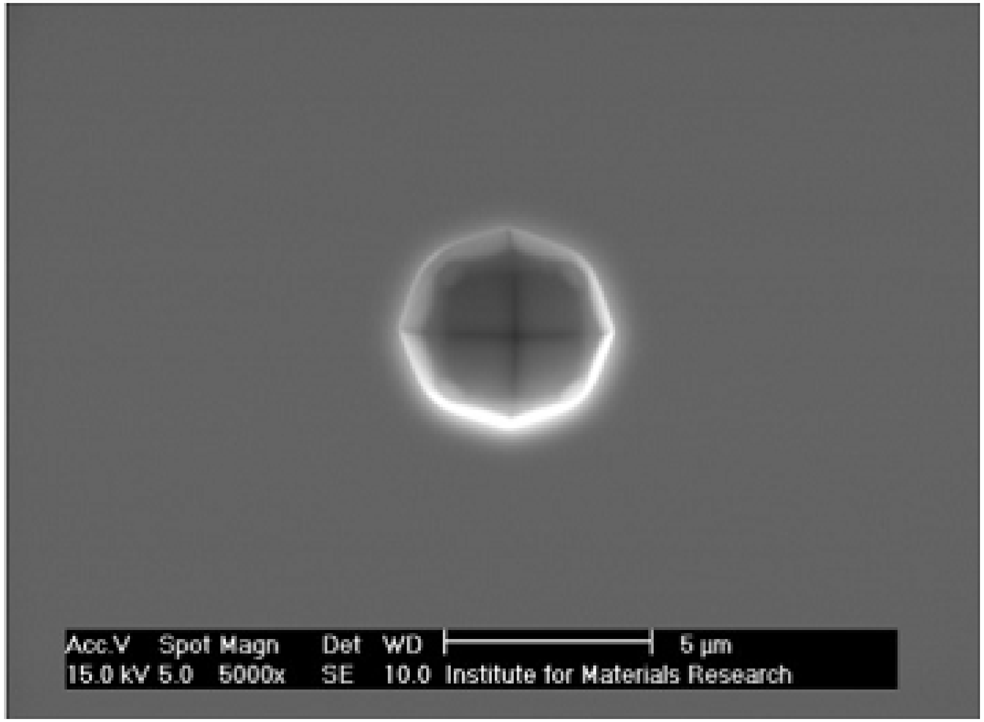
COP'S on Cz germanium wafers?



- Image obtained with a SURFSCAN surface inspection tool, revealing the presence of large COP's on a polished germanium wafer.

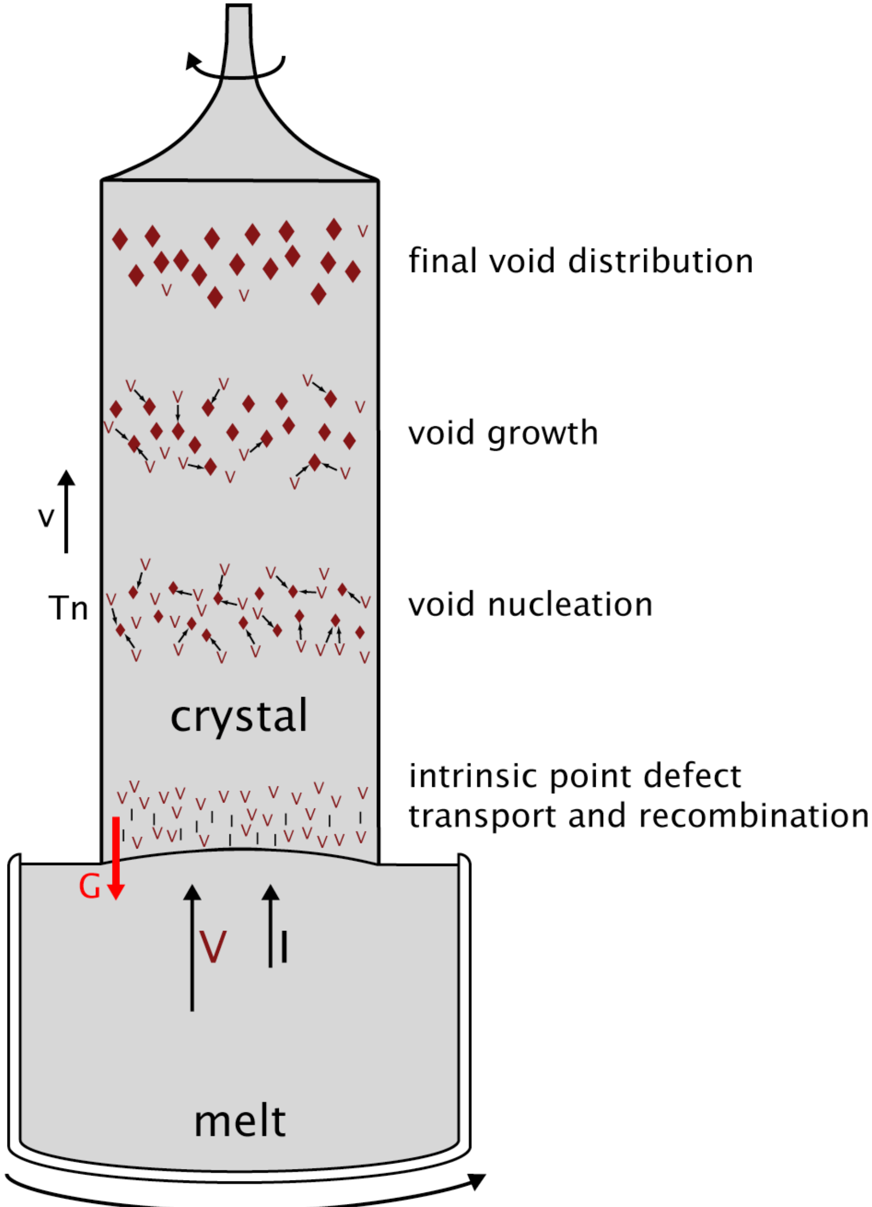
SEM after coordinate transfer of COP positions





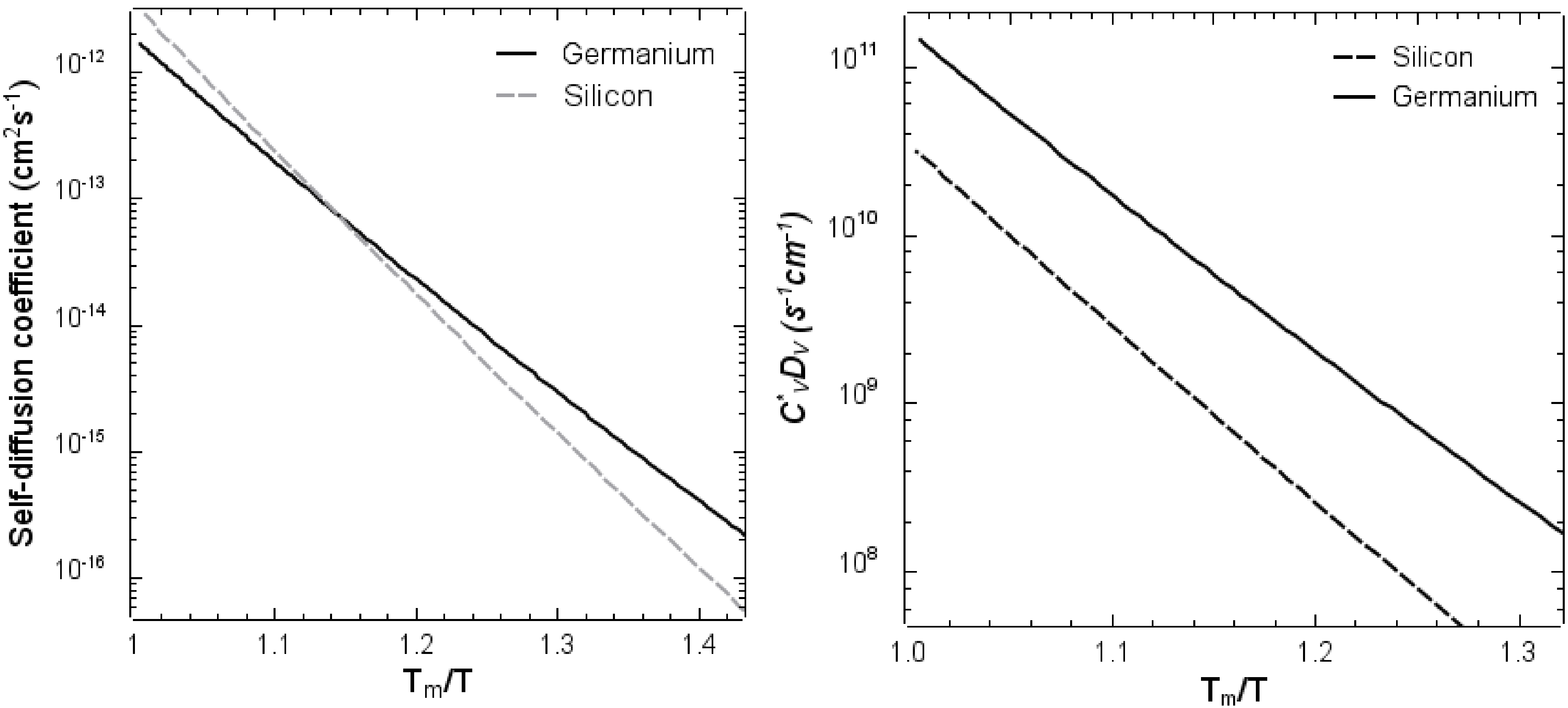
- SEM images of surface pits on Ge wafer surfaces, corresponding with and octahedral (left) and truncated octahedral void (right).

Void formation in Czochralski germanium



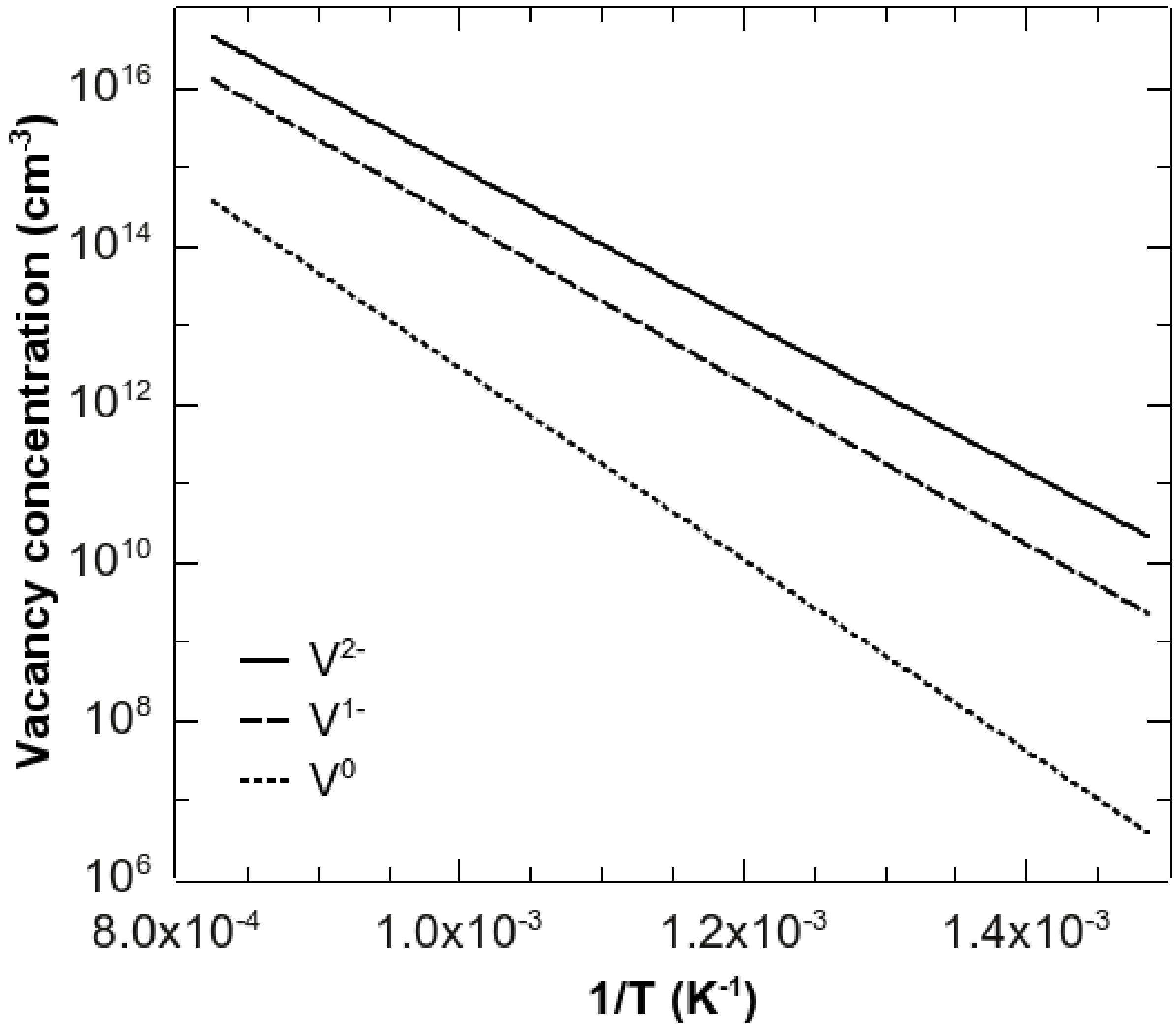
- Schematic view of a growing Ge crystal as a solid-state reactor for point defects.
- Tweet JAP 30, 2002 (1959):
  - pit size depending on thermal history;
  - pit density reduction when pulling slower or post-heating the crystal in the puller;
  - density reduction accompanied by size increase;
  - vacancy clustering mechanism.

Self-diffusion and vacancy transport capacity



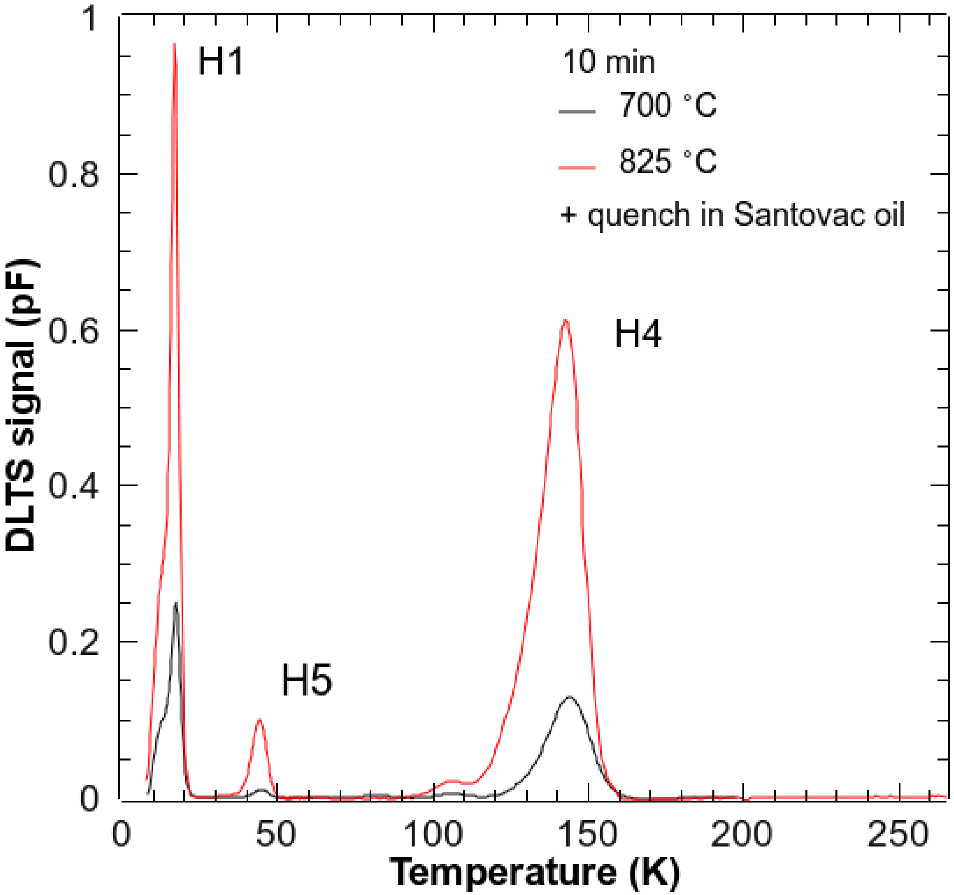
- Self-diffusion coefficient (left) and vacancy transport capacity (right) in Si and Ge as a function of temperature normalized with respect to the melt temperature.

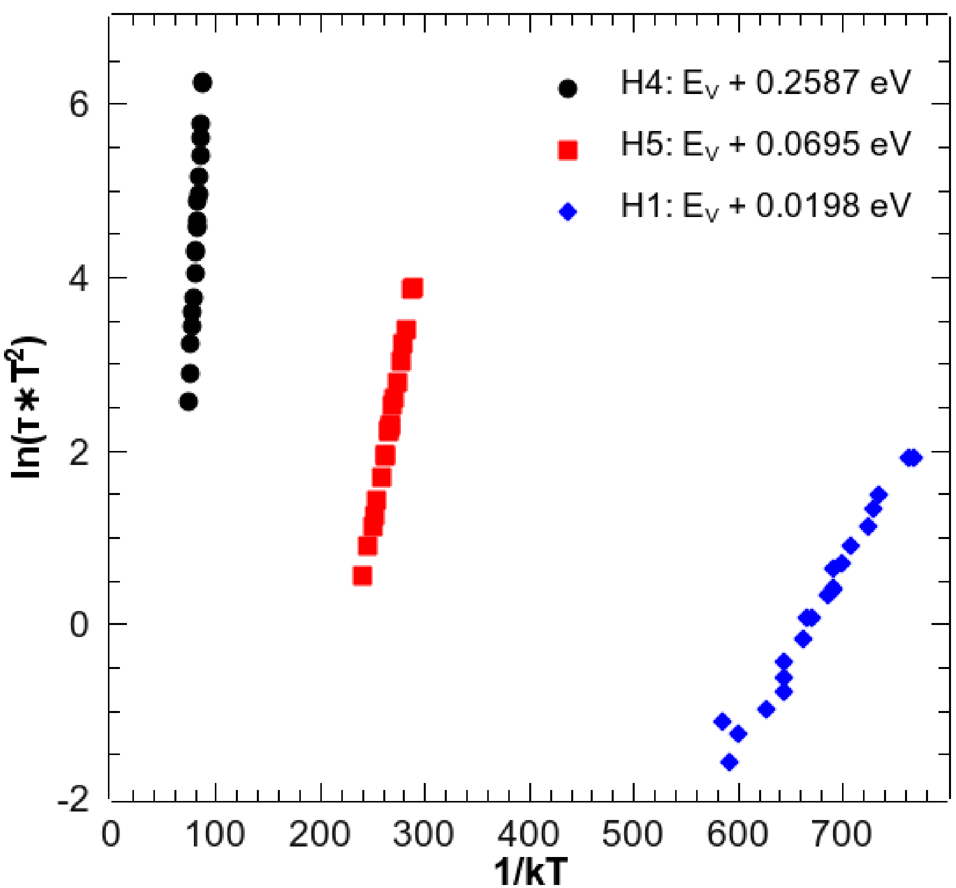
Vacancies in germanium: quenching experiments



- Thermal equilibrium concentration of different charge states of the vacancy.

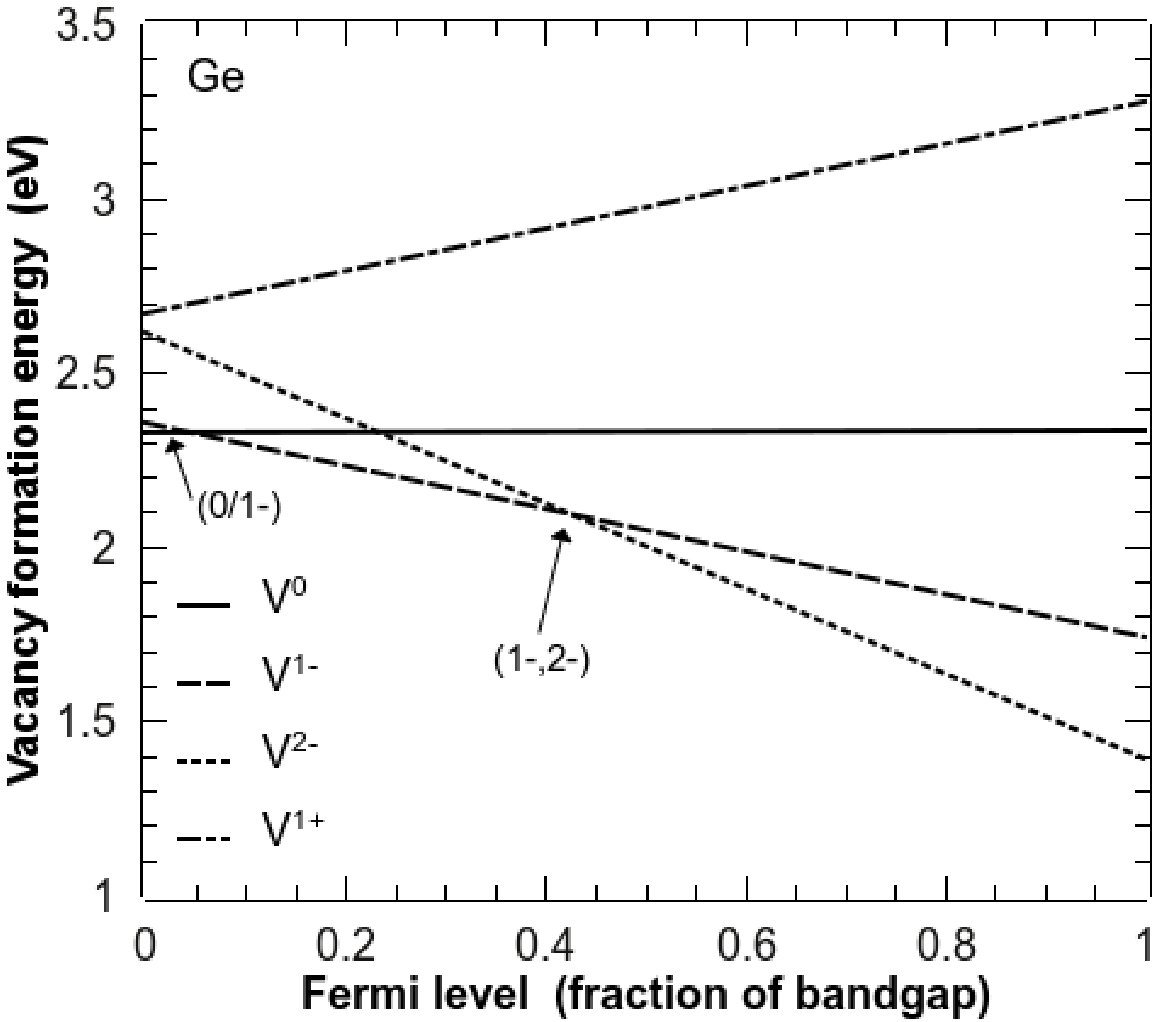
Quenching experiments: DLTS





- DLTS spectra measured in quenched samples. No known Cu-related deep levels are observed.

Ge vacancy formation energy: impact of Fermi level



- Formation energy of the vacancy calculated ab initio with LDA+U as a function of the position of the Fermi level in the bandgap and of the charge state.

Charged vacancies in Ge

- Calculated vacancy formation energies in eV ($E_F = 0.305$ eV).

Charge state	2−	1−	0	1+	2+
LDA+*U* PAW *3d*	2.00	2.05	2.33	2.97	4.01
Quenching	2.19 +/− 0.11	1.98 +/− 0.11	2.35 +/− 0.11	−	−

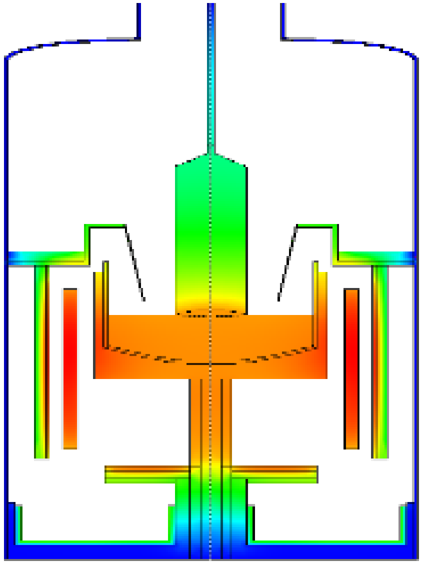
- Acceptor levels in eV for the Ge vacancy.

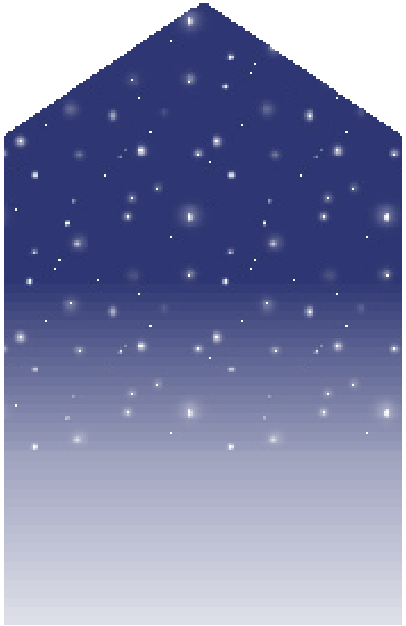
Reference	0/1-	1-/2-	Method
This work	**0.02**	**0.26**	**DFT LDA**
This work	**0.02**	**0.26**	**DLTS**
Konorova (1969)	0.025 +/- 0.005	0.15 +/- 0.05	Hall effect
Hiraki (1965)	0.03-0.05	0.15 - 0.20	Hall effect
Zhidkov (1961)	0.04	0.25	Hall effect

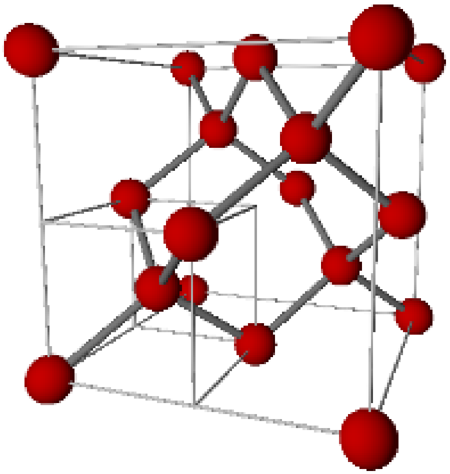
Multiscale model for defect dynamics during Cz growth

temperature distribution

material parameters





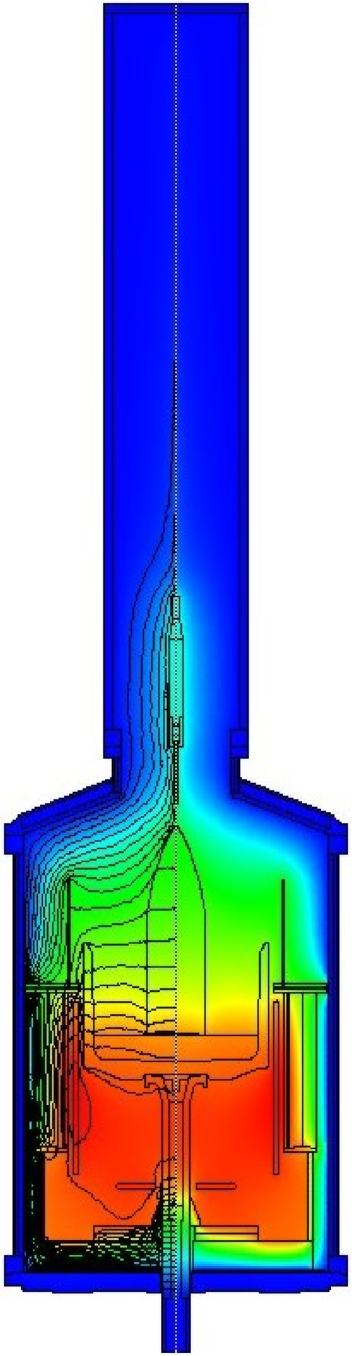


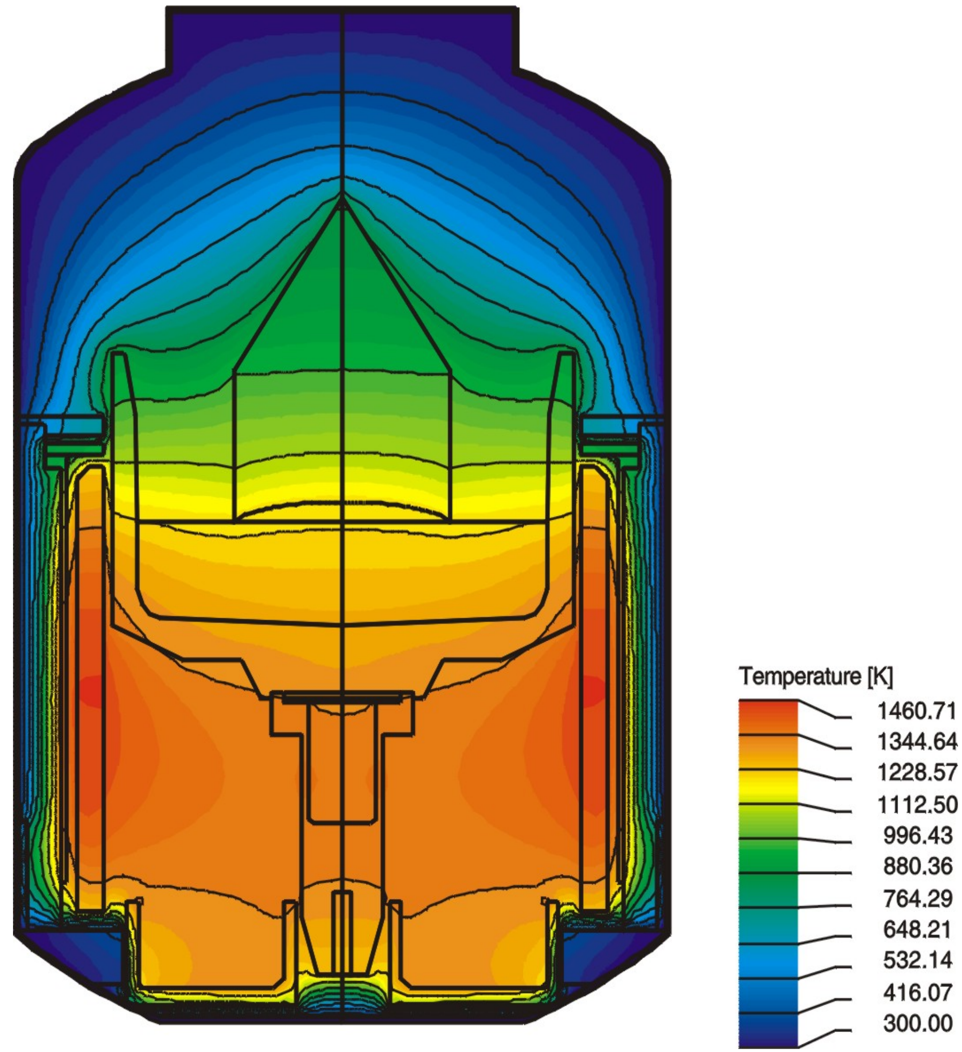
macro scale
(macroscopic process simulation)

meso scale
(microscopic defect dynamics)

atomistic scale
(atomistic models)

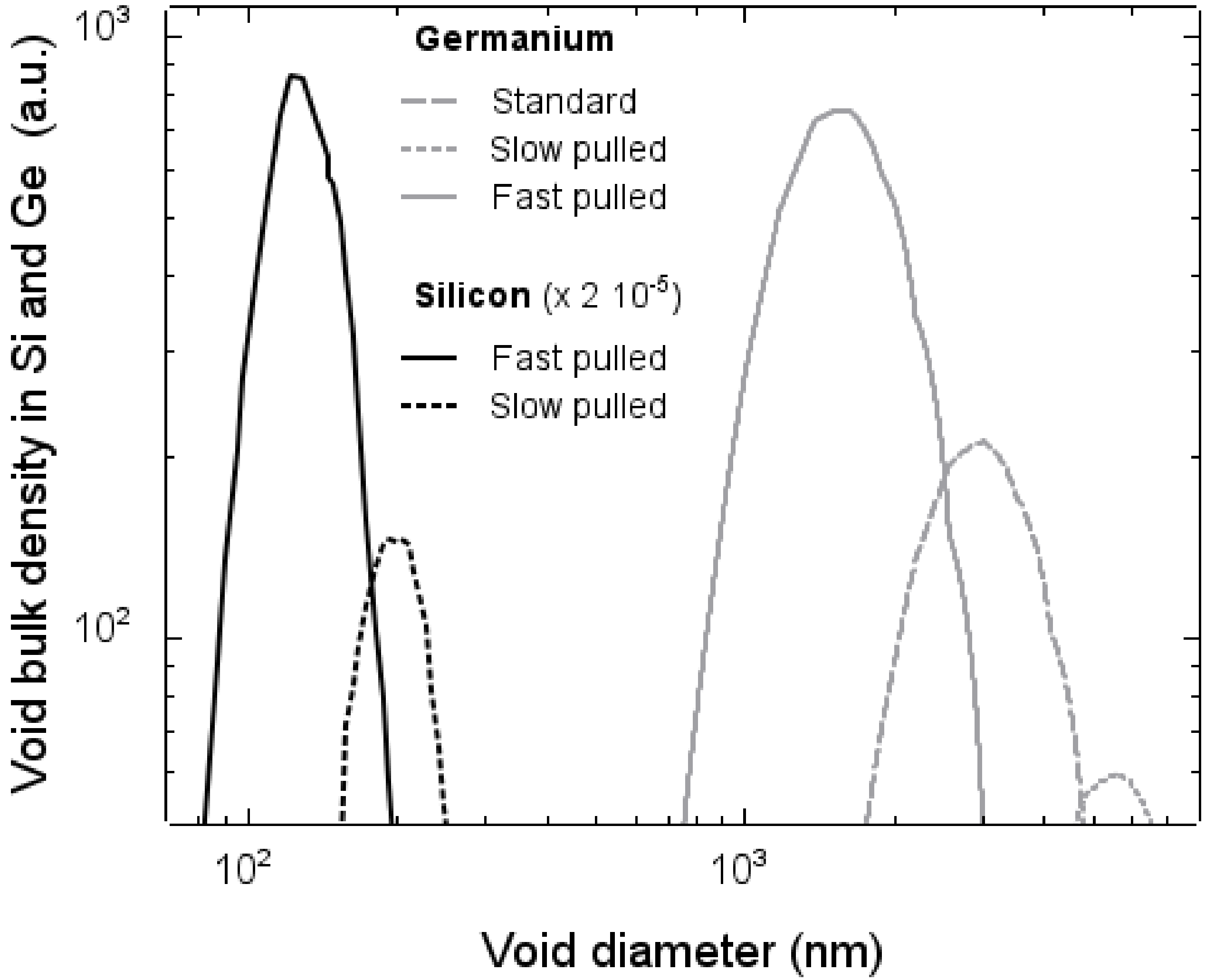
Thermal simulations





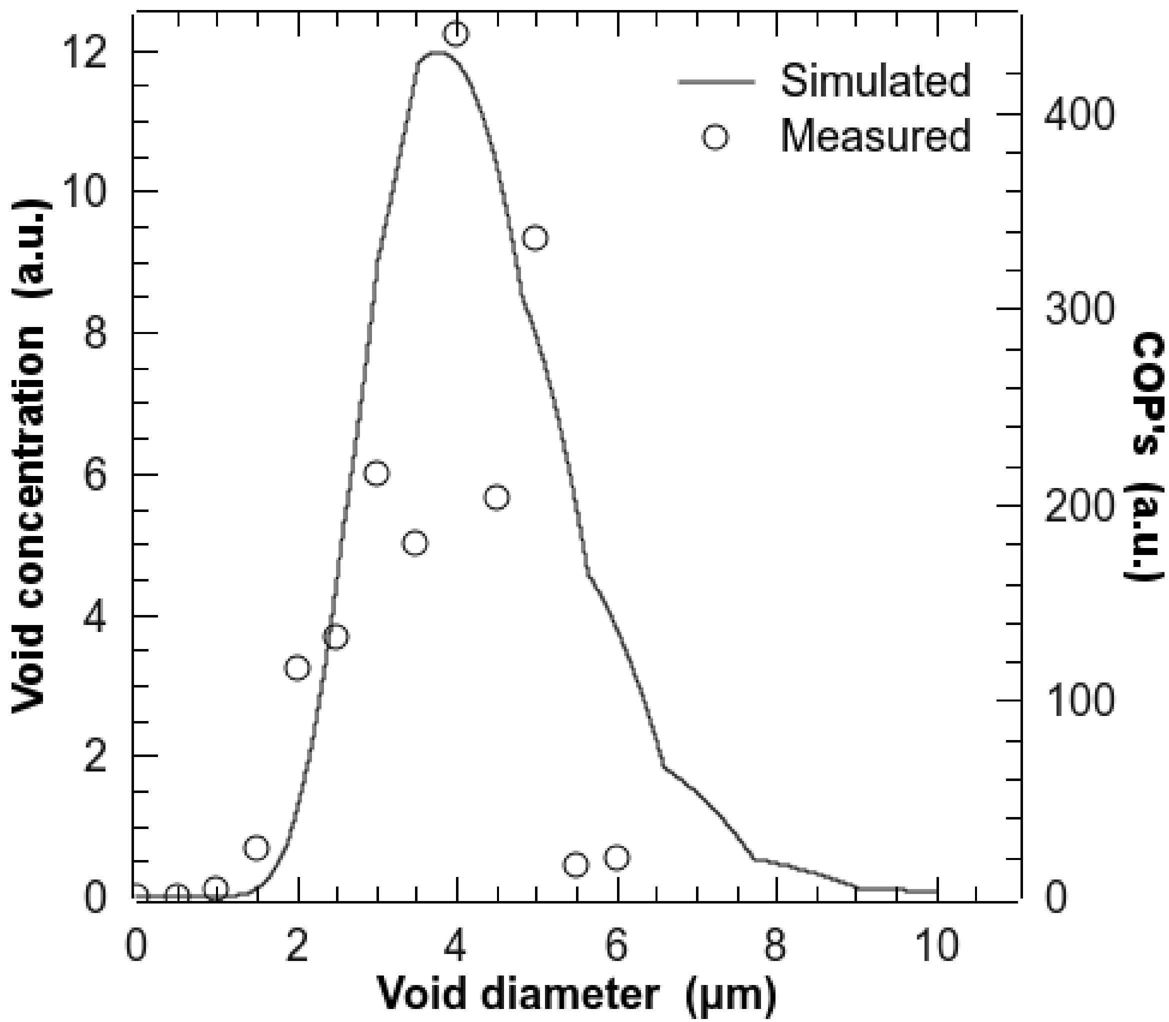
- Thermal simulations of 200 and 300 mm Ge crystal growth.

Simulation of intrinsic point defect clustering



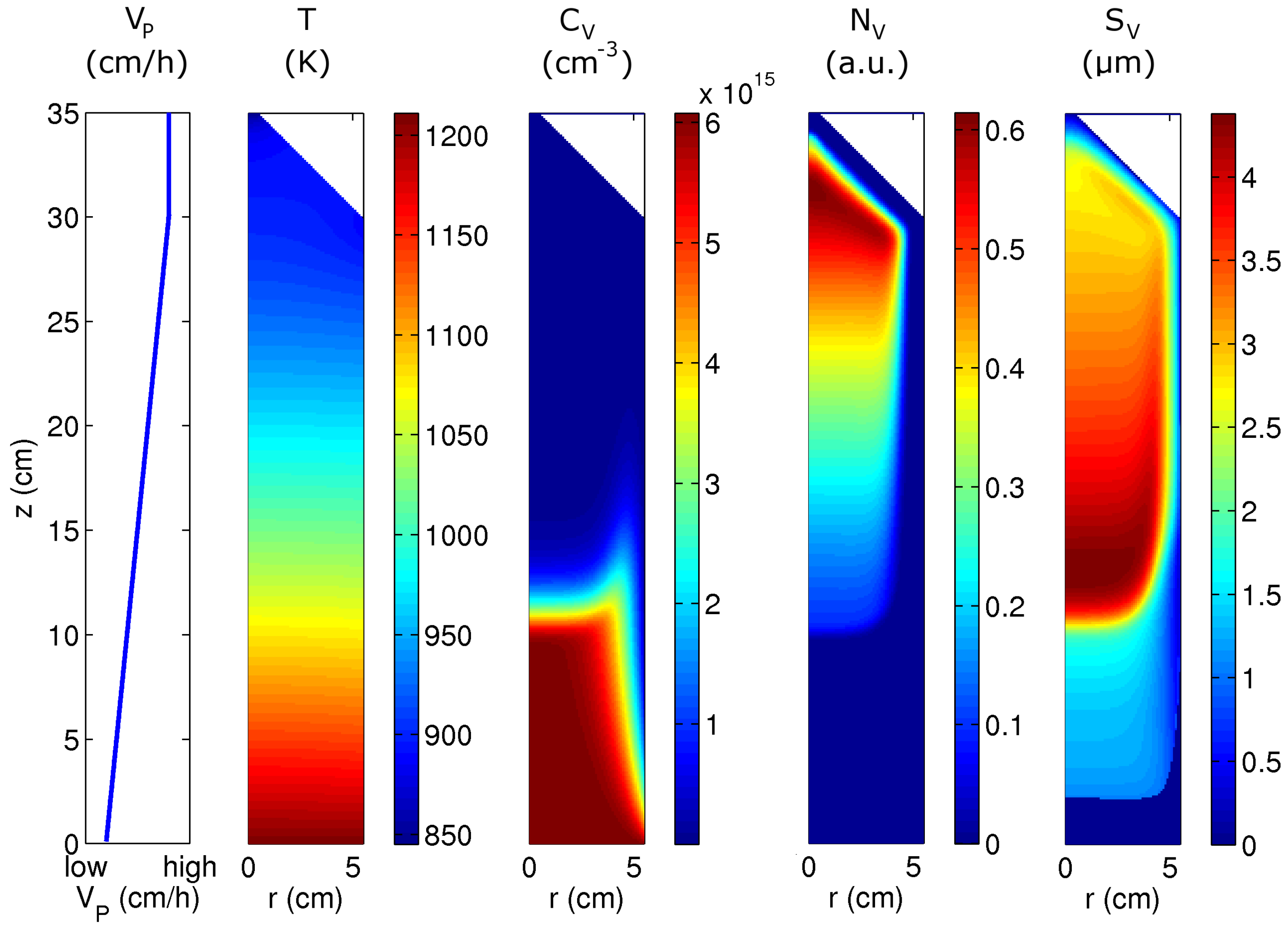
- Simulations illustrating the one order of magnitude larger void size in Ge and the four orders of magnitude lower volume density compared to Si.

Simulation of vacancy clustering in Cz Ge



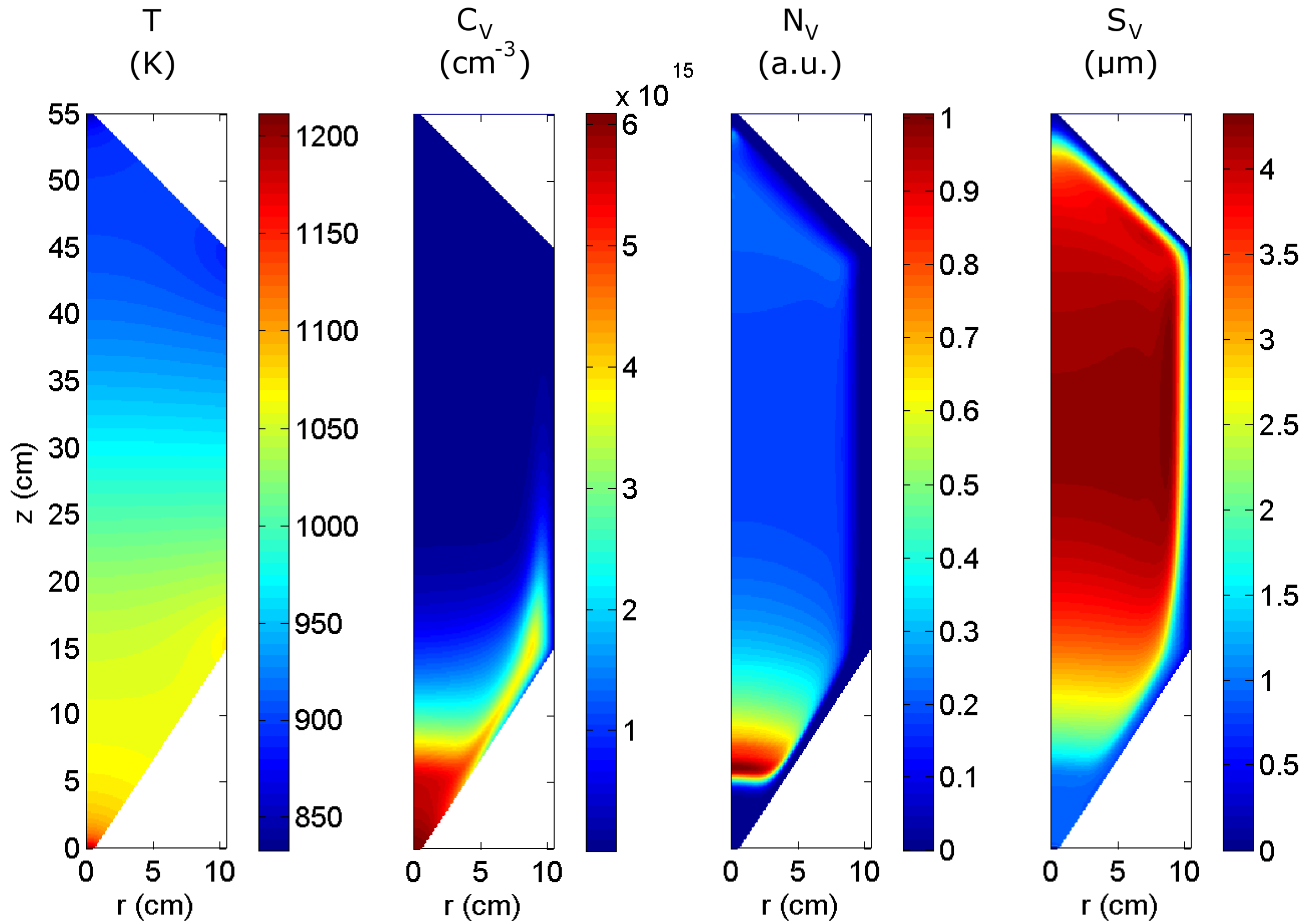
- Comparison between measured COP and simulated void distribution. The COP distribution was measured using a confocal review station.

2D unsteady-state simulations: decreasing pull rate



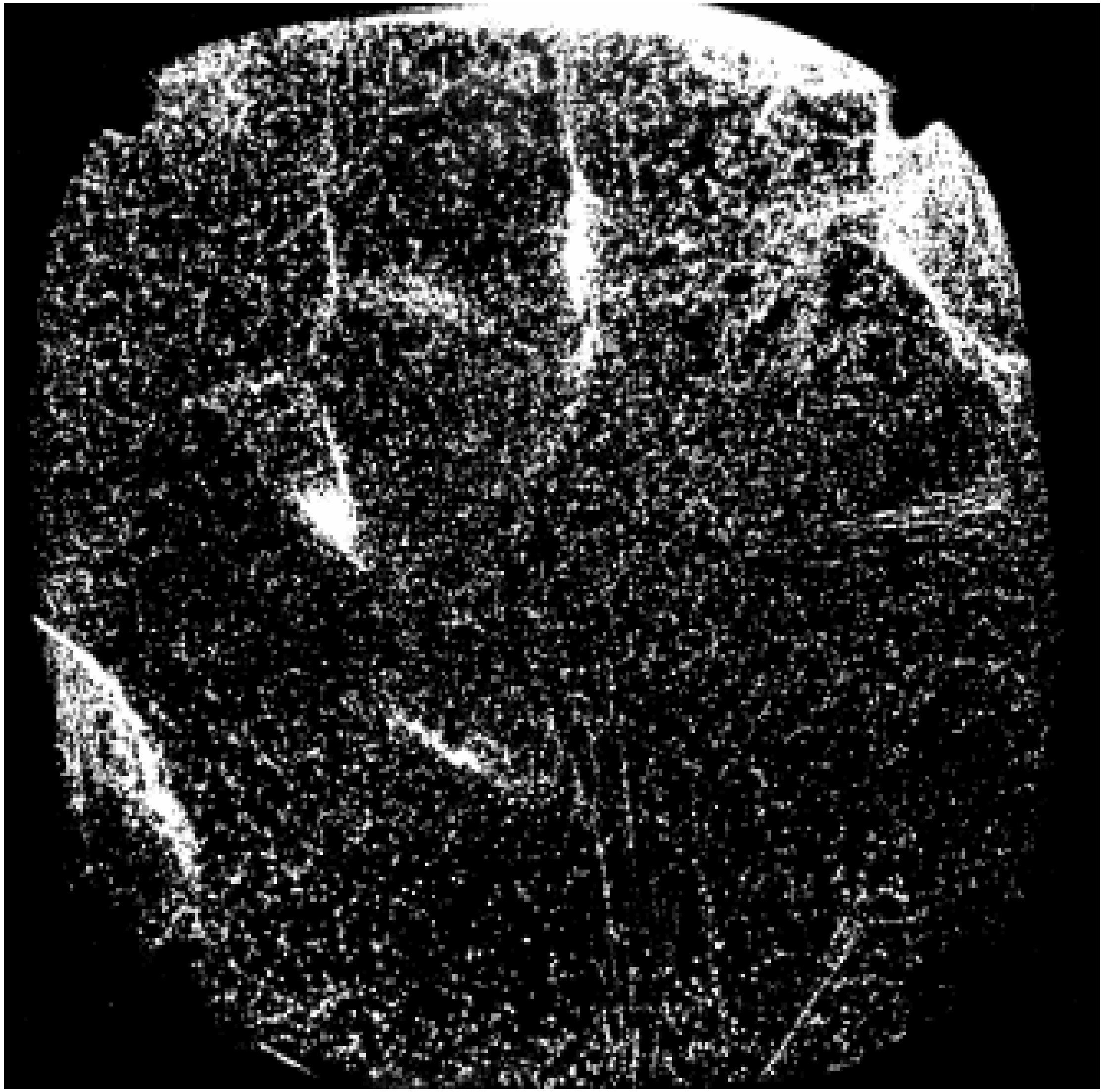
- Temperature, vacancy concentration, vacancy cluster concentration and size distributions for increasing pull rate.

2D unsteady-state simulations: full crystal



• 2D distributions of T, V concentration, V cluster concentration and size distribution in a 8" Ge crystal grown with constant pull rate.

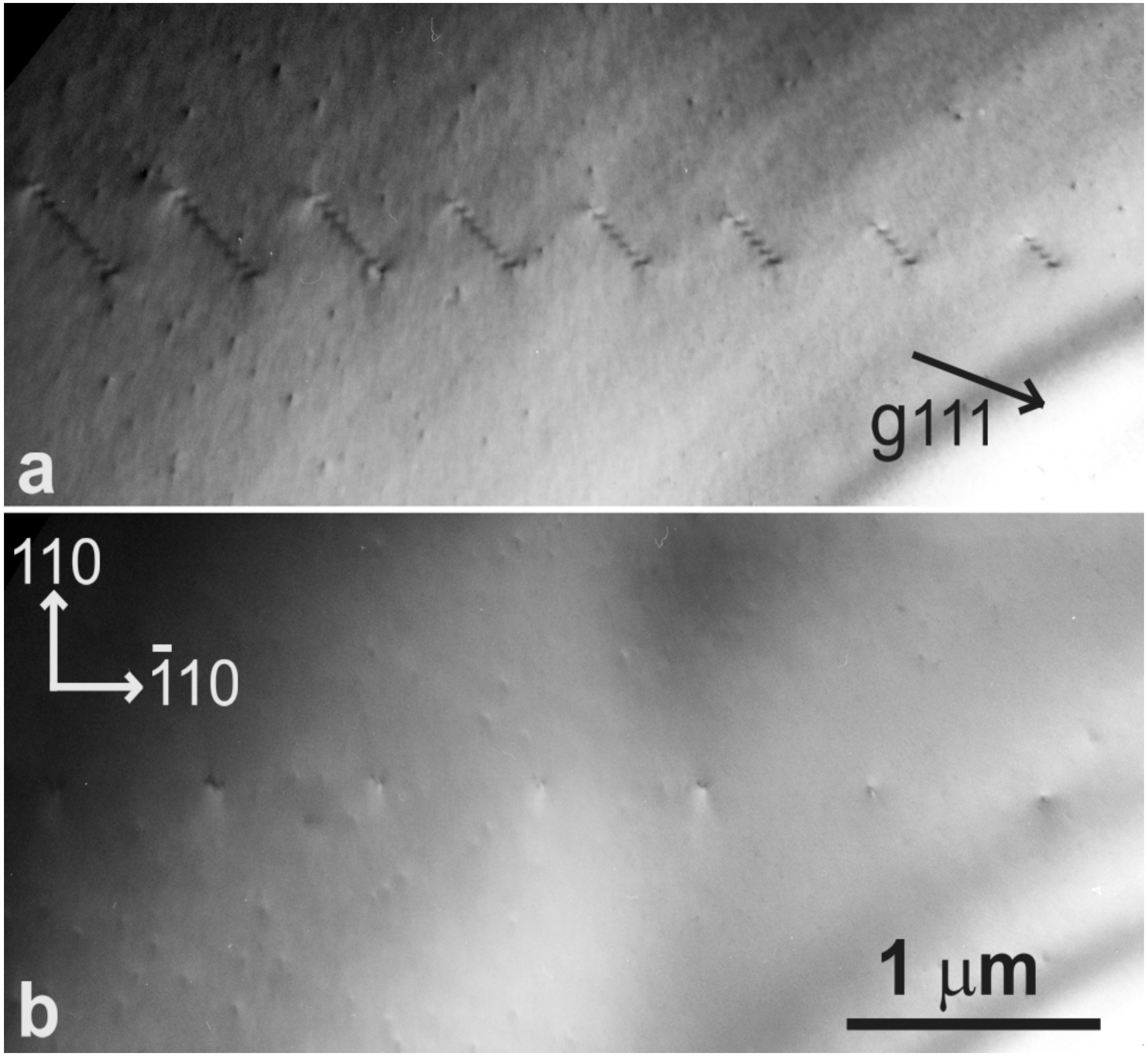
Epilogue: grown-in dislocations in HR-Ge



- Optical micrograph of preferentially etched HR-Ge crystal slice revealing dislocation lineage and mosaic structures as well as isolated dislocations.

Van Sande et al, Appl.Phys. A **40**, 257 (1986).

Grown-in dislocations



- HVEM of lineage dislocations (Class 1) in a HR germanium crystal. Top) Tilted about 35° away from the [001] crystal pulling axis. Bottom) The same area viewed along the [001] axis. Dislocations are seen end-on.

Epilogue: grown-in dislocations in HR-Ge

- HR-Ge is grown with well defined dislocation density to suppress V_2H and void formation:
  - 90° (class 1) dislocations form low angle grain boundaries showing up as lineage or mosaic structures of etch pits;
  - 60° (class 2) dislocations: few thousand per cm^2;
  - 30° (class 3) and 90° (class 4) difficult to avoid and radial distribution.

- Dislocation and impurity specs HR Ge crystals:

Deep Levels	p-type	Total Cu concentration, as measured by DLTS : $Cu_{tot} \leq 4{,}5\ 10^9\ cm^{-3}$
	n-type	Deep level point defects as measured by DLTS : $< 5\ 10^8\ cm^{-3}$

Crystallographic perfection		p-type	n-type
	Dislocation density (EPD, cm^{-2})	≤ 10000	≤ 5000
	Lineage (unit length = slice radius)	≤ 3	≤ 2
	Mosaic structures (unit surface = $100mm^2$)	≤ 5	≤ 2
	Saucers (cm^2)	≤ 500	≤ 500

Conclusions

- The (negatively charged) vacancy is the dominant intrinsic point defect in germanium.
- Quantitative simulation of vacancy introduction and clustering during Czochralski pulling is possible.
- Further work:
  - impact of extrinsic point defects on vacancy thermal equilibrium concentration;
  - experimental data on vacancy and self-interstitial formation energy, diffusivity and recombination;
  - (impact of dislocations).