Precipitation Models

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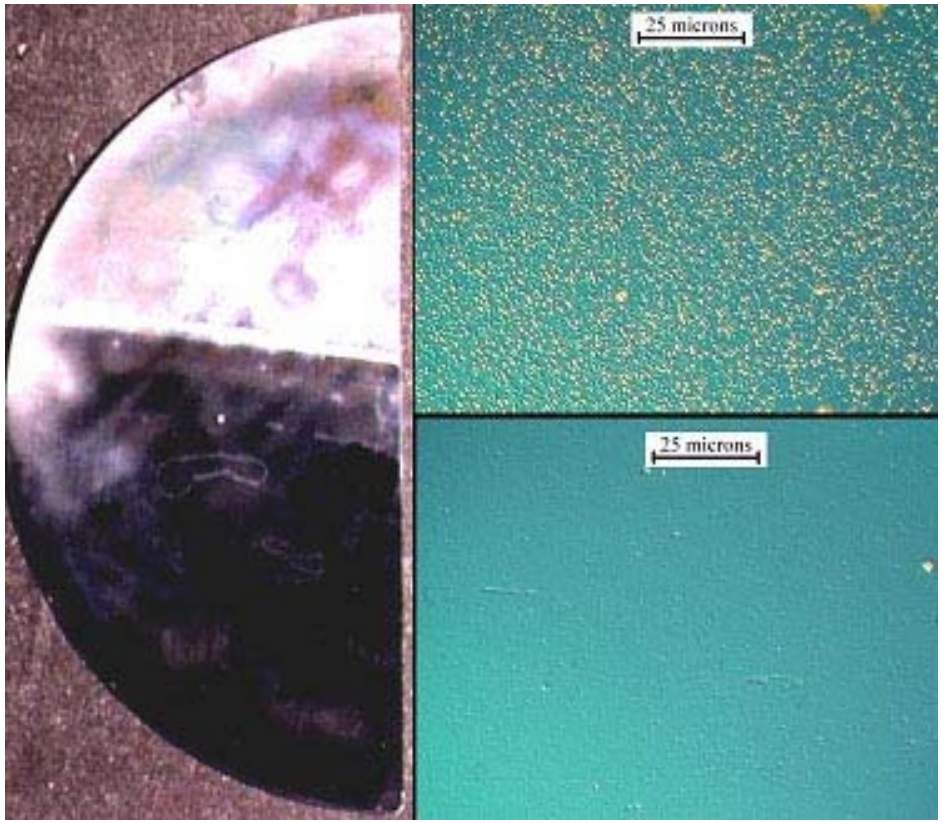
Outline

- **Motivation**
  - **Precipitation in Silicon**
  - **Why Do We Care?**
  - **TCAD: Technology Computer-Aided Design**
- The Problem
- Modeling of Precipitation
- Reduced Kinetic Precipitation Model
- RKPM Example: Dislocations
- Oxygen Precipitation

Precipitation in Silicon

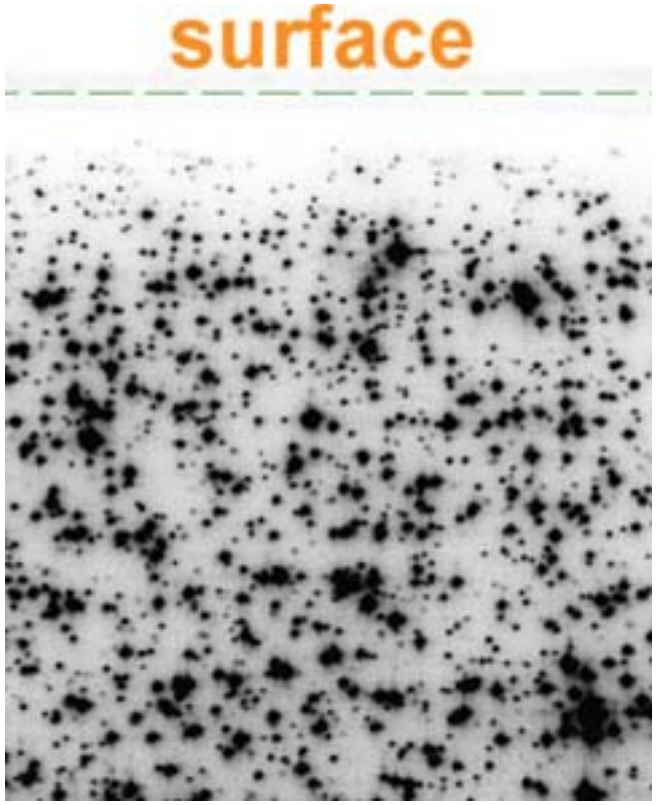
At sufficiently high concentrations, impurity atoms want to "stick" together to lower their energy, forming their own phase.

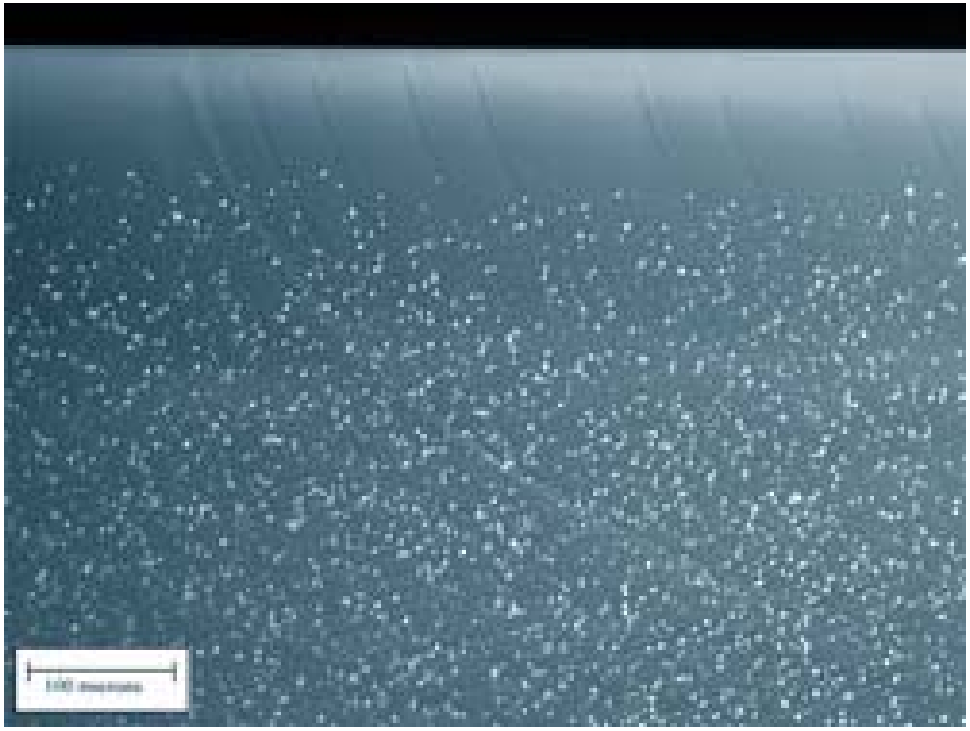


Copper precipitates on the surface of a silicon wafer.

Precipitation in Silicon

Oxygen is present in CZ-grown silicon, which is widely used in the VLSI and PV industries.

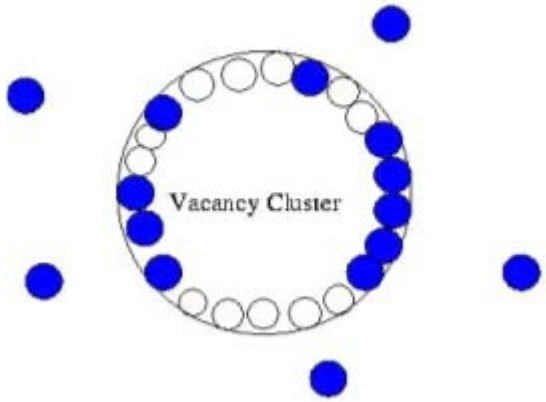


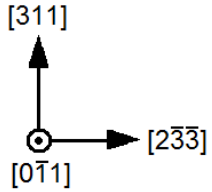


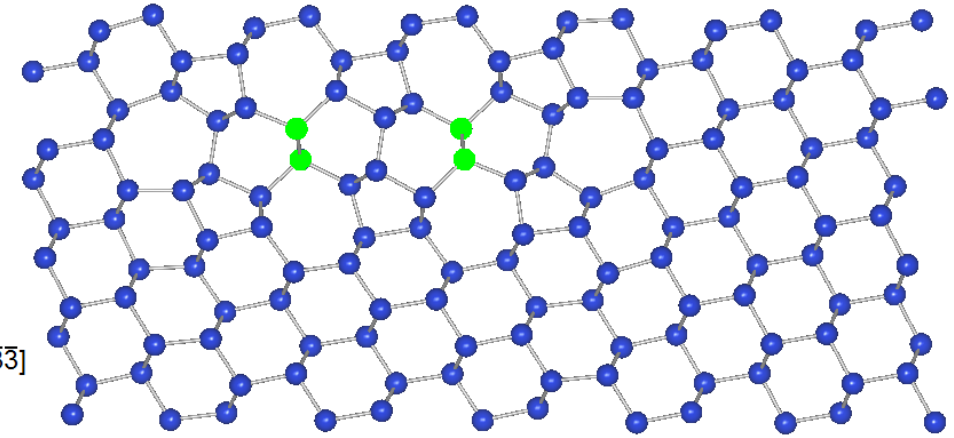
Cross-sectional images of oxygen precipitates in wafers.

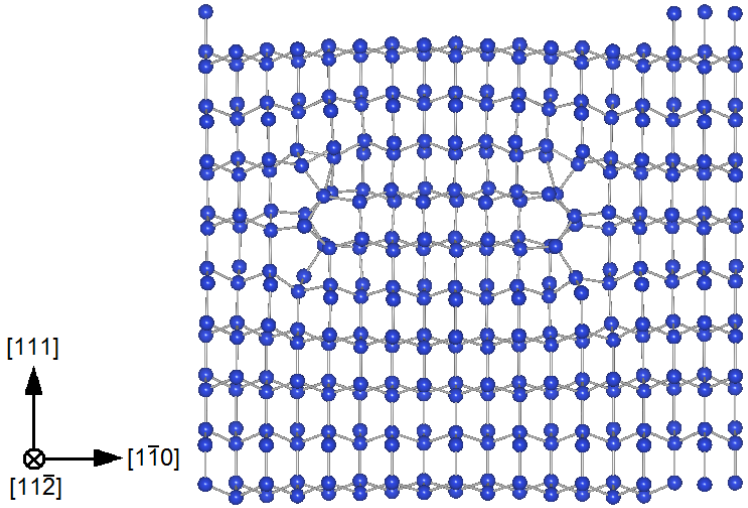
Precipitation in Silicon

Extended defects are precipitates, too.









Above: *{311} defect chains (green).*
Left: *Faulted edge dislocation.*

Why Do We Care?

- Metals
  - Shallow donors (esp. Cu)
  - Recombination active
  - Fast diffusing, may segregate to active areas of device
- Oxygen
  - Improves stiffness
    - Wafers less susceptible to slip and warp during high-T processing
  - Oxygen interstitials form thermal (shallow) donor defects
  - BO_2 clusters
    - Highly recombination-active, big concern in PVs
  - Dislocation nucleation
- Extended defects
  - Act as sinks for silicon interstitials, impurities, dopants

The Problem

- Nucleation/growth models require a solution for each possible precipitate size. Dozens or hundreds of equations!

$$\frac{df_1}{dt} = -2I_1 - \sum_{i=2}^{\infty} I_n$$

$$\frac{df_n}{dt} = I_{n-1} - I_n$$

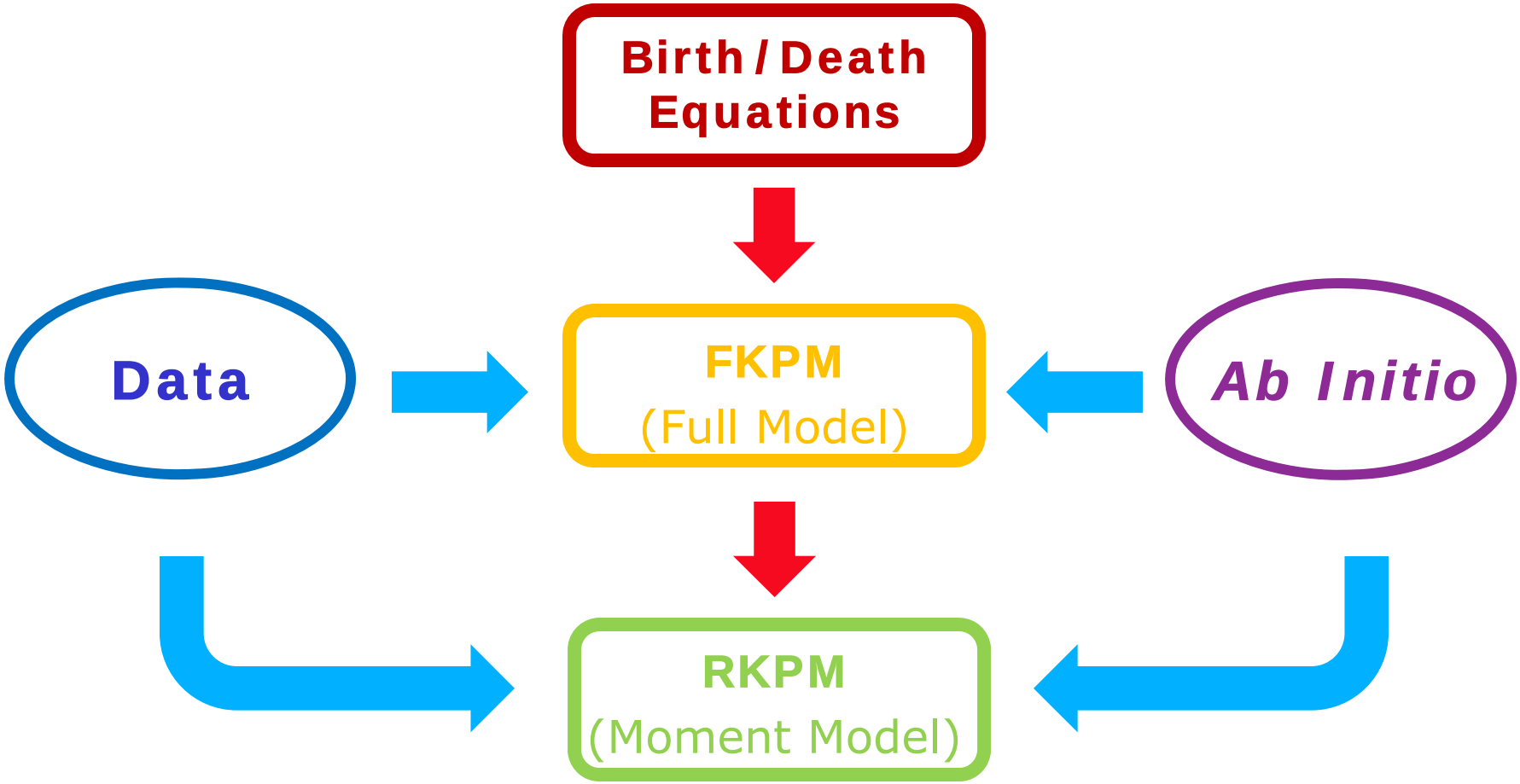
• • •

- Device geometries (esp. 2D and 3D) can have hundreds of sample points. **Computationally intractable.**

- **No stress dependence.**

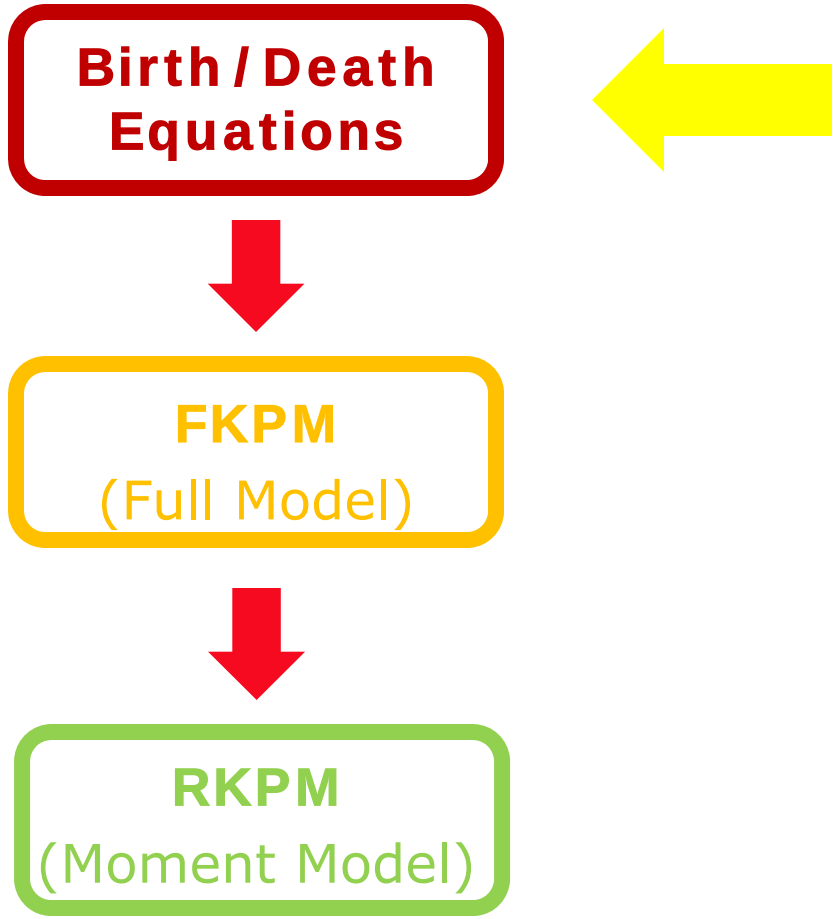
The Solution

Development of a moment-based (RKPM) model.



Modeling Flowchart

Development of a moment-based (RKPM) model.



Precipitate Energetics

- Precipitate free energy
  - C: Solute concentration (e.g.. interstitial oxygen atoms)
  - C_{ss}: Solid solubility (want to precipitate when solute concentration exceeds this)
  - $G_{exc}(n)$: Excess (surface) energy.

$$G_n = -n \cdot kT \ln \frac{C}{C_{SS}} + G_{exc}(n)$$

Growth Kinetics

- Nucleation and growth reactions

$$X + X \Leftrightarrow f_2$$

$$X + f_{n-1} \Leftrightarrow f_n$$

- Solute concentration at equilibrium with precipitate of size *n*

$$C_n^* = C_{SS} \exp\left\{\frac{-\left(G_n - G_{n-1}\right)}{kT}\right\}$$

Full Kinetic Precipitation Model

Birth/death equation for each possible precipitate size:

$$\frac{\partial f_2}{\partial t} = g_1 \cdot C - d_2 f_2 - \left(g_2 f_2 - d_3 f_3\right)$$

$$\frac{\partial f_3}{\partial t} = g_2 f_2 - d_3 f_3 - \left(g_3 f_3 - d_4 f_4\right)$$

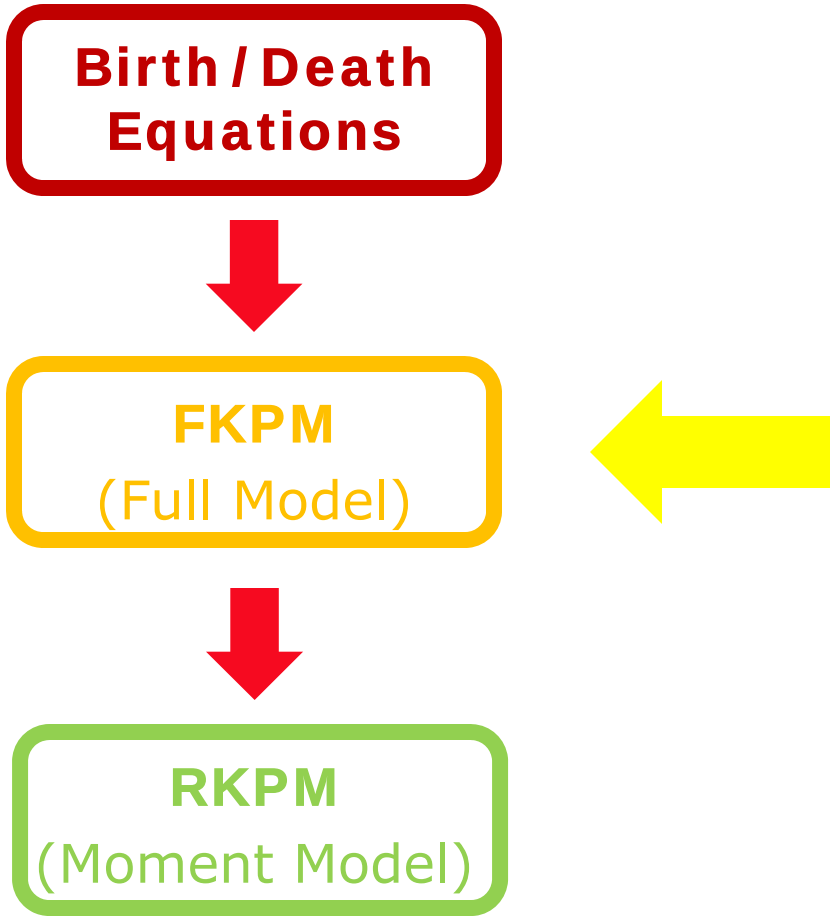
...

Problem: **Too many equations!**

Solution: **Discretization.**

Modeling Flowchart

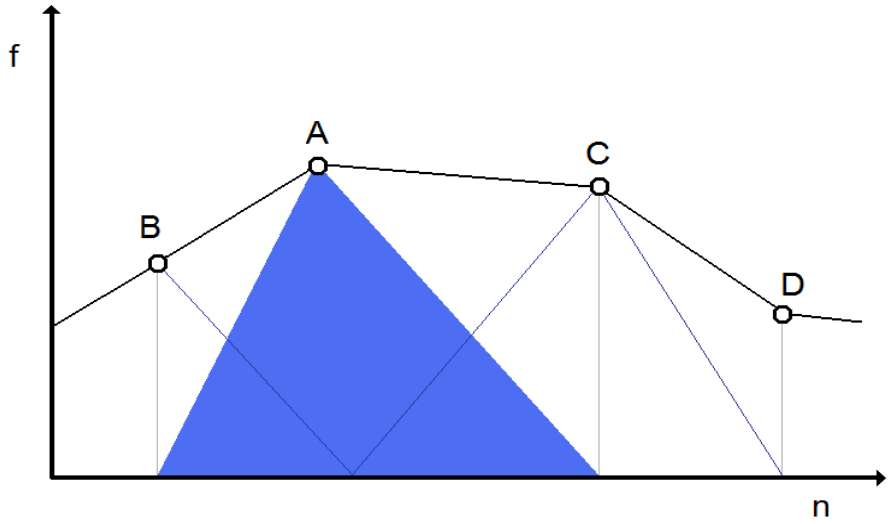
Development of a moment-based (RKPM) model.

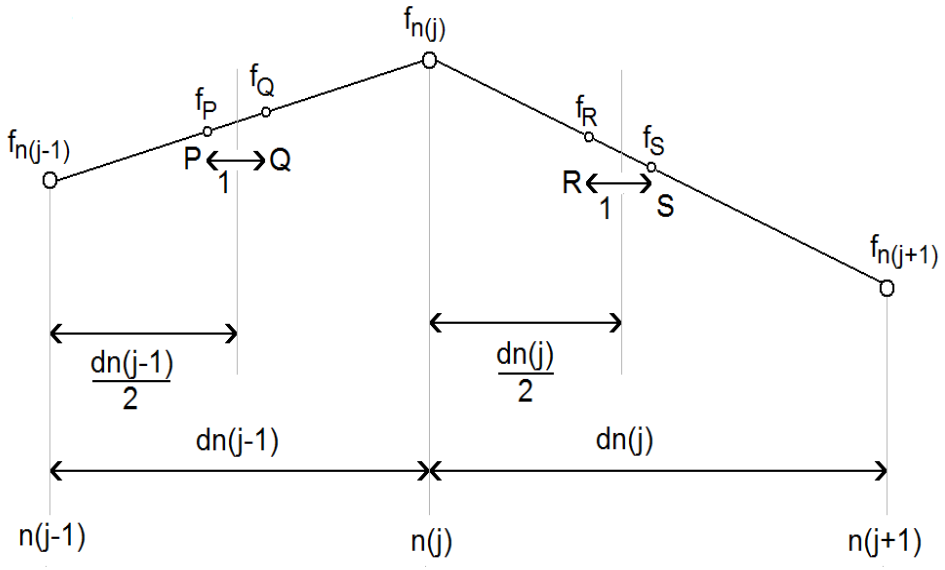


Discretization

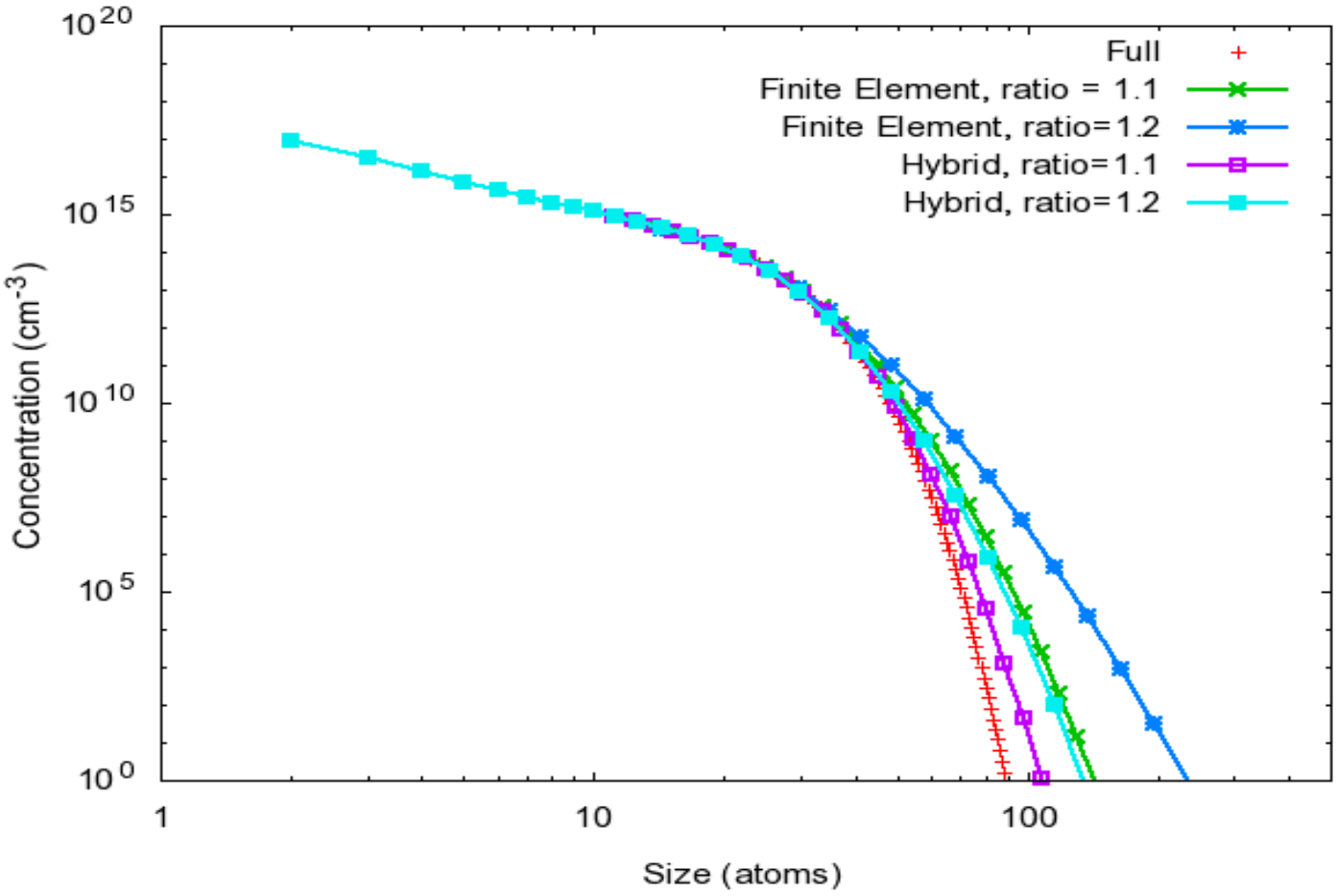
Sample in size space. Compute samples w/ interpolation:

- Linear
- Exponential
- Finite element (linear)
- Hybrid (FEM, exponential)





Discretization



Comparison of different discretization methods.

Outline

- Motivation
- The Problem
- Modeling of Precipitation
- **Reduced Kinetic Precipitation Model**
  - **A More Efficient Approach**
  - **Closure Assumptions**
- RKPM Example: Dislocations
- Oxygen Precipitation
- Proposed Research

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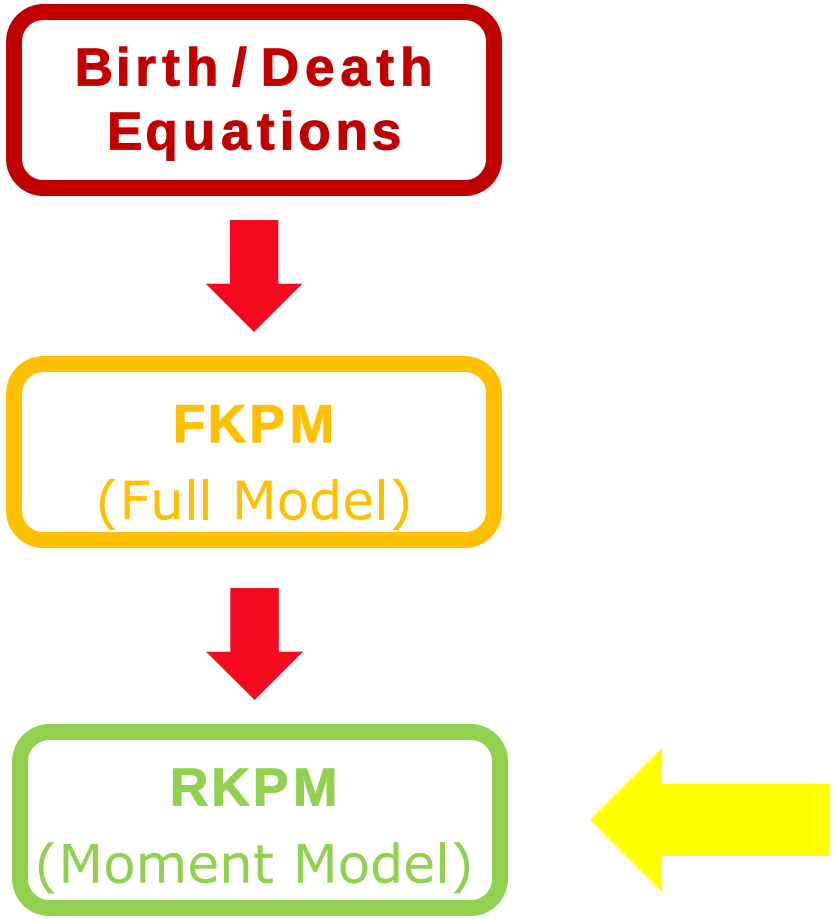
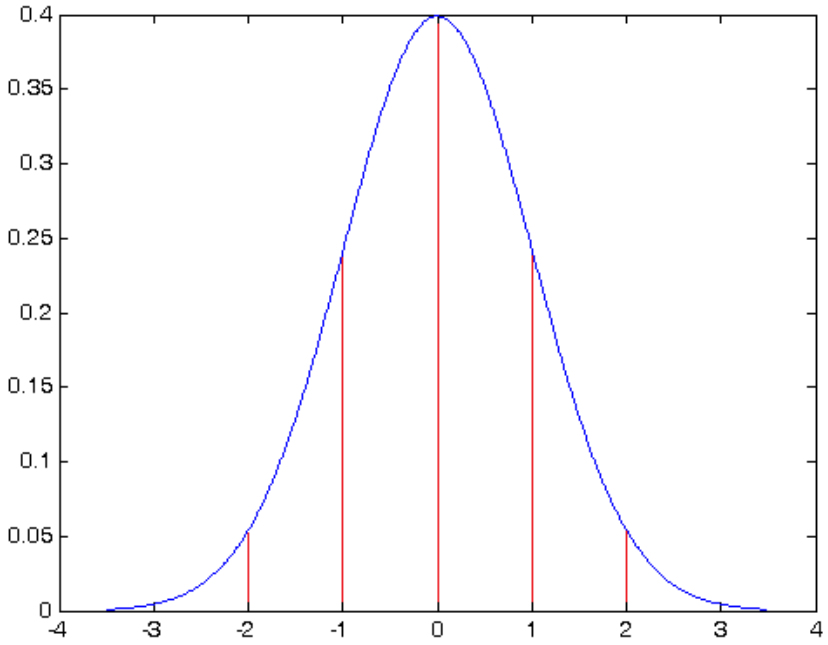
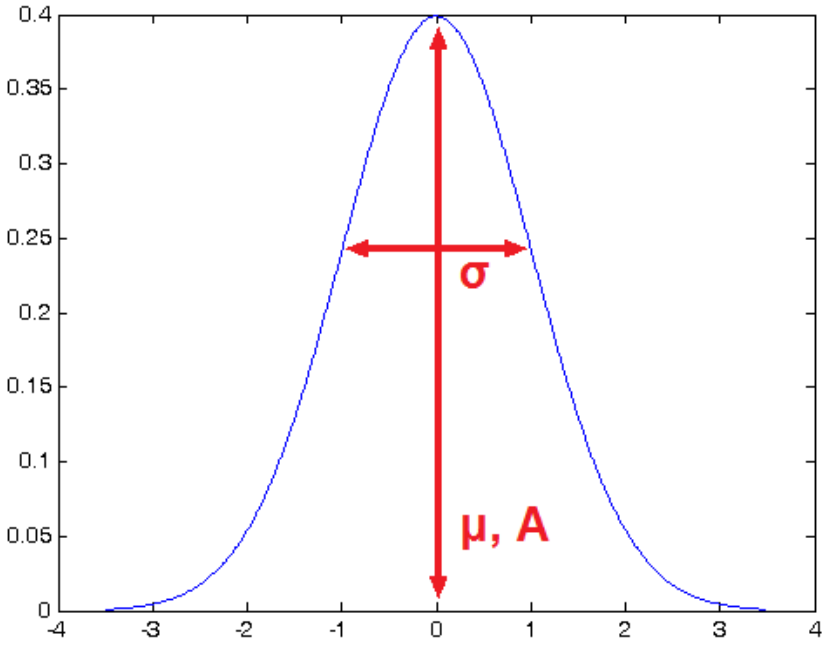


A More Efficient Approach



We *could* track every possible defect size independently (conceptually easy)…



… but why not be more clever about it and track only the bare minimum of information needed to describe a distribution?

Growth Rate

- Growth rate [3]

$$I_{n-1} = D_I \lambda_{n-1} \left(C_I f_{n-1} - C_n^* f_n \right)$$

  - D_I: Diffusivity of interstitials
  - C_I: Interstitial concentration
  - λ_n: A kinetic growth factor
  - C_n^*: Local equilibrium constant associated with size-n defects for interstitials

$$C_n^* = C_{SS} \exp\left\{ - \frac{\left(\Delta G_n^{exc} - \Delta G_{n-1}^{exc} \right)}{k_B T} \right\}$$

- Change in free energy upon defect formation

$$\Delta G_n = -n \cdot k_B T \ln \frac{C_I}{C_{SS}} + \Delta G_n^{exc}$$

  - C_{SS}: Solid solubility
  - ΔG_n^{exc}: Excess formation energy (perimeter)

RKPM

- Continuity equations rewritten in terms of moments

$$\frac{dm_i}{dt} = k^i I_{k-1} + \sum_{n=k}^{\infty} \left[(n+1)^i - n^i \right] I_n = k^i I_{k-1} + D_I m_0 \left(C_I \gamma_i^+ - C_{SS} \gamma_i^- \right)$$

$$\gamma_i^+ = \sum_{n=k}^{\infty} \left[(n+1)^i - n^i \right] \cdot \lambda_n \hat{f}_n$$

$$\gamma_i^- = \sum_{n=k}^{\infty} \left[n^i - (n+1)^i \right] \cdot \lambda_n \frac{C_{n+1}^*}{C_{SS}} \hat{f}_{n+1}$$

  - Note: Using the definition of moments, these infinite summations can be written in terms of the moments, which is what the model actually computes

$$\hat{f}_n = \frac{f_n}{m_0}$$

A More Efficient Approach

Moments

- m_0: Number of precipitates
- m_1: Number of atoms inside precipitates
- m_2: Breadth of distribution
- m_n: Related to shape

$$m_i = \sum_{n=k=2} n^i \cdot f(n)$$

$$\frac{\partial C}{\partial t} = \nabla \bullet \left(D \nabla C\right) - 2I_1 - Dm_0\left(C\gamma_1^+ - \gamma_1^-\right)$$

$$\frac{\partial m_0}{\partial t} = I_1$$

$$\frac{\partial m_1}{\partial t} = 2I_1 + Dm_0\left(C\gamma_1^+ - \gamma_1^-\right)$$

$$\frac{\partial m_2}{\partial t} = 4I_1 + Dm_0\left(C\gamma_2^+ - \gamma_2^-\right)$$

Closure Assumptions

Finite set of moments insufficient to describe a complete distribution. Need a closure assumption to allow γ terms to be written in terms of moments.

- Delta Function Approximation
  - Assumes all precipitates are of average size (m_1/m_0)
  - Still need to estimate distribution for nucleation of smallest precipitate
- Free energy-minimizing distribution
  - Results in a non-linear system of equations that must be solved.
    - Can be pre-computed and interpolated during the simulation; need m_2.
- Other distributions
  - Log-normal observed for dislocation loops.
    - Can be pre-computed. Need m_2 (or model for $m_2(m_1/m_0)$).

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- Motivation
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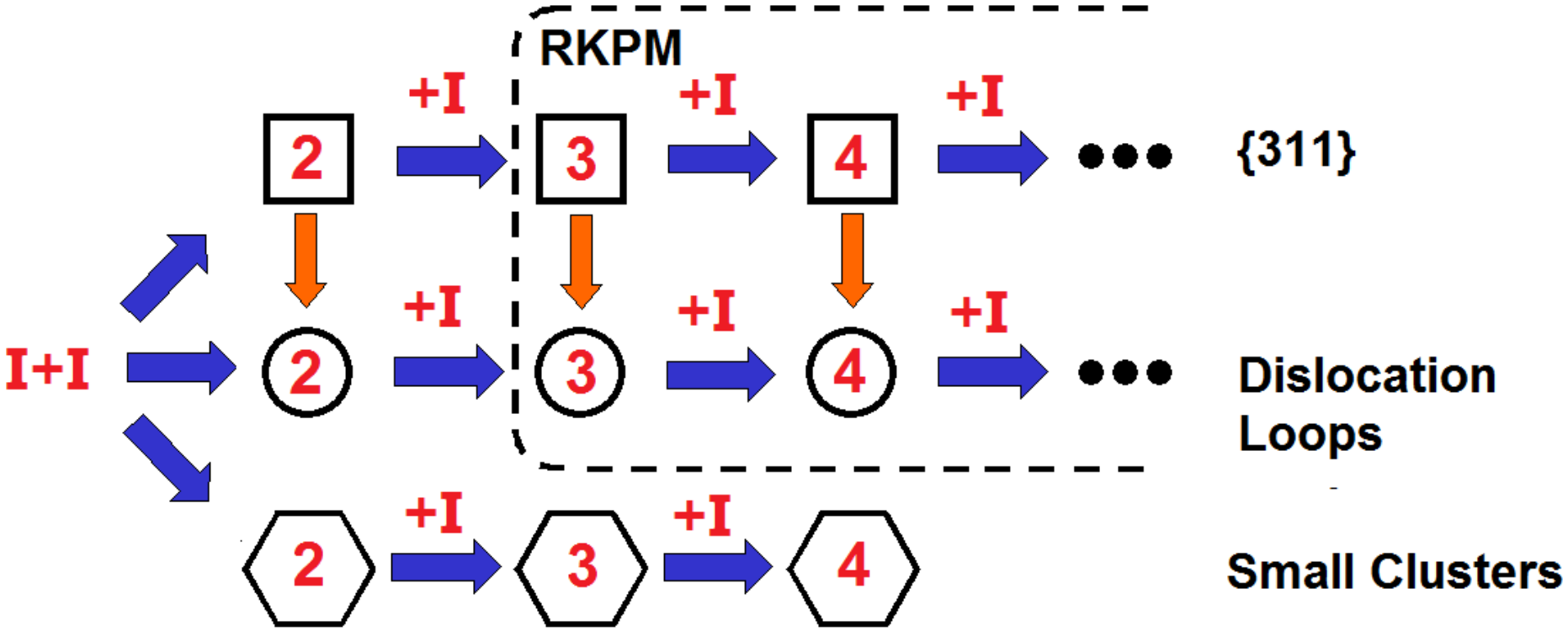
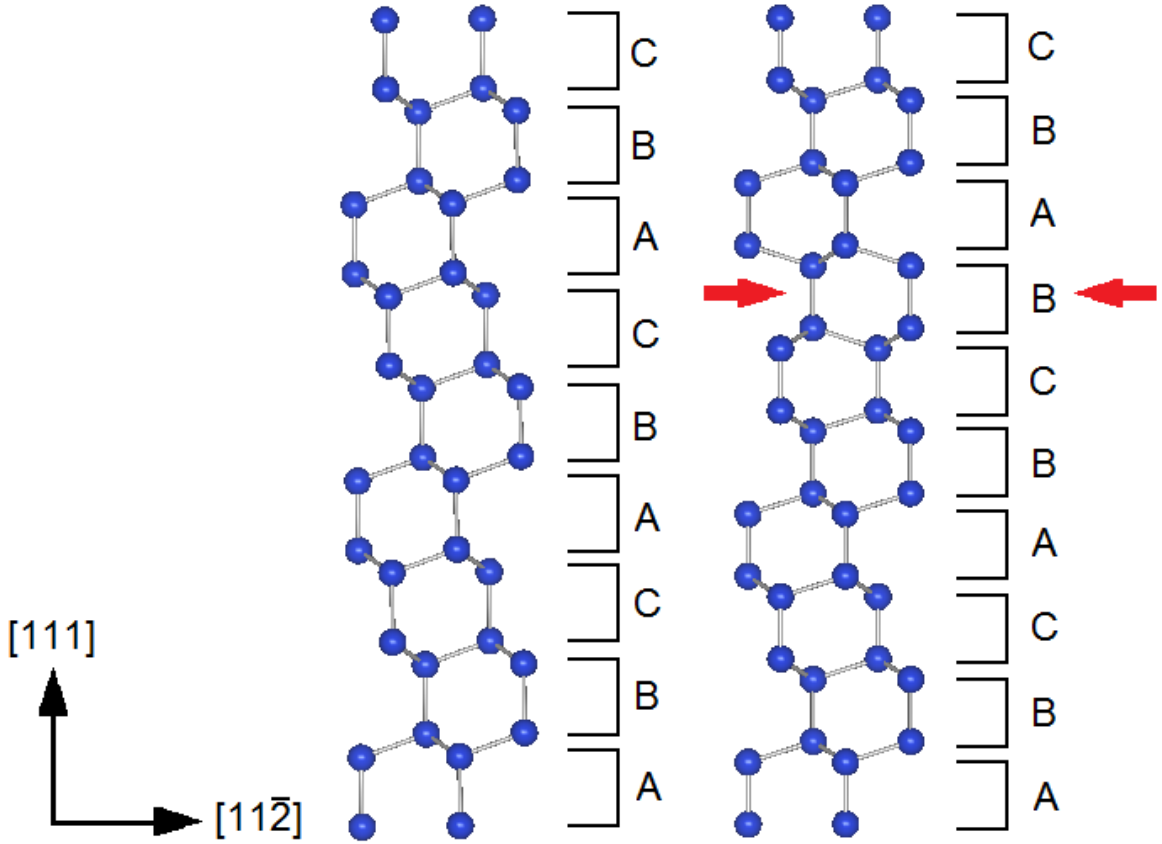
- Modeling of Precipitation
- Reduced Kinetic Precipitation Model
- **RKPM Example: Dislocations**
  - **Big Picture Overview**
  - ***Ab Initio* Calculations**
  - **Stress Effects**
  - **Loop Energy**
  - **Results**
- Oxygen Precipitation
- Proposed Research

Big Picture Overview



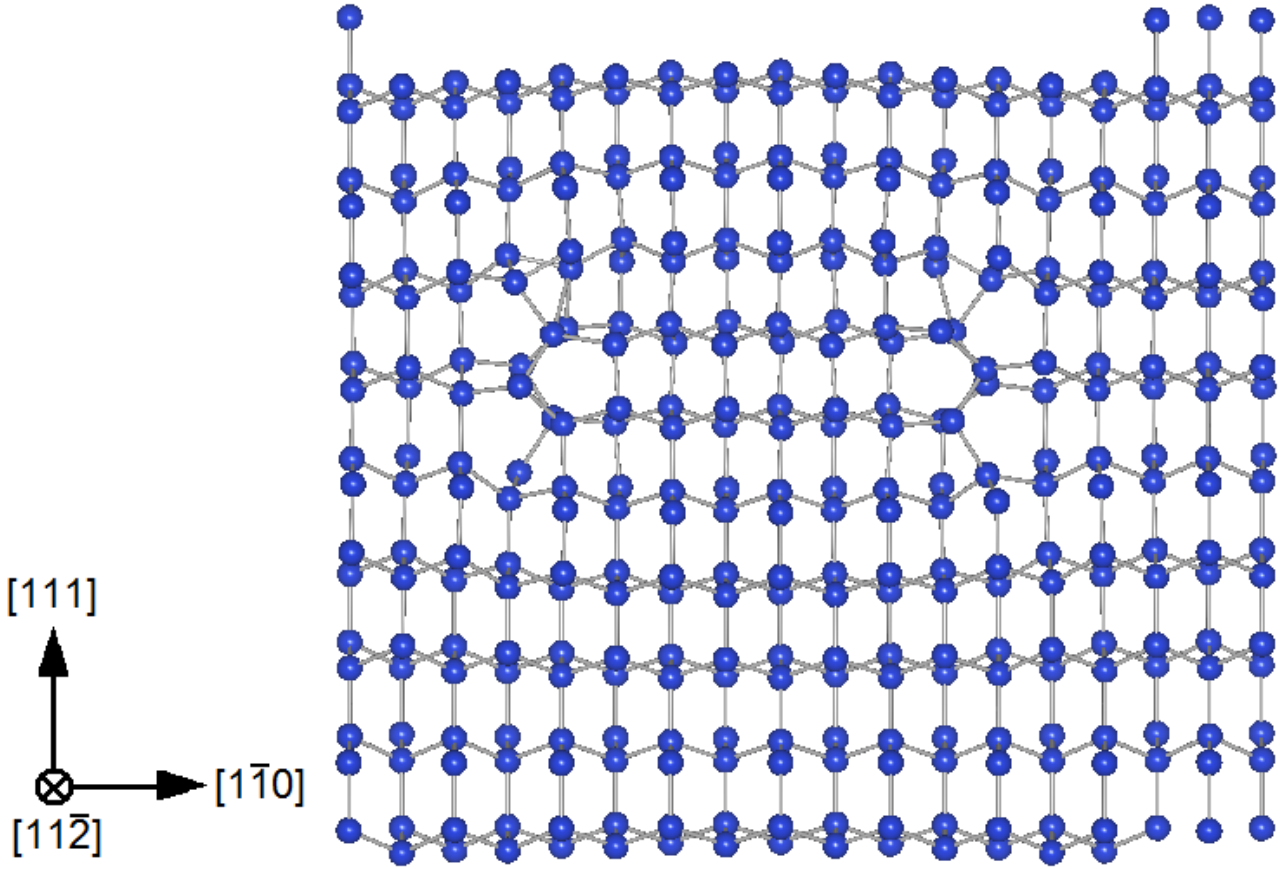
Note: Vacancy interactions omitted for clarity.

Ab Initio Calculation of Stacking Fault



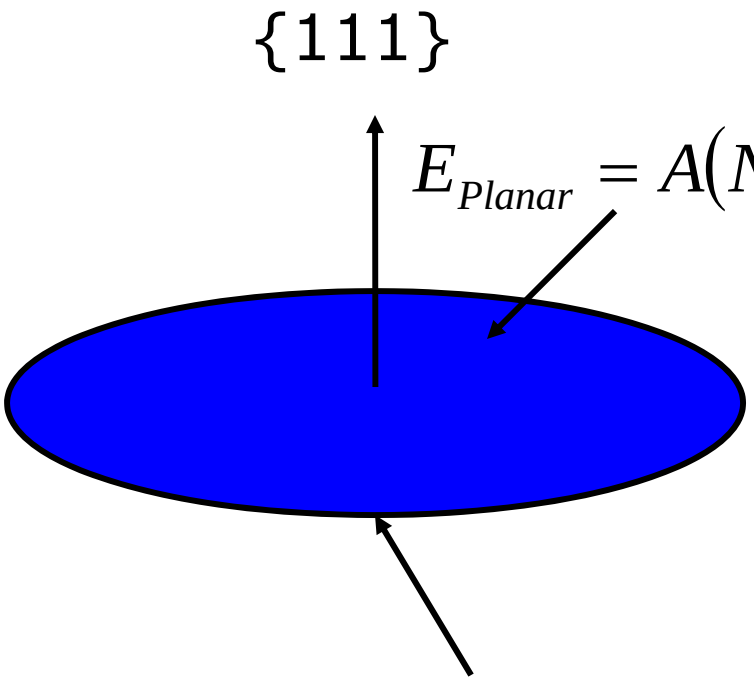
An extrinsic stacking fault. E_f = 0.01525 eV/atom

Dislocation Dipole



Dislocation dipole system.

Loop Energy



Total formation energy of loop:

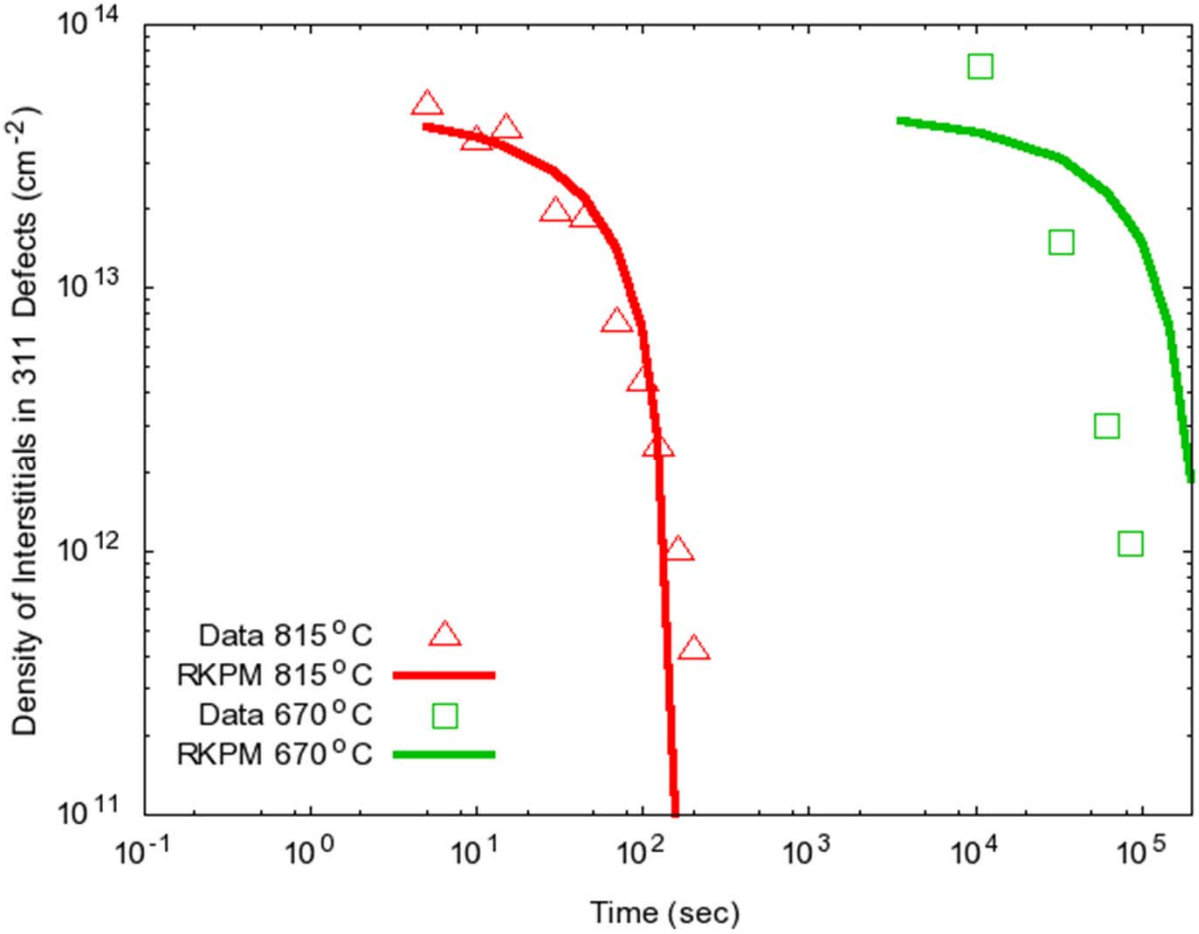
$$E_f = E_{Perimeter} + E_{Planar} + E_S$$

E_s = Elastic self-energy

Change with applied strain:

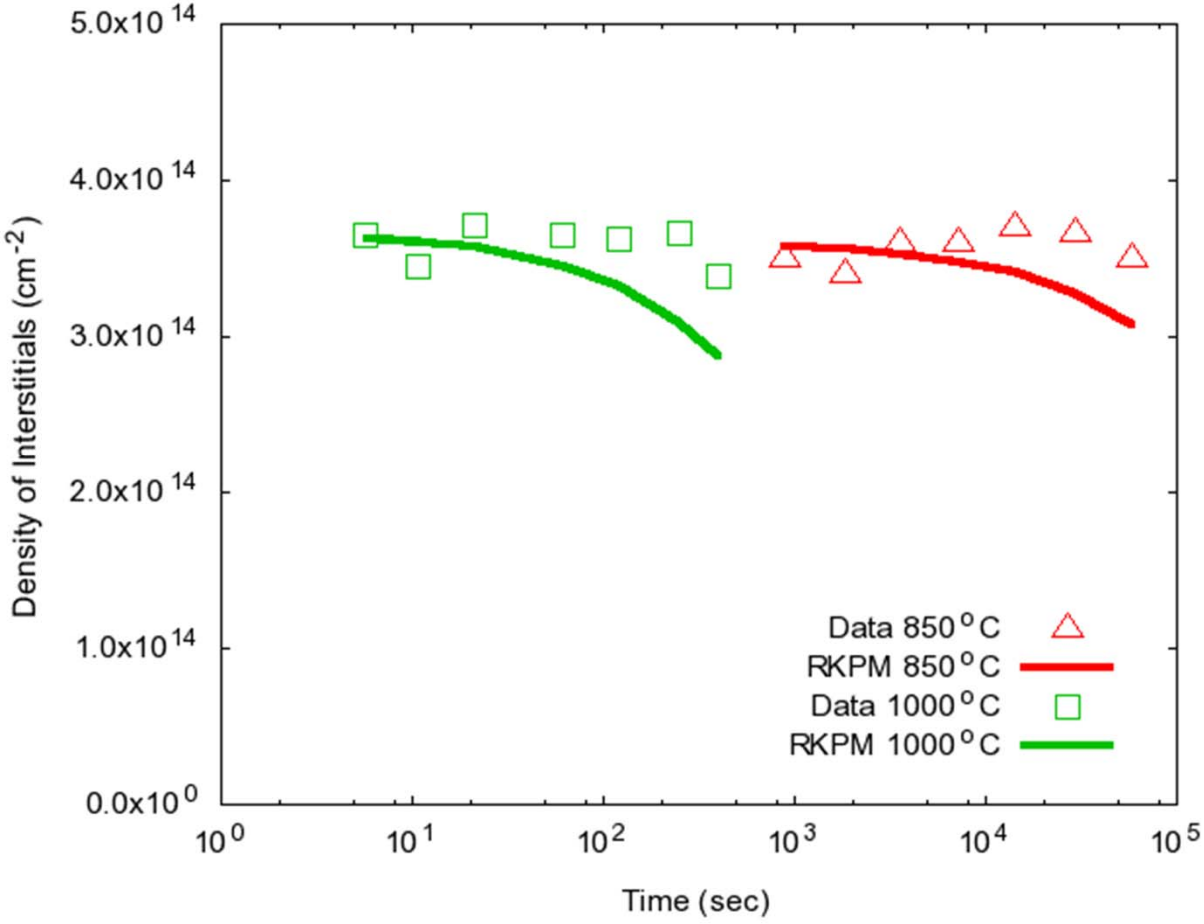
$$\Delta E_f = -\frac{V}{2}\sum_{i=1}^{3}\sum_{j=1}^{3}\Delta\varepsilon_{ij}\sigma_{ij}$$

Results



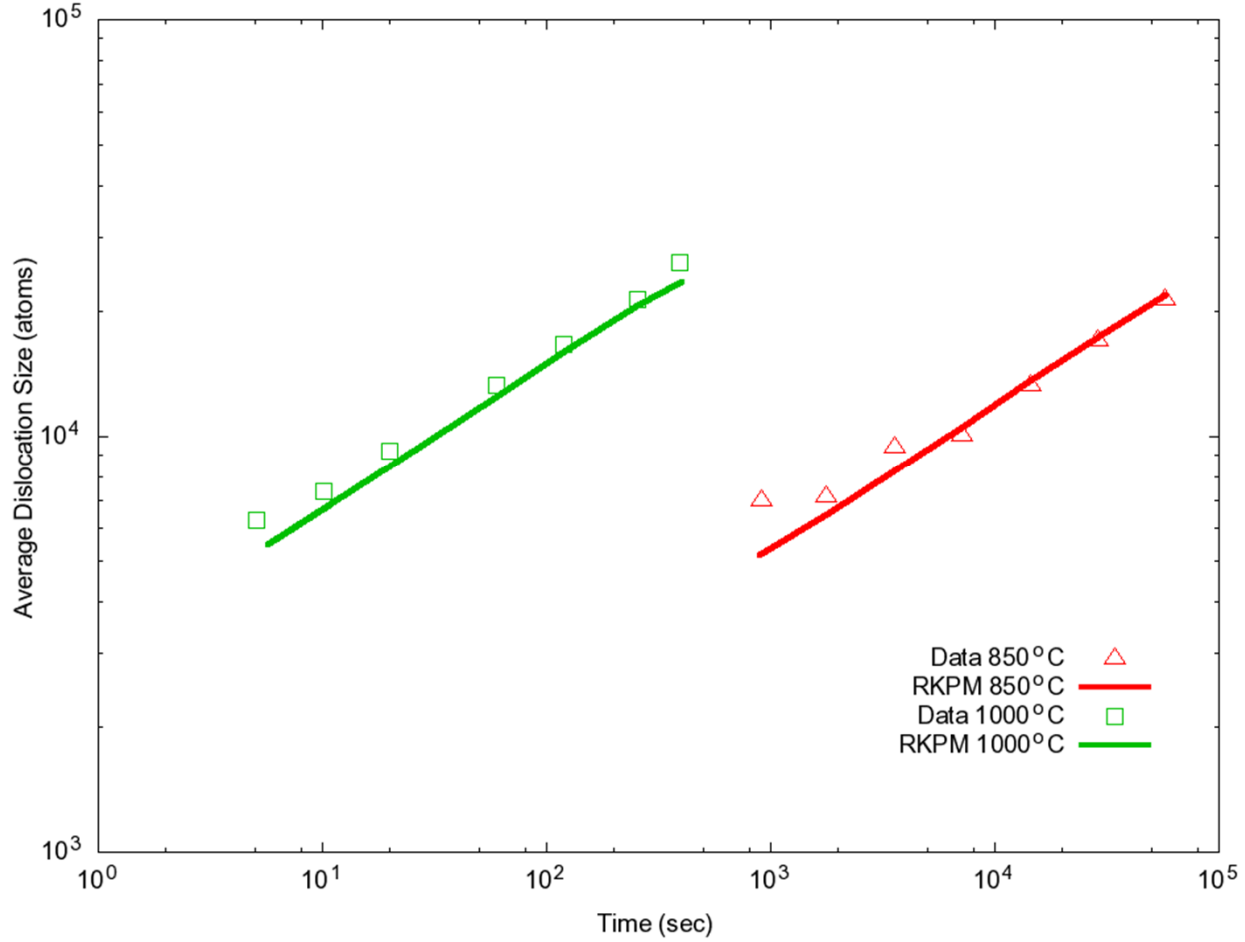
Density of interstitials bound to {311} defects compared to data (Eaglesham *et al*).

Results



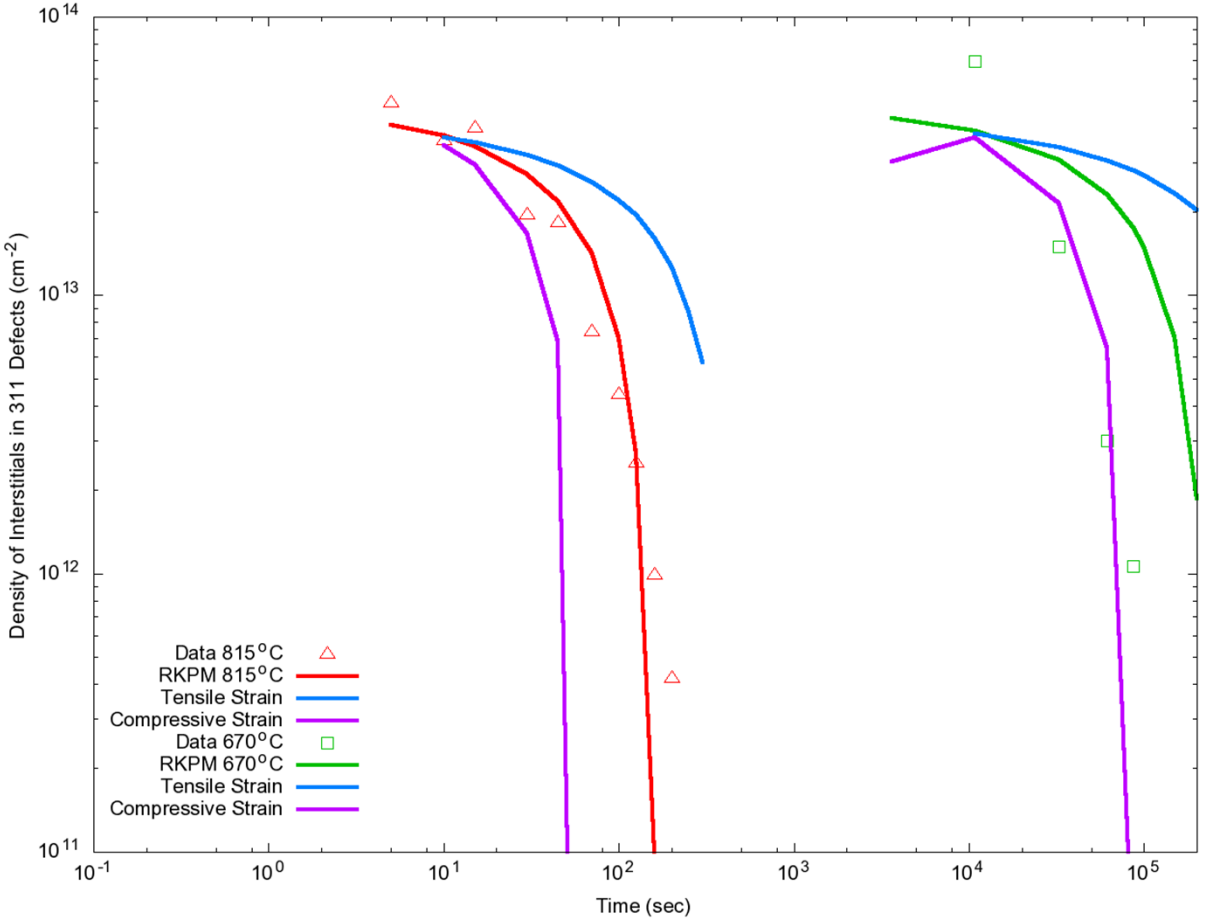
Density of interstitials bound to dislocation loops compared to data (Pan *et al*).

Results



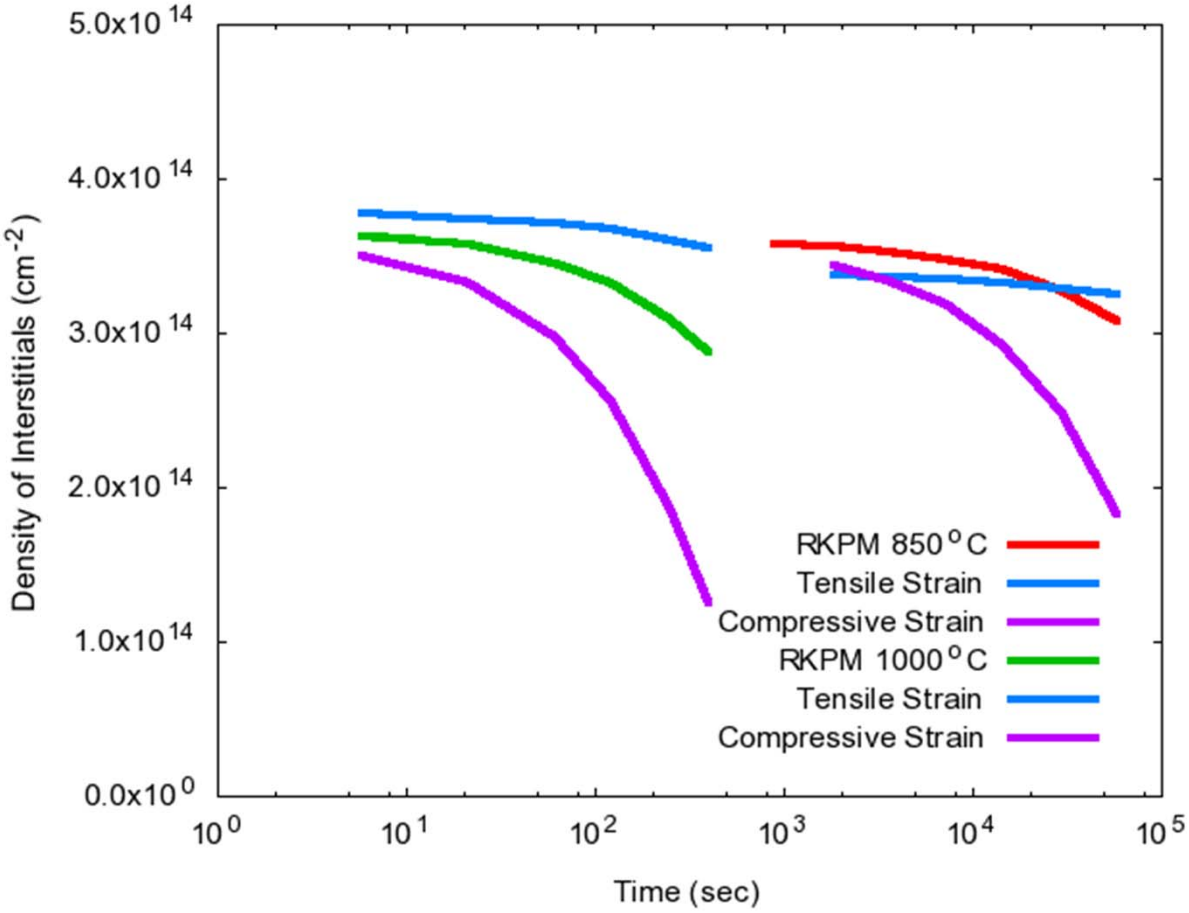
Growth in average dislocation size over time compared to data (Pan *et al*).

Results



Impact of 1.5% biaxial strain on {311} defects.

Results



Impact of 1.5% biaxial strain on dislocation loops.

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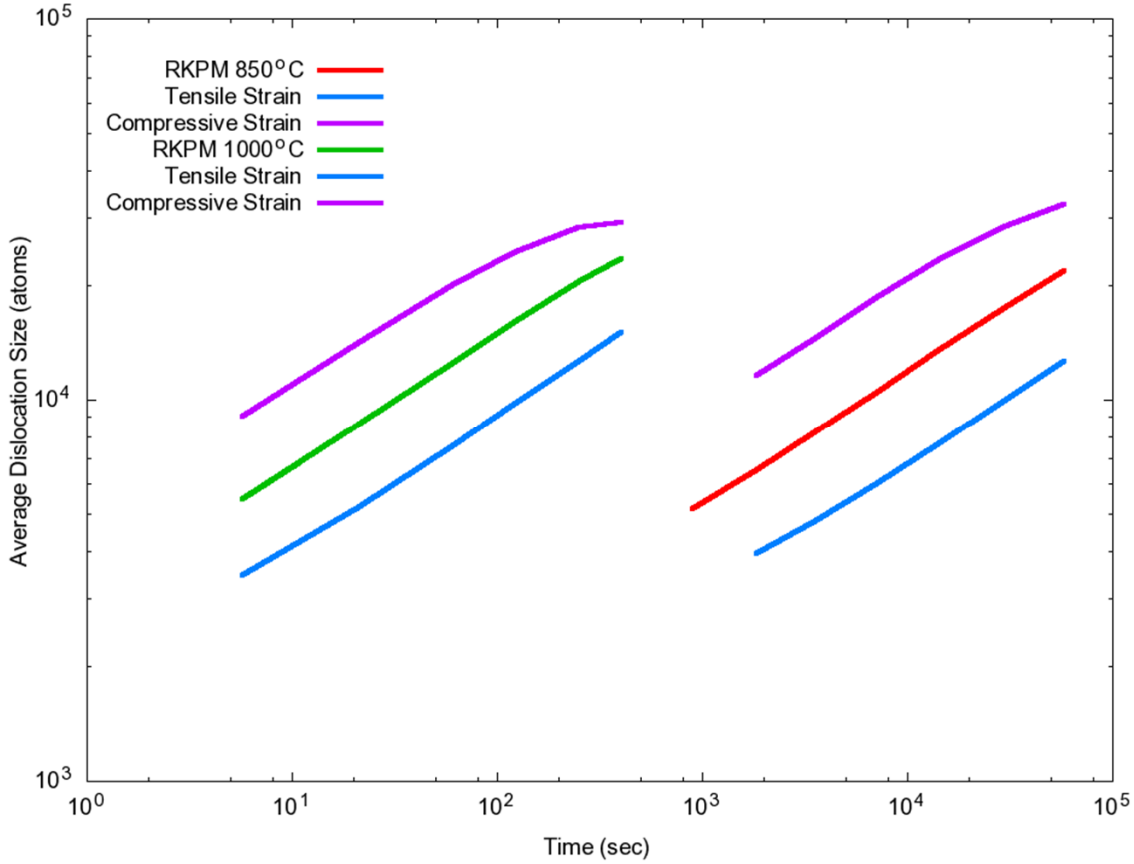

Impact of 1.5% biaxial strain on loop growth rates.

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- **Oxygen Precipitation**
  - **Oxygen Growth / Dissolution Model**
  - **Oxygen / Silicon Interface**
  - **Oxygen Data**
  - **Interaction w / Dislocation Loops**
- Proposed Research

Oxygen Growth/Dissolution Model

$$\left(\frac{1}{2}+\gamma_I\right)\mathrm{Si}+\mathrm{O}\Leftrightarrow\frac{1}{2}\mathrm{SiO}_2+\gamma_I\mathrm{I}+\mathrm{stress}$$

Energy

$$G_0=-nk_BT\ln\left(\frac{C_O}{C_O^*}\right)$$

$$G_{if}=4\pi r^2\alpha$$

$$G_s=\frac{4}{3}\pi r^3 6\mu_{Si}e_Ce_T$$

$$G_i=\gamma_I nk_BT\ln\left(\frac{C_I}{C_I^*}\right)$$

$$G_v=-\gamma_V nk_BT\ln\left(\frac{C_V}{C_V^*}\right)$$

Strain

$$e_T=e_C\left(1+\frac{4\mu_{Si}}{3K_{SiO2}}\right)$$

$$e_C=\frac{k_BT}{4\mu_{Si}V_{Si}}\ln\left(\frac{C_I}{C_I^*}\right)+\frac{\alpha}{4\mu_{Si}r_p}\left(1-\frac{3K_{SiO2}}{3K_{SiO2}+4\mu_{Si}}\right)$$

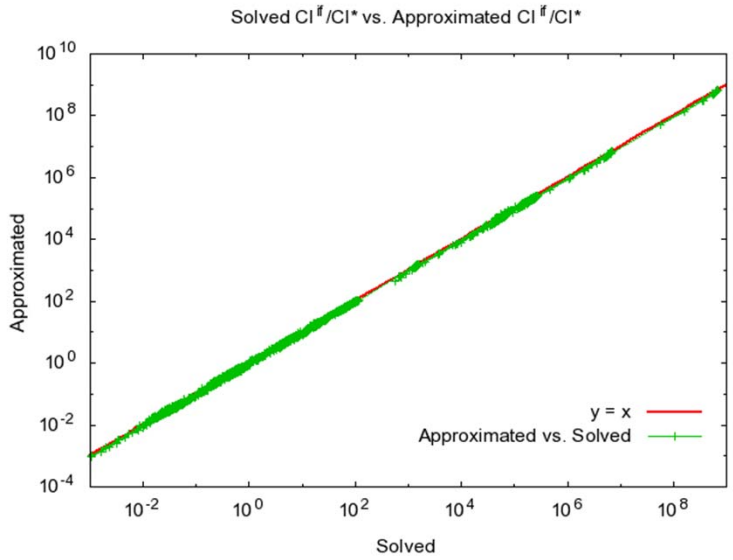
$$\gamma_I=\frac{1}{2}\left[\frac{V_{SiO2}}{V_{Si}}\left(1+e_T\right)^{-3}-1\right]$$

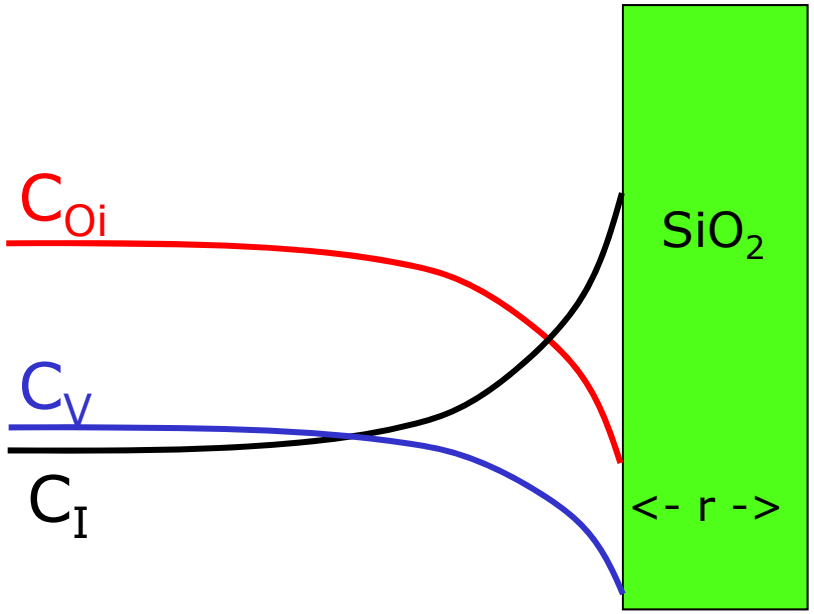
Oxygen/Silicon Interface

Interfacial Oxygen, Interstitial Silicon

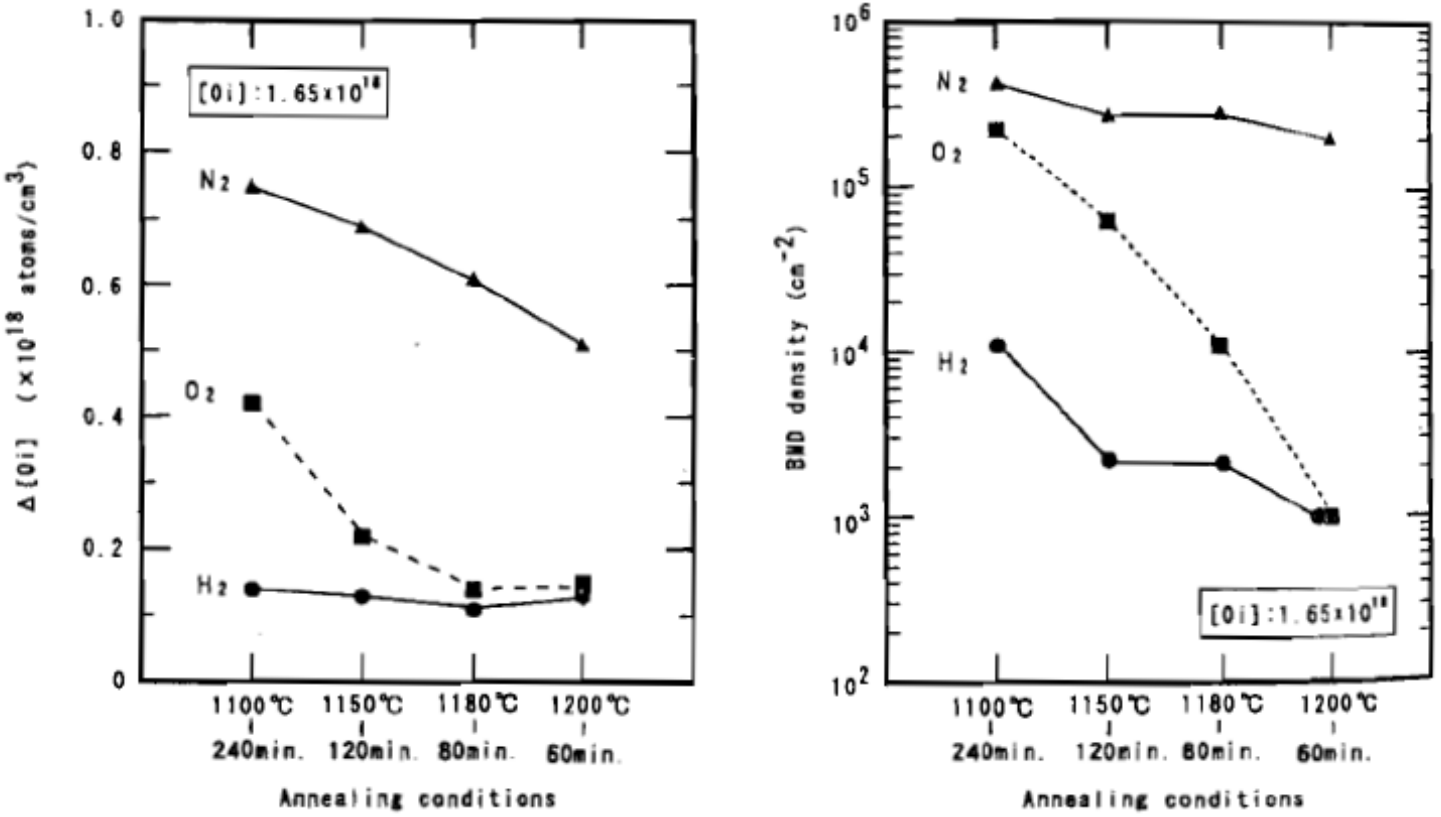
$$D_O \frac{C_O - C_O^{if}}{r} = k_r \left(C_O^{if} - C_O^* \right) = \frac{D_I}{\gamma_I} \frac{C_I^{if} - C_I}{r}$$

Result is a transcendental equation. Can approximate numerically.



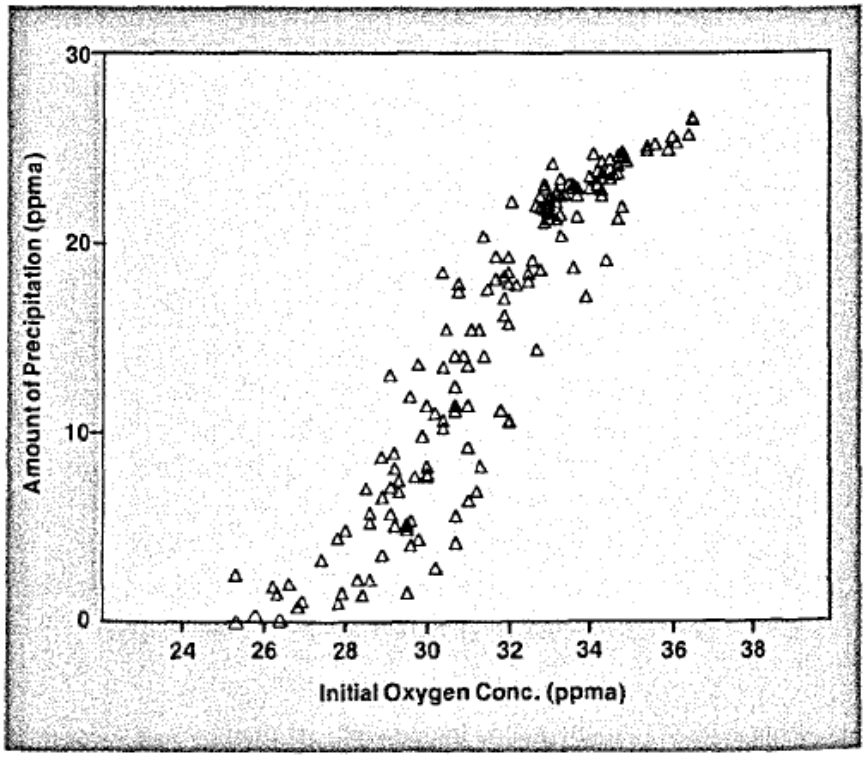


Oxygen Data

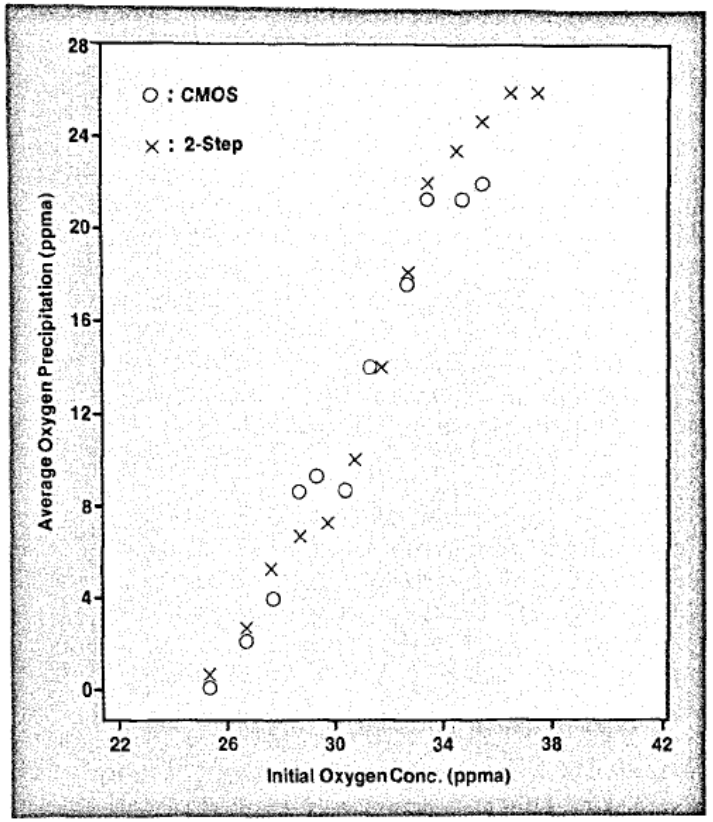


Abe, Suzuki and Koya, *J. Electrochem. Soc.* **144**, 306 (1997)

Oxygen Data



Series of 800°C/2h + 1050°C/16h

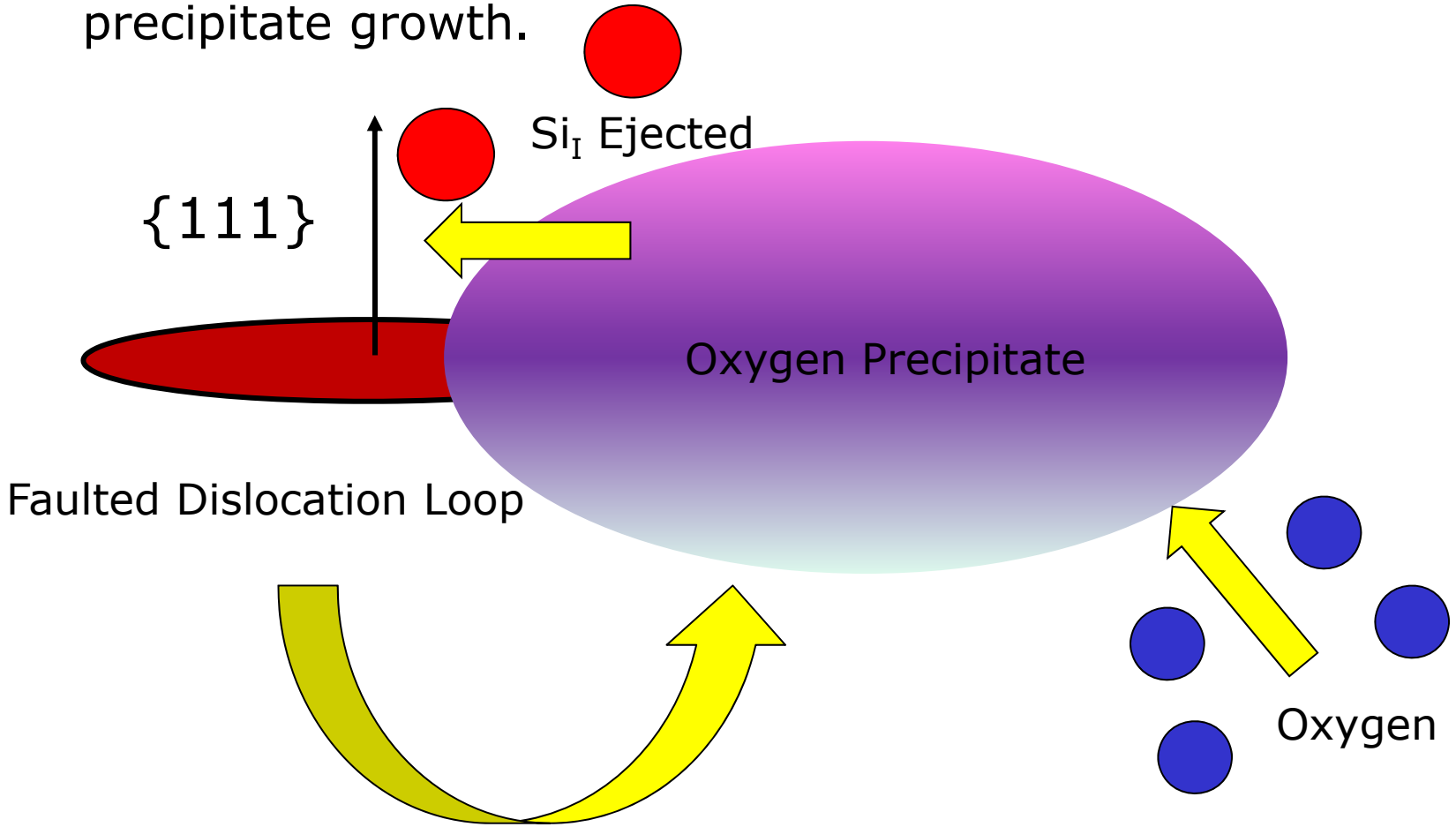


CMOS simulation and 800°C/2h + 1050°C/16h

H-D. Chiou, *Solid State Tech.* **30**, 77 (1987)

Interaction w/ Dislocation Loops

Faulted dislocation loops generated in regions of high stress and large Si interstitial concentrations. Accelerate precipitate growth.



Precipitate Energetics

Per-atom free energy of infinitely large precipitate:

$$G_\infty = G_P - kT \ln \frac{C}{C_{Si}}$$

Define *solid solubility* as concentration at which $G_\infty = 0$:

$$C_{SS} = C_{Si} \exp\left\{\frac{G_P}{kT}\right\}$$

Interpret C_{SS} as concentration above which precipitates form. For finite precipitates, a surface (excess) energy term is needed:

$$G_n = -n \cdot kT \ln \frac{C}{C_{SS}} + G_{exc}(n)$$

Precipitate Energetics

Formation and growth reactions:

$$X + X \Leftrightarrow f_2$$

$$X + f_{n-1} \Leftrightarrow f_n$$

In equilibrium:

$$f_n^* = K_n \cdot C \cdot f_{n-1}^*$$

Equilibrium concentration of precipitate depends on number of lattice sites it can sit on and energy:

$$f_n^* = C_{Si} \exp\left\{\frac{-G_n}{kT}\right\}$$

$$K_n = \frac{f_n^*}{C \cdot f_{n-1}^*} = \frac{1}{C} \exp\left\{\frac{-\left(G_n - G_{n-1}\right)}{kT}\right\}$$

Growth Kinetics

Birth death process of discrete precipitate sizes:

$$\frac{\partial n}{\partial t} = g_{n-1} - d_n$$

g_n: Growth rate, n -> n+1

d_n: Dissolution rate, n -> n-1

Flux in size-space from n to n+1 (ie. concentration of precipitates growing from size n to n+1):

$$R_n = g_n f_n - d_{n+1} f_{n+1}$$

Leading to equation for precipitates of size n:

$$\frac{\partial f_n}{\partial t} = R_{n-1} - R_n$$