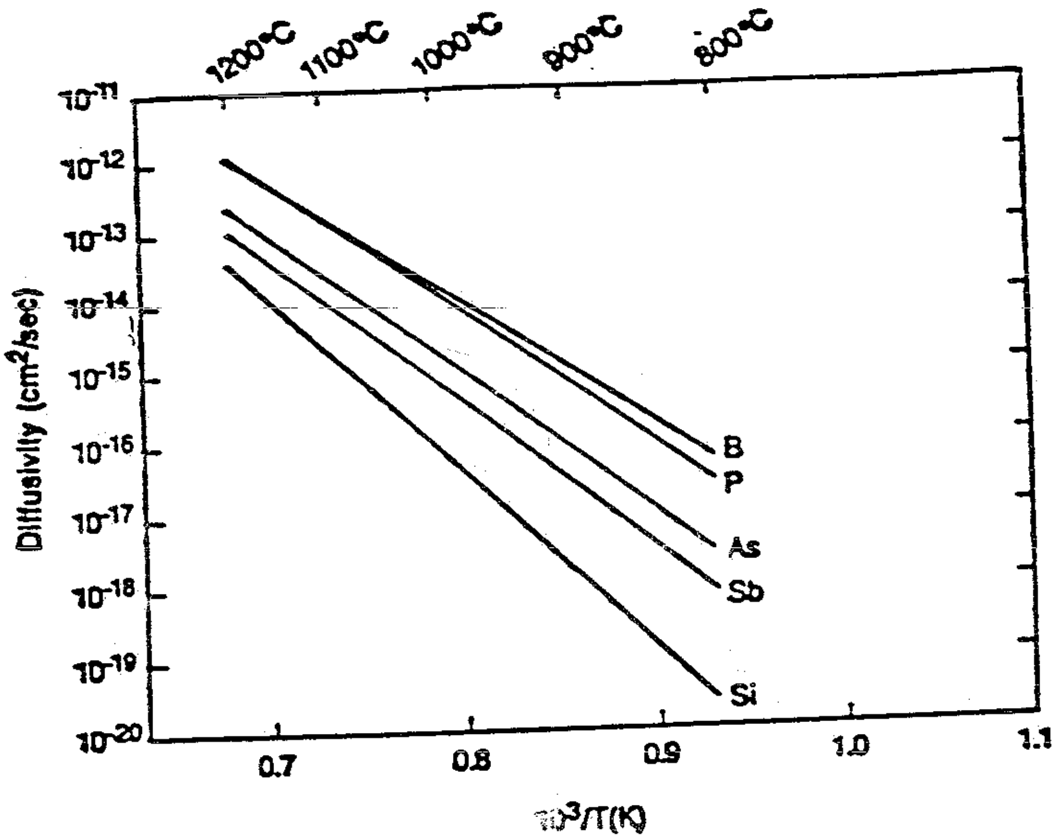
Pair Diffusion Models

- Dopant diffusivity is much larger than self-diffusion



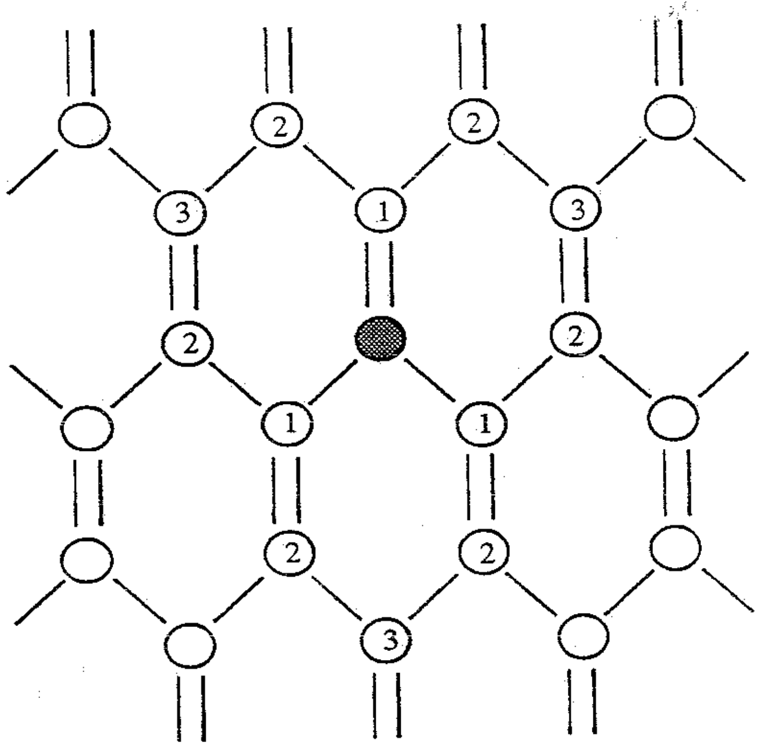
(Fahey *et al.*)

- Therefore:
  - Defects preferentially interact with dopants
  - Attractive potential between dopants and defects
  - Single defect participates in multiple dopant hops
- Modeled as diffusion of dopant/defect pair

$$D_D = D_{DX}\left(\frac{C_{DX}}{C_D}\right)$$

Vacancy Mediated Diffusion

- Pair diffusion is no problem for interstitials, but vacancy and dopant move in opposite directions
- Dopant/vacancy pair must dissociate to third-nearest neighbor distance for long-range migration.



- Third-nearest neighbor sites play critical role in dopant/vacancy pair diffusion.

Hopping Diffusion – Dopants

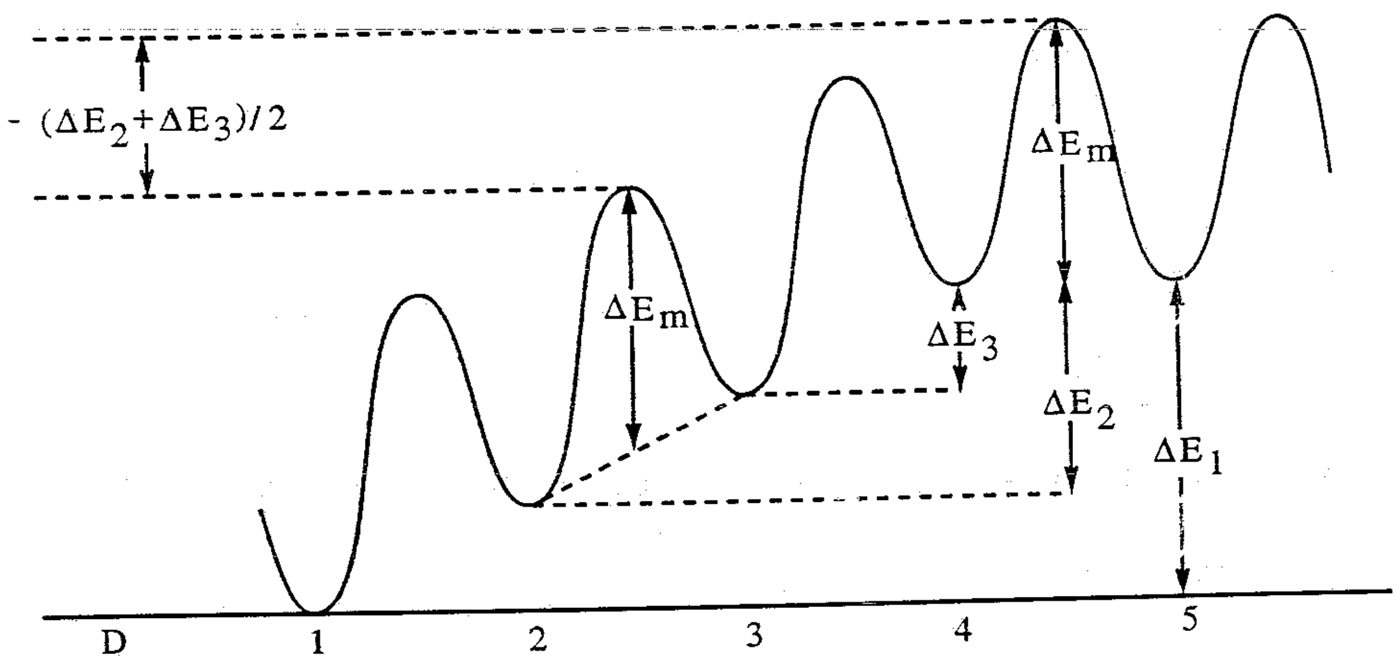
- Due to the pair binding energy, there are many vacancies adjacent to dopants and thus many dopants hops.
- However, dopant and vacancy primarily just keep exchanging places over and over.
  - No long range migration
- Third nearest neighbor sites serve as bridging configuration.
- Critical rate is third- to second-nearest neighbor transition:

$$\nu_{\text{eff}} = \frac{1}{2}\left[C_{DV}^{3\text{nn}}/C_D\right](\nu_{32}) \tag{2}$$

  - $C_{DV}^{3\text{nn}}$ is number of third-nearest neighbor pairs
  - ν_{32} is rate of hopping from third- to second-nearest neighbor position
  - Assumes all transitions to second-nearest neighbor sites result in exchanges with dopant, but half result in vacancy exiting by same path.

Atomistic Model

- Consider a dopant/defect interaction out to third-nearest neighbor.
- Assume change in energy with distance linear between sites.



- Substituting in Eq. (1) and (2):

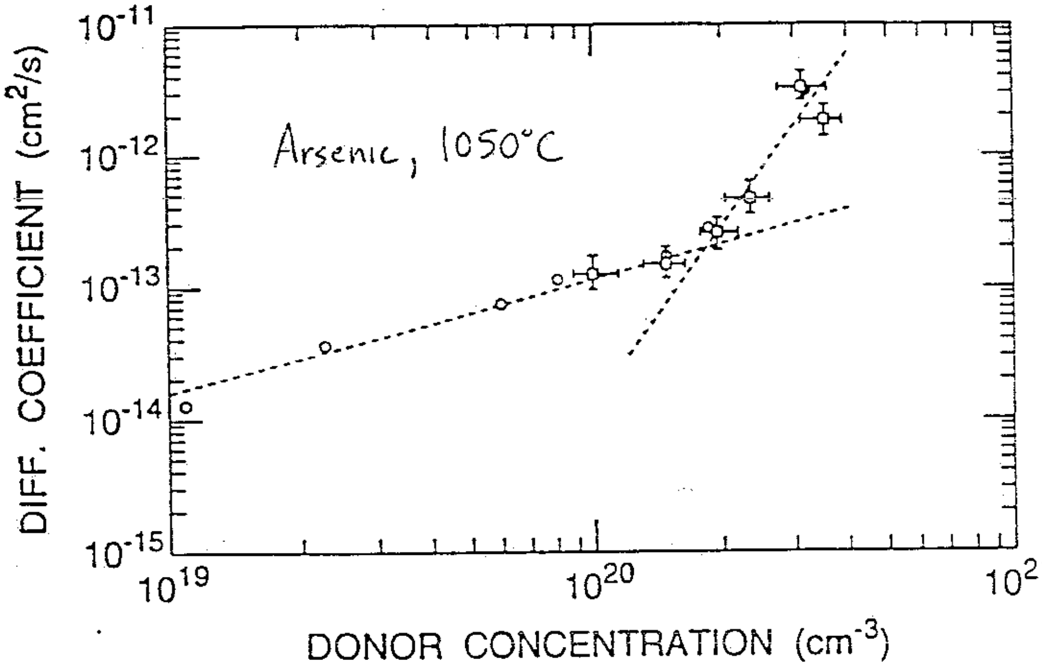
$$D = \frac{\alpha^2}{4}\left[12\left(\frac{C_V^0}{C_s}\right)\exp\left(\frac{\Delta E_3}{kT}\right)\right]\left[\nu_V^0 \exp\left(\frac{\Delta E_2 - \Delta E_3}{2kT}\right)\right]$$

$$= 3\alpha^2\left(\frac{C_V^0}{C_s}\right)\nu_V^0 \exp\left(\frac{\Delta E_2 + \Delta E_3}{2kT}\right) \qquad (3)$$

- Represents improvement on analysis by Hu.

Quantitative Coupled Diffusion Model for Phosphorus

- $D \propto (n/n_i)^4$ at donor concentrations above $2 \times 10^{20}\text{cm}^{-3}$ for As, Sb and Sn (Larsen *et al.*).

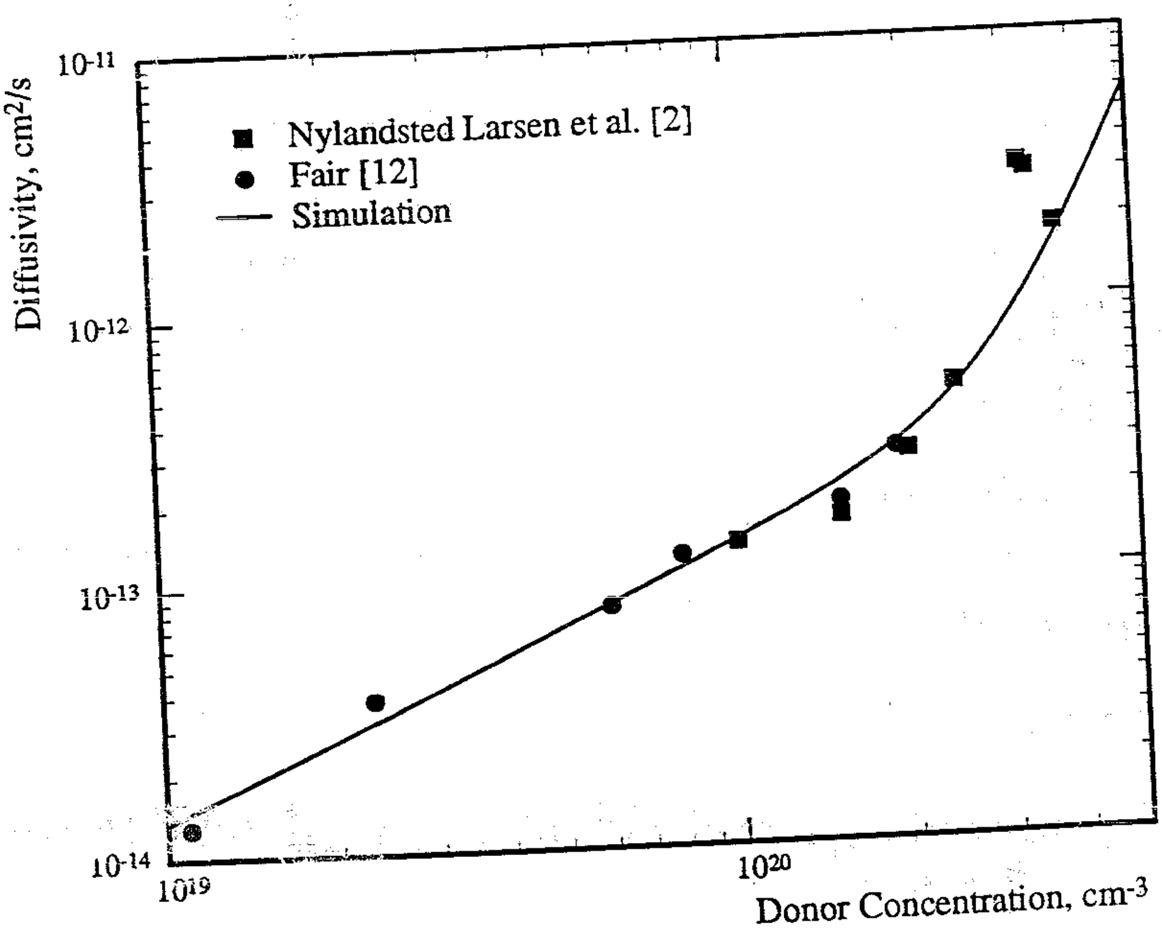


- Pair diffusion limited by activation energy required for vacancies to reach third-nearest neighbor site of dopant.
- At high concentrations, the presence of other dopants reduces that energy and thus increases diffusivity.
- Assume $D_{(\mathrm{PV})^0} \propto (n/n_i)^3$, so $D_{\mathrm{P}}^{V^-} \propto (n/n_i)^4$.
- Optimized $k_{\mathrm{I/V}}$ and $D_{\mathrm{P}}^{V^-}|_{(C_{\mathrm{P}^+}=n_i)}$ to match data.

Simulation Results – Comparison to Experiment

- Can compare predictions of simulation to experimental data from Larsen *et al.*
- Diffusivity at moderate doping extended to very high doping based on lattice Monte-Carlo simulations.

$$D = D^0 + D^-\left(\frac{n}{n_i}\right)\left[1 + \left(\frac{C_A}{C_{\text{ref}}}\right)^3\right]$$



- Atomistic simulations predict experimental results.

Model for Coupled Diffusion of Dopants and Defects via Pairs

- Pairing Reactions:

$$P^+ + I^i \Leftrightarrow (PI)^{i+1}$$

$$P^+ + V^i \Leftrightarrow (PV)^{i+1}$$

[i represents charge state (−, 0, +, etc.)]

- Ionization Reactions:

$$I^i + e^- \Leftrightarrow I^{i-1}$$

$$V^i + e^- \Leftrightarrow V^{i-1}$$

$$(PI)^i + e^- \Leftrightarrow (PI)^{i-1}$$

$$(PV)^i + e^- \Leftrightarrow (PV)^{i-1}$$

- Recombination Reactions:

$$I^i + V^j \Leftrightarrow (-i-j)e^-$$

$$(PI)^i + V^j \Leftrightarrow P^+ + (1-i-j)e^-$$

$$(PV)^i + I^j \Leftrightarrow P^+ + (1-i-j)e^-$$

$$(PI)^i + (PV)^j \Leftrightarrow 2P^+ + (2-i-j)e^-$$

- Diffusion and Drift of Mobile Species:

  – I^i, V^i, $(PI)^i$, $(PV)^i$

Model Assumptions

- Assumptions used:
  - Ionization reactions are near equilibrium.

$$C_{\mathrm{I}^i} \cong K_{\mathrm{I}}^i \left(\frac{n}{n_i}\right)^i C_{\mathrm{I}^0}$$

$$C_{(\mathrm{PI})^{i+1}} \cong K_{\mathrm{PI}}^i \left(\frac{n}{n_i}\right)^i C_{(\mathrm{PI})^+}$$

  - Isolated dopant atoms are immobile.
  - Charge neutrality.
- Other possible assumptions:
  - Defect pairing reactions near equilibrium.

$$C_{(\mathrm{PI})^{i+1}} \cong K_{\mathrm{P/I}}^i C_{\mathrm{I}^i} C_{\mathrm{P}^+}$$

  - Defect recombination reactions near equilibrium.

$$C_{\mathrm{I}^i} C_{\mathrm{V}^j} \cong C_{\mathrm{I}^i}^* C_{\mathrm{V}^j}^*$$

Coupled Diffusion Model

- Recombination rates depend on Fermi level due to changing fraction of charged species.

$$R_{\mathrm{I/V}} = \left[\sum_{i,j} k^{i,j}_{\mathrm{I/V}} K^i_{\mathrm{I}} K^j_{\mathrm{V}} \left(\frac{n_i}{n}\right)^{i+j}\right] \left[C_{\mathrm{I}^0} C_{\mathrm{V}^0} - C^*_{\mathrm{I}^0} C^*_{\mathrm{V}^0}\right]$$

- Point defect recombination enhanced in heavily doped material via PI + V and PV + I reactions.

$$R_{\mathrm{PI/V}} = \left[\sum_{i,j} k^{i,j}_{\mathrm{PI/V}} K^i_{\mathrm{PI}} K^j_{\mathrm{V}} \left(\frac{n_i}{n}\right)^{i+j}\right] K^0_{\mathrm{P/I}} C_{\mathrm{P}^+} \left[C_{\mathrm{I}^0} C_{\mathrm{V}^0} - C^*_{\mathrm{I}^0} C^*_{\mathrm{V}^0}\right]$$

- Considering charged species results in an effective diffusion coefficient which is dependent on the Fermi level.

$$\begin{aligned} J_{\mathrm{I}^i} &= -D_{\mathrm{I}^i}\left(\nabla C_{\mathrm{I}^i} - \frac{iq\vec{\mathcal{E}}}{kT} C_{\mathrm{I}^i}\right) \\ &= -D_{\mathrm{I}^i} K^i_{\mathrm{I}} \left(\frac{n_i}{n}\right)^i \nabla C_{\mathrm{I}^0} \end{aligned}$$

$$J_{\mathrm{I}} = \sum_i J_{\mathrm{I}^i} = -\left[\sum_i D_{\mathrm{I}^i} K^i_{\mathrm{I}} \left(\frac{n_i}{n}\right)^i\right] \nabla C_{\mathrm{I}^0}$$

$$J_{(\mathrm{PI})} = -\left[\sum_i D_{(\mathrm{PI})^{i+1}} K^i_{\mathrm{PI}} \left(\frac{n_i}{n}\right)^i\right] \left[\nabla C_{(\mathrm{PI})^+} + C_{(\mathrm{PI})^+} \left(\frac{n_i}{n}\right) \nabla \left(\frac{n}{n_i}\right)\right]$$

- J_{V} and $J_{(\mathrm{PV})}$ are analogous.

Model – Continuity Equations

- Need to consider five continuity equations:

$$\frac{\partial C_{\mathrm{P+}}}{\partial t} = -R_{\mathrm{P/I}} - R_{\mathrm{P/V}} + R_{\mathrm{PI/V}} + R_{\mathrm{PV/I}}$$

$$\frac{\partial C_{\mathrm{I}}}{\partial t} = -\nabla J_{\mathrm{I}} - R_{\mathrm{P/I}} - R_{\mathrm{I/V}} - R_{\mathrm{PV/I}}$$

$$\frac{\partial C_{\mathrm{V}}}{\partial t} = -\nabla J_{\mathrm{V}} - R_{\mathrm{P/V}} - R_{\mathrm{I/V}} - R_{\mathrm{PI/V}}$$

$$\frac{\partial C_{\mathrm{(PI)}}}{\partial t} = -\nabla J_{\mathrm{(PI)}} + R_{\mathrm{P/I}} - R_{\mathrm{PI/V}}$$

$$\frac{\partial C_{\mathrm{(PV)}}}{\partial t} = -\nabla J_{\mathrm{(PV)}} + R_{\mathrm{P/V}} - R_{\mathrm{PV/I}}$$

Model Parameters

- Defect energy levels (K_{I}^{i}, K_{V}^{i})
- Pair energy levels (K_{PI}^{i}, K_{PV}^{i})
- Defect diffusivities (D_{I^i}, D_{V^i})
- Pair diffusivities ($D_{(\mathrm{PI})^i}$, $D_{(\mathrm{PV})^i}$)
- Dopant/defect pair binding ($K_{\mathrm{P/I}}^{0}$, $K_{\mathrm{P/V}}^{0}$)
- Equilibrium defect concentrations (C_{I^0}, C_{V^0})
- Forward reaction rates ($k_{\mathrm{P/I}}^{i}$, $k_{\mathrm{I/V}}^{i,j}$, etc.)

Quantifying Model

- Dependence of pair diffusion on Fermi level from isoconcentration studies (Wittel and Dunham) ($K^0_{P/I} K^i_{PI} D_{(PI)^i}$).
- Defect equilibrium concentrations and diffusivities from metal diffusion (Bracht) (D_I, C^*_I, D_V, C^*_V).
- Relative importance of interstitial versus vacancy mechanisms at low concentrations from diffusion during point defect injection/extraction (Fahey, *et al.*).

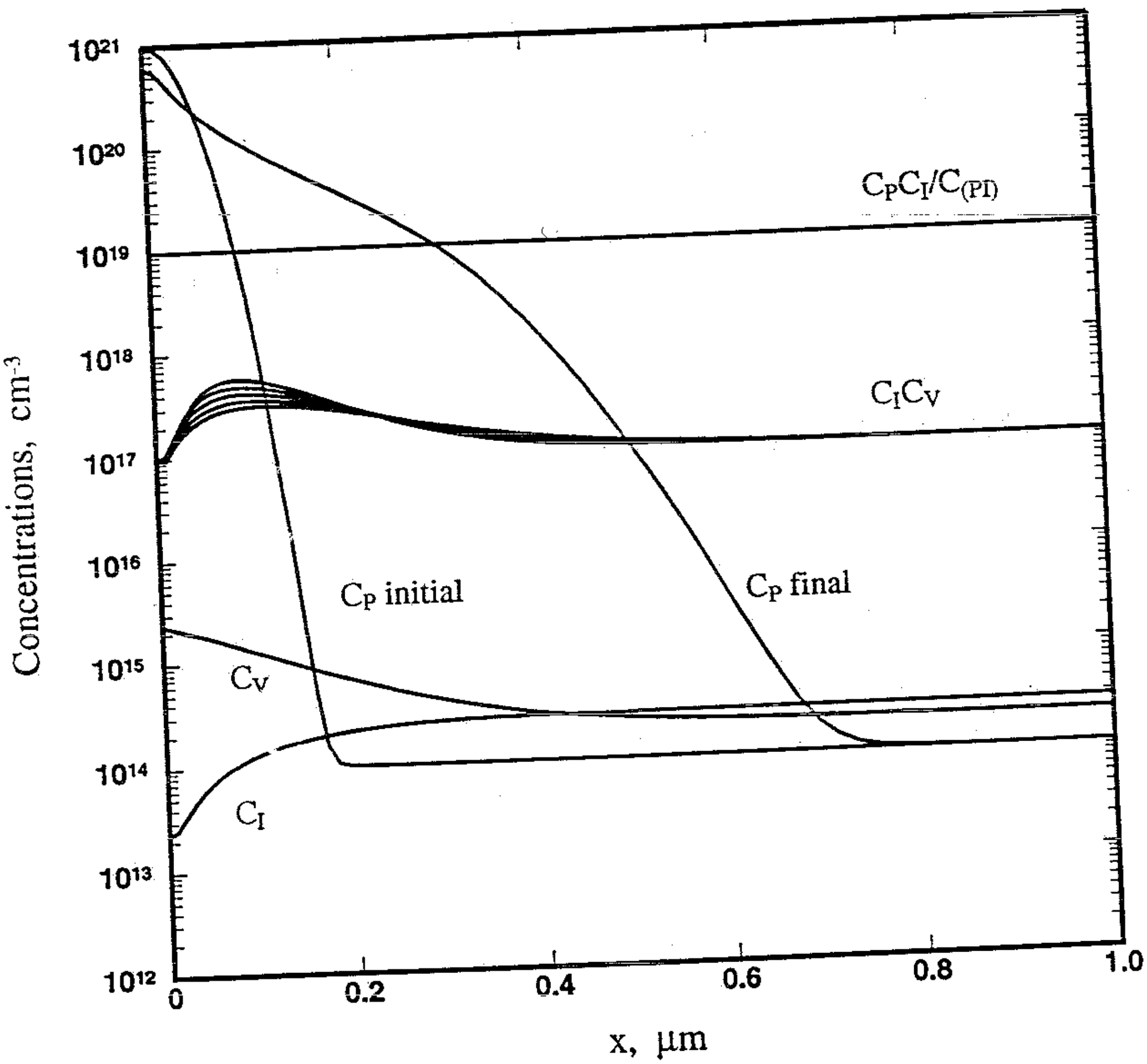
$$\frac{K^0_{P/I} \sum_i K^i_{PI} D_{(PI)^i}}{K^0_{P/V} \sum_i K^i_{PV} D_{(PV)^i}}$$

- Location of defect charge states from EPR (vacancies, Watkins) and OED and TED in heavily doped material (interstitials, Giles).
- Estimate forward reaction rates from simple kinetic approximation (diffusion-limited for $\Delta E = 0$):

$$k_{AB} = \sigma_{AB} (D_A + D_B) \exp\left(-\frac{\Delta E}{kT}\right)$$

Testing Assumptions

- Simulate general system (pairs considered explicitly) to evaluate possible assumptions.



- Dopant/defect pairing reactions near equilibrium?

$$C_{(PI)} = K_{PI}C_{P+}C_I \Rightarrow \textbf{Yes}$$

- Defect recombination reaction near equilibrium?

$$C_IC_V \neq C_I^*C_V^* \Rightarrow \textbf{No}$$

Simplified Model – Continuity Equations

- Simplified model (and SUPREM IV) assumes pairing is near equilibrium.
- Reduces continuity equations from 5 to 3 (pairs no longer need to be considered explicitly).

$$\frac{\partial C_{\mathrm{P}}{}^{\mathrm{T}}}{\partial t} = \frac{\partial\left(C_{\mathrm{P+}} + C_{(\mathrm{PI})} + C_{(\mathrm{PV})}\right)}{\partial t} = -\nabla\cdot\left(J_{(\mathrm{PI})} + J_{(\mathrm{PV})}\right)$$

$$\frac{\partial C_{\mathrm{I}}{}^{\mathrm{T}}}{\partial t} = \frac{\partial\left(C_{\mathrm{I}} + C_{(\mathrm{PI})}\right)}{\partial t} = -\nabla\cdot\left(J_{\mathrm{I}} + J_{(\mathrm{PI})}\right) - R$$

$$\frac{\partial C_{\mathrm{V}}{}^{\mathrm{T}}}{\partial t} = \frac{\partial\left(C_{\mathrm{V}} + C_{(\mathrm{PV})}\right)}{\partial t} = -\nabla\cdot\left(J_{\mathrm{V}} + J_{(\mathrm{PV})}\right) - R$$

$$R = R_{\mathrm{I/V}} + R_{\mathrm{PI/V}} + R_{\mathrm{PV/I}}$$

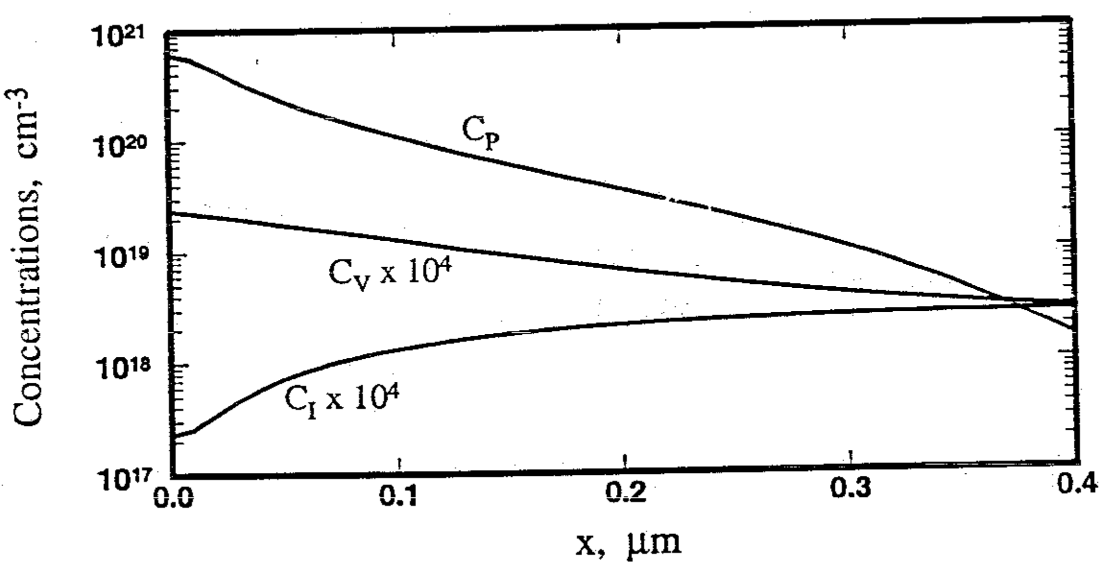
Cause of Phosphorus Profile Anomalies

- For pair diffusion, the flux of pairs depends on the gradient in the product of the dopant and defect concentrations.

$$J_{(PI)} \propto \nabla C_{(PI)^0} = C_{P+}\nabla C_{I^0} + C_{I^0}\nabla C_{P+}$$

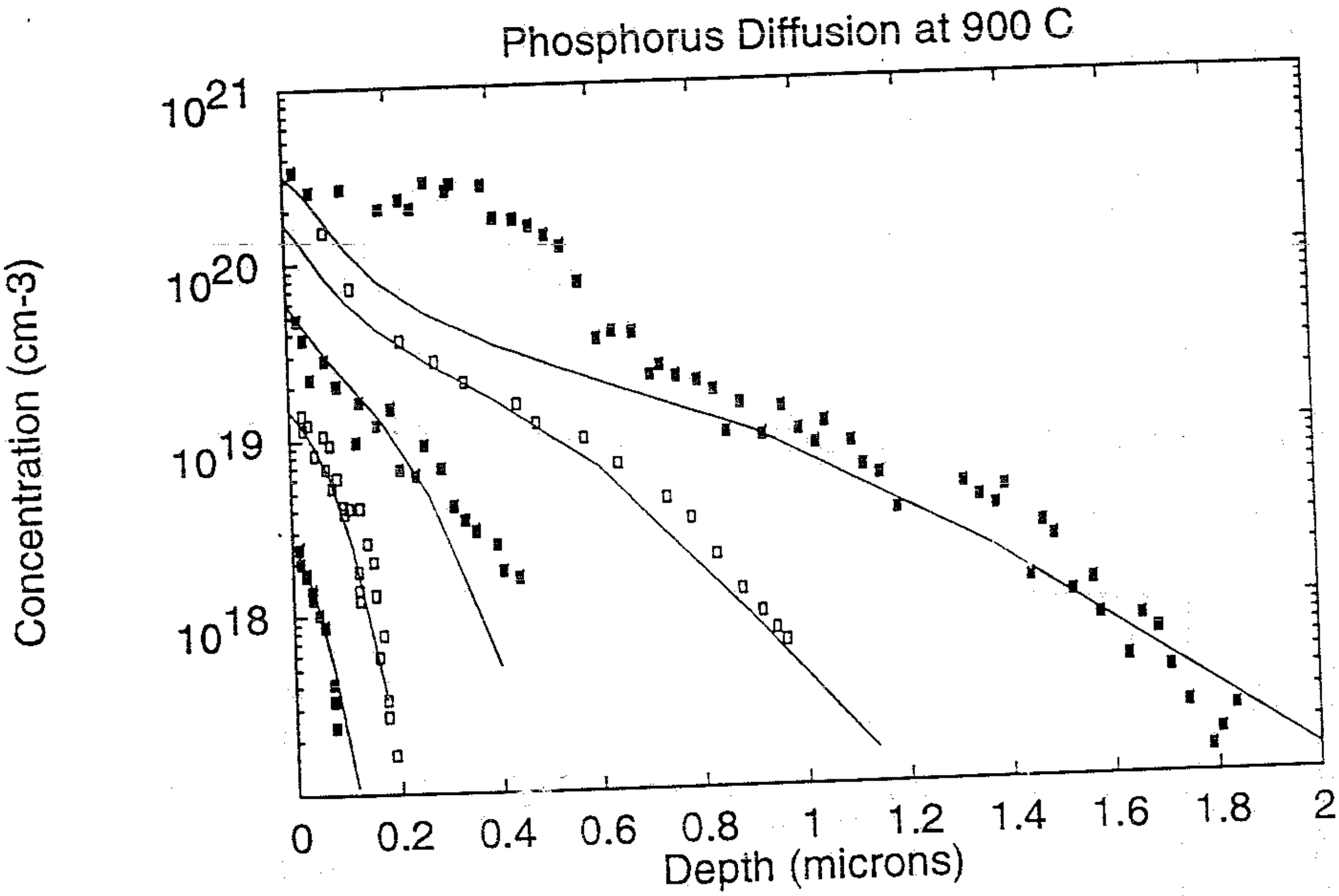
  – Gradient in either concentration drives pair flux.

- Initially, doping gradient causes flux of pairs into bulk.



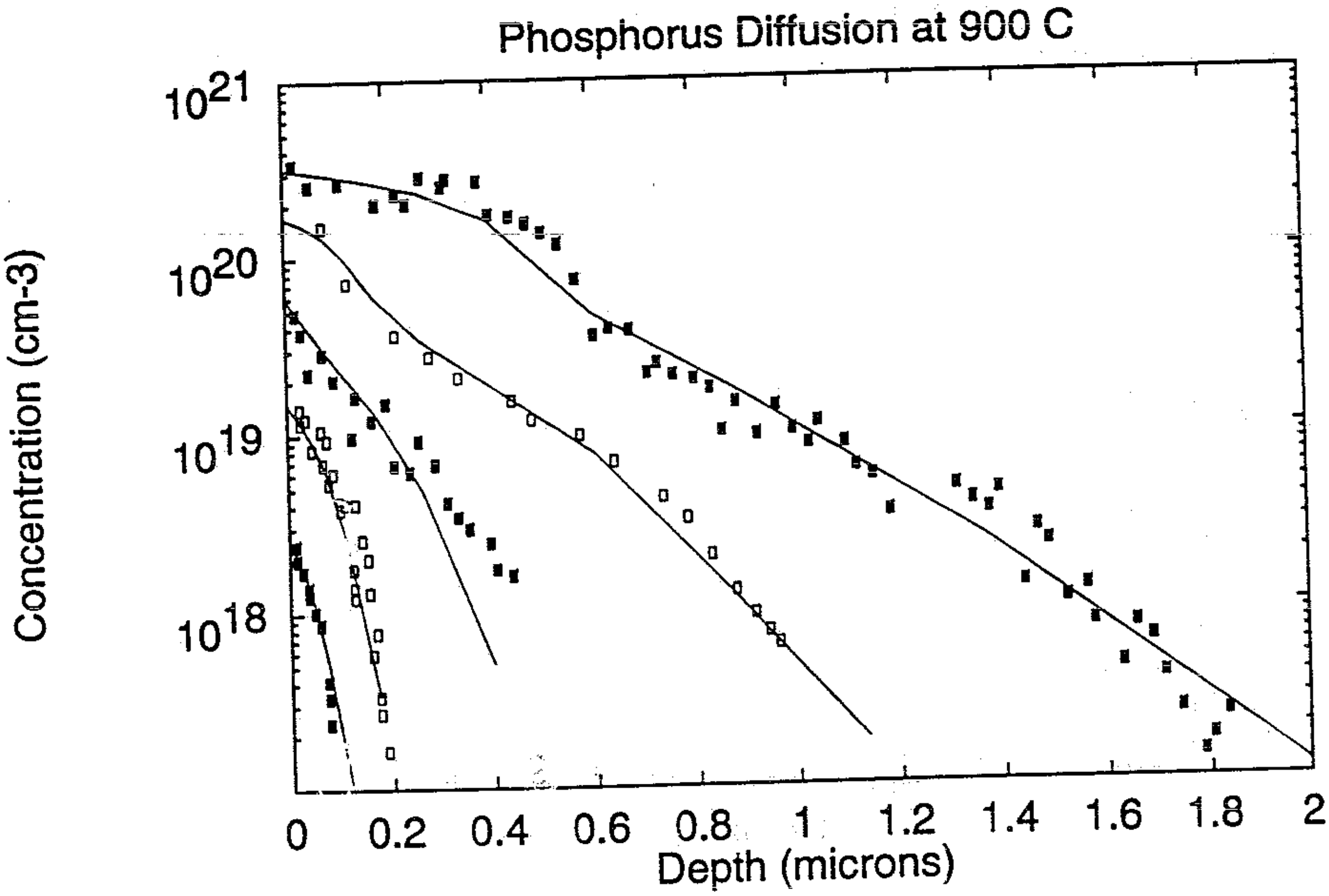
- Pairs dissociate as dopant concentration reduces – interstitial supersaturation (base push).
- Interstitials diffuse back towards surface.
- Gradient in defect concentration compensates for doping gradient reducing pair flux and causing kink.

Comparison to Experiment – No (PV) Pairs



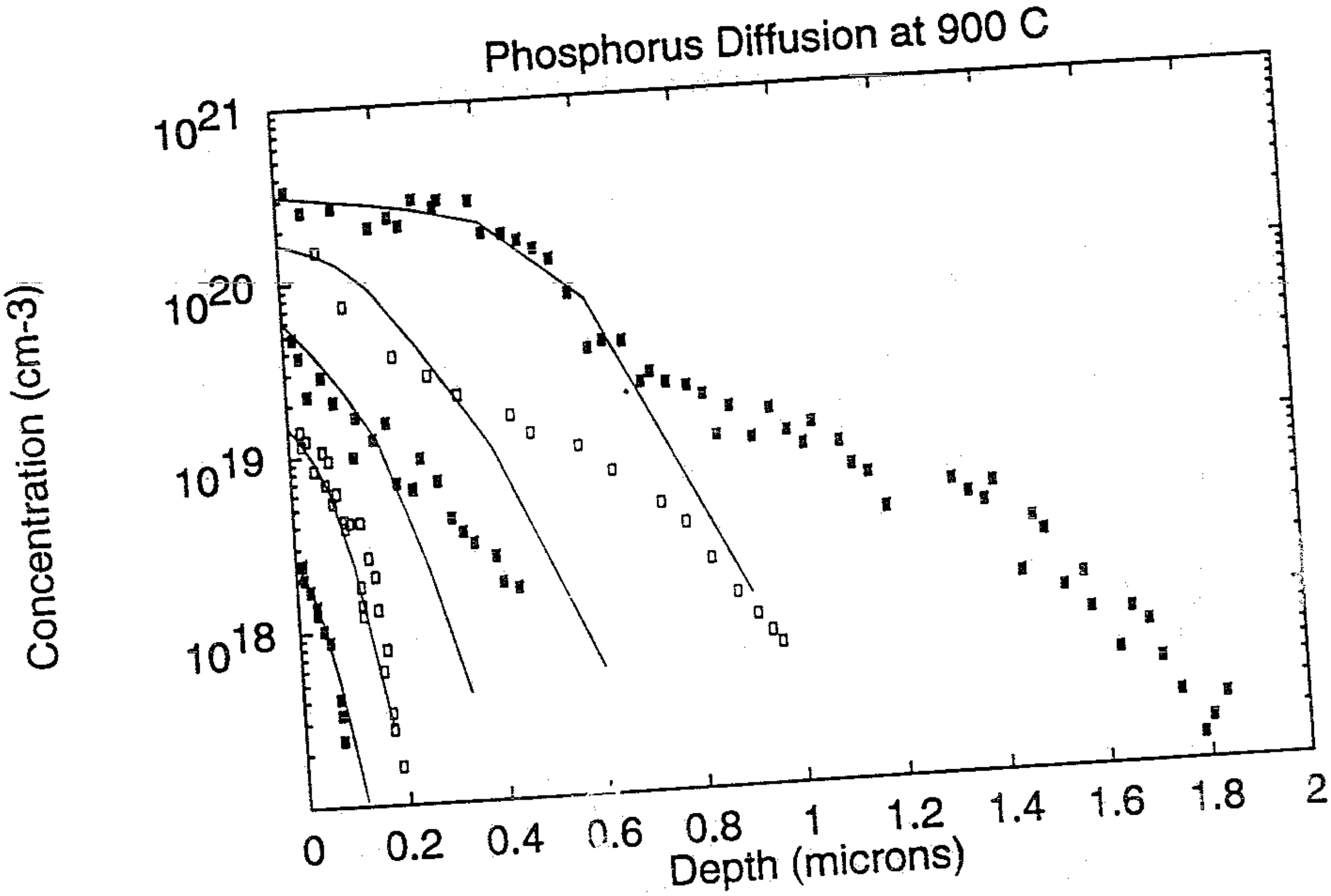
- Cannot match full range of data.

Comparison to Experiment – Concentration-Dependent $D_{(PV)}$



- Excellent match to data over full range of doping levels.

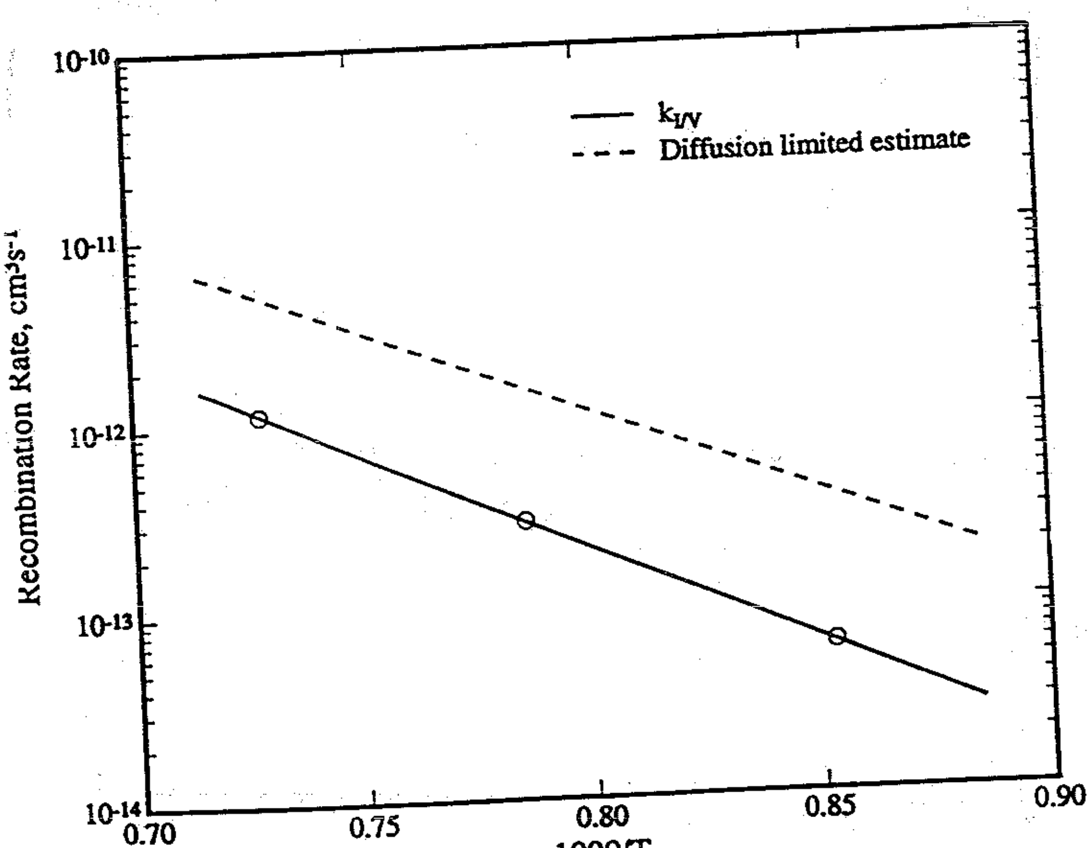
Comparison to Experiment – Point Defect Equilibrium ($C_I C_V = C_I^* C_V^*$)



- Finite defect recombination rate essential for quantitative model.

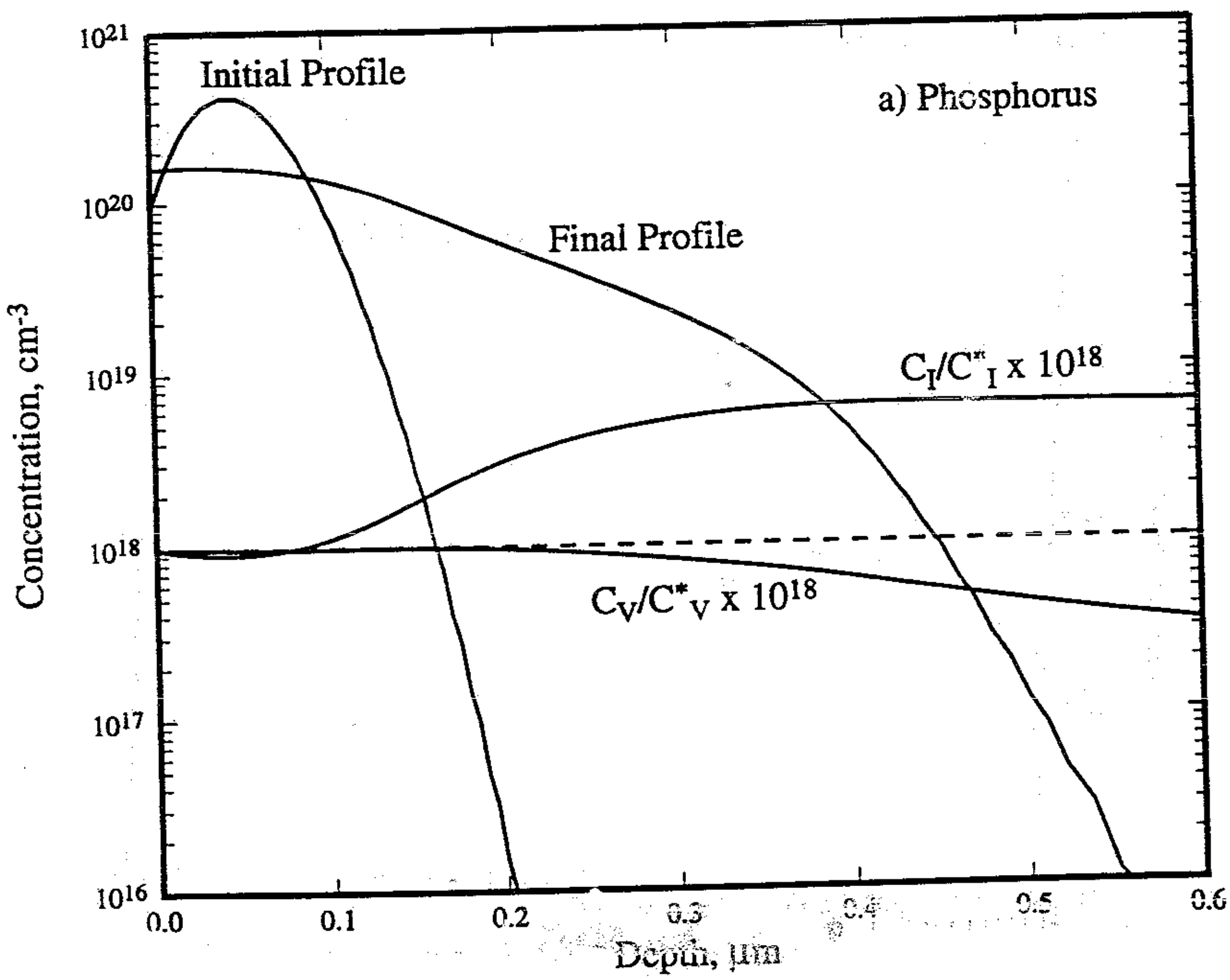
Comparison to Experiment – Bulk Recombination Rate

- Calculated effective recombination rate similar to diffusion-limited estimate.
  - Small ($\sim 0.2\,\text{eV}$) recombination barrier.
  - Includes effects of dopant-mediated recombination.



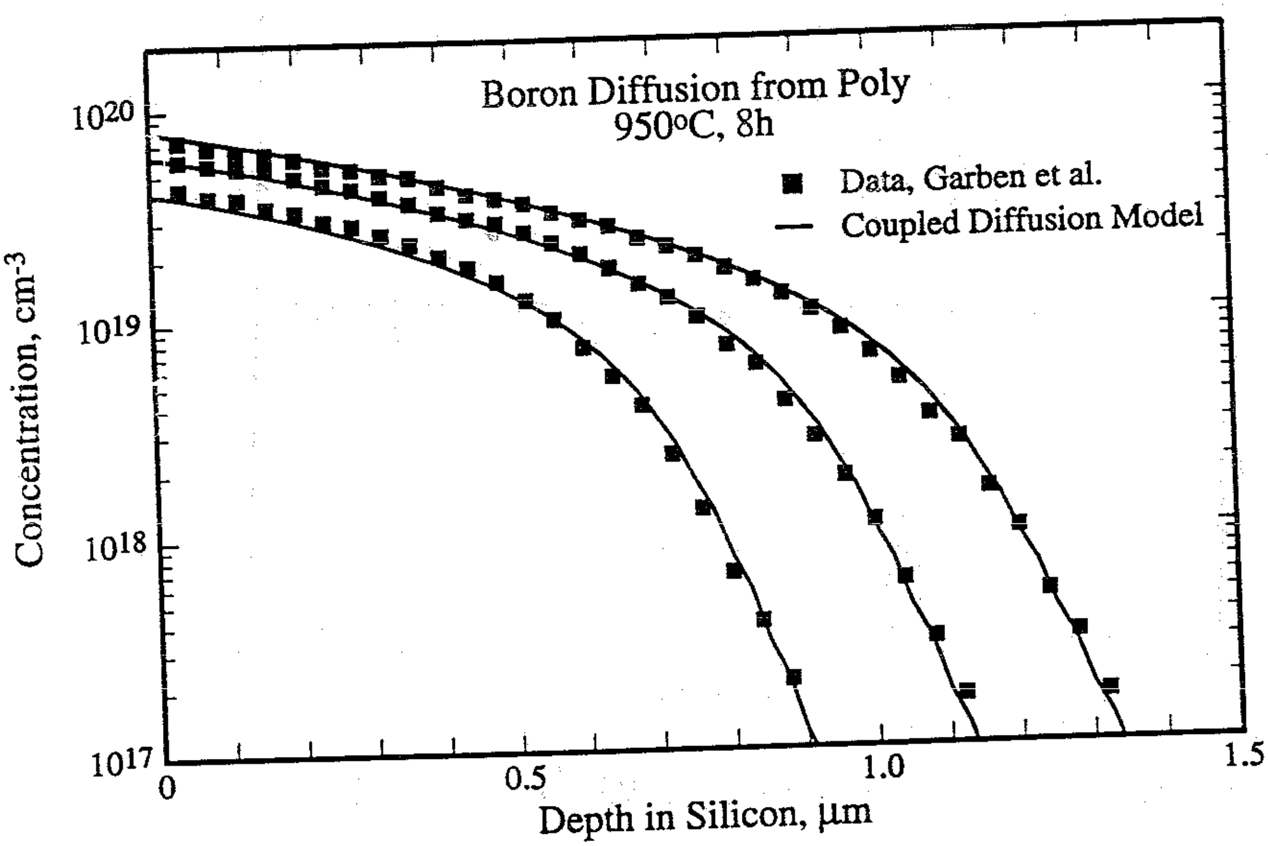
Differences Between Dopant Diffusion Profiles

- Can extend models developed to phosphorus to other dopants.
- Explains differences between profiles (why phosphorus behaves "anomalously").
- Phosphorus: Kink and tail and an order of magnitude interstitial supersaturation in bulk.



Extension of Phosphorus Model to Boron

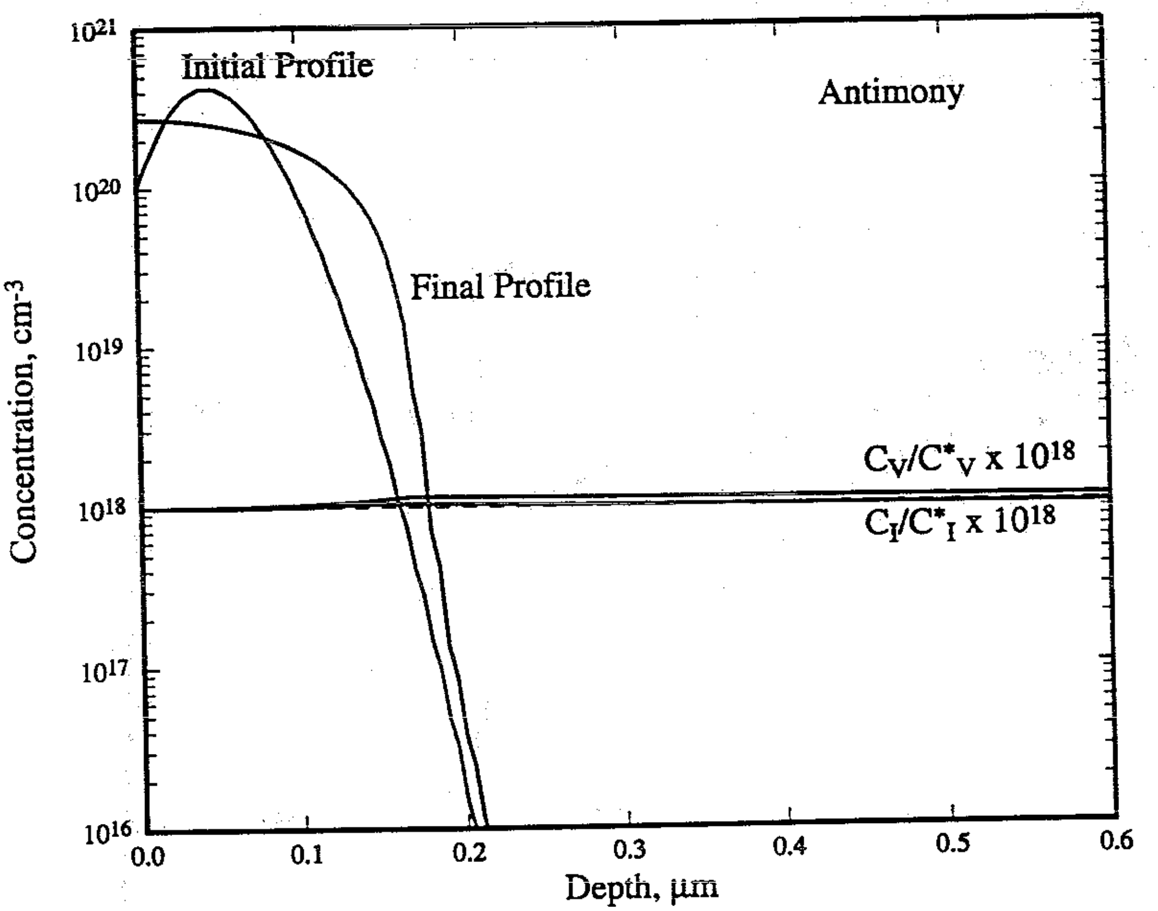
- Use point defect parameters from phosphorus analysis.
- Use boron diffusion parameters from isoconcentration experiments.
- Diffusion from polysilicon (Garben *et al.*).



- Predicts experimental boron profiles.
- Substantial enhanced tail diffusion ($C_I/C_I^* \sim 3$).

Differences Between Dopant Diffusion Profiles

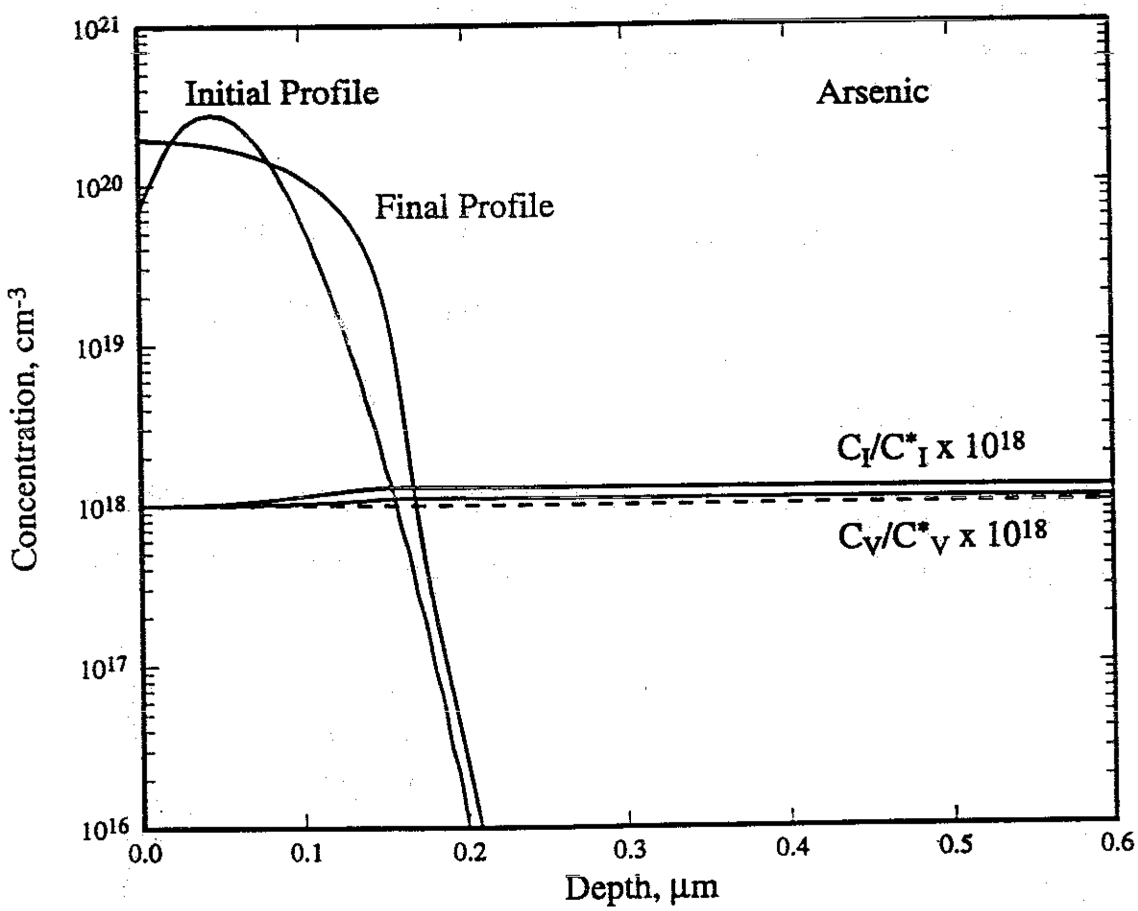
- Antimony: ($f_I^{Sb} \cong 0$) Single dominant pair-type like phosphorus (vacancies instead of interstitials), but no tail or defect supersaturation.



- Difference due to $C_V^* > C_I^*$ and $D_{Sb} < D_P$.

Differences Between Dopant Diffusion Profiles

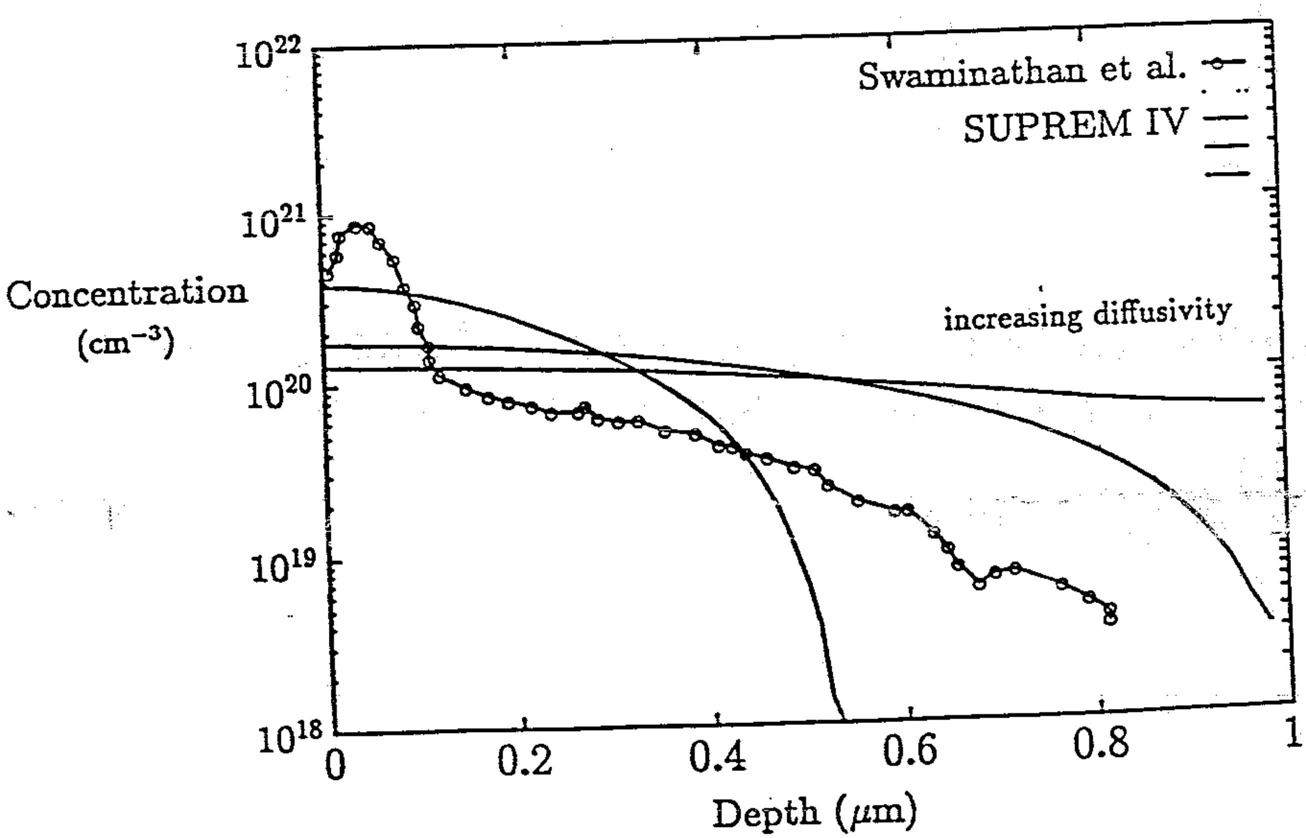
- <u>Arsenic:</u> ($f_I^{As} \cong 0.4$) No kink or tail. Small interstitial (not vacancy) supersaturation despite $f_I^{As} < 0.5$ because $C_V^* > C_I^*$.



- Diffusivity of P with f_I of As and diffusivity of As with f_I of P show that both factors are important.

Dopant Diffusion in/from Polysilicon

- Dopant diffusion is greatly enhanced in polysilicon relative to silicon.
- Segregation to poly/substrate interface.
- Diffusion in poly is due to combination of diffusion in grain and grain boundary.
  - Normal diffusion in grain.
  - Segregation of dopant to grain boundary.
  - Fast diffusion of dopant in grain boundary.
- SUPREM IV uses an increased diffusivity (×100)
  - Cannot account for experimental data except for high thermal budgets (flat profiles in poly).



Two-Stream Model

- Continuity equations:

$$\frac{\partial C_{\text{A}}^{\text{grain}}}{\partial t} = \frac{\partial}{\partial x}\left(D_{\text{A}}^{\text{grain}}\frac{\partial C_{\text{A}}^{\text{grain}}}{\partial x}\right) - k_{\text{eff}}\left(C_{\text{A}}^{\text{grain}} - \frac{C_{\text{A}}^{\text{gb}}}{s}\right)$$

$$\frac{\partial C_{\text{A}}^{\text{gb}}}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_{\text{A}}^{\text{gb}}}{L_g}\frac{\partial\left(C_{\text{A}}^{\text{gb}}L_g\right)}{\partial x}\right) + k_{\text{eff}}\left(C_{\text{A}}^{\text{grain}} - \frac{C_{\text{A}}^{\text{gb}}}{s}\right)$$

- k_{eff} is effective transfer rate between the grains and grain boundaries.
- s is effective segregation coefficient (normalized by relative volumes).

$$s = m_{seg}W_{gb}/L_g.$$

  - W_{gb} is grain boundary thickness
  - L_g is the grain diameter

Effective Transfer Rate

- Transfer rate is composed of a two components

$$k_{\text{eff}} = k_D + k_v$$

  – Diffusion within the grain:

$$k_D = D_{\text{A}}^{\text{grain}} \left(\frac{2\beta}{{L_g}^2} \right)$$

  $\beta = 2.9$ is geometrical factor from quasi-steady state diffusion in cylindrical grains.

  – Grain boundary motion:

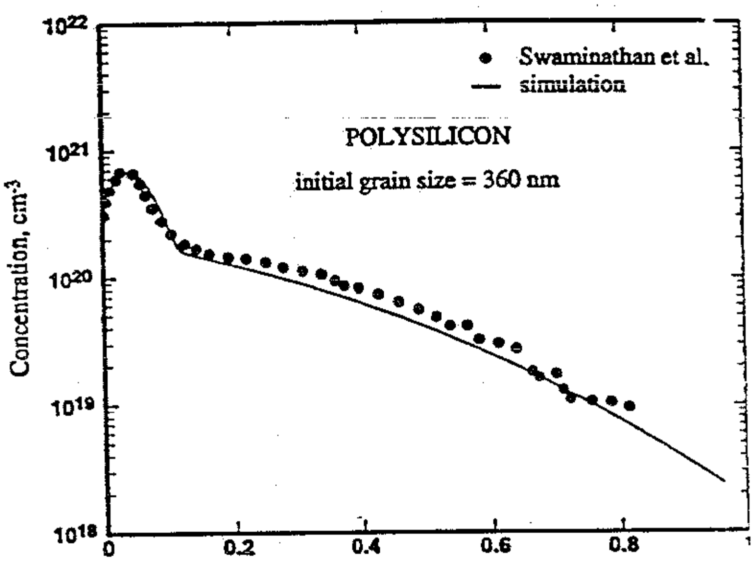
$$k_v = \frac{2v}{L_g} = \frac{2}{L_g} \frac{dL_g}{dt}$$

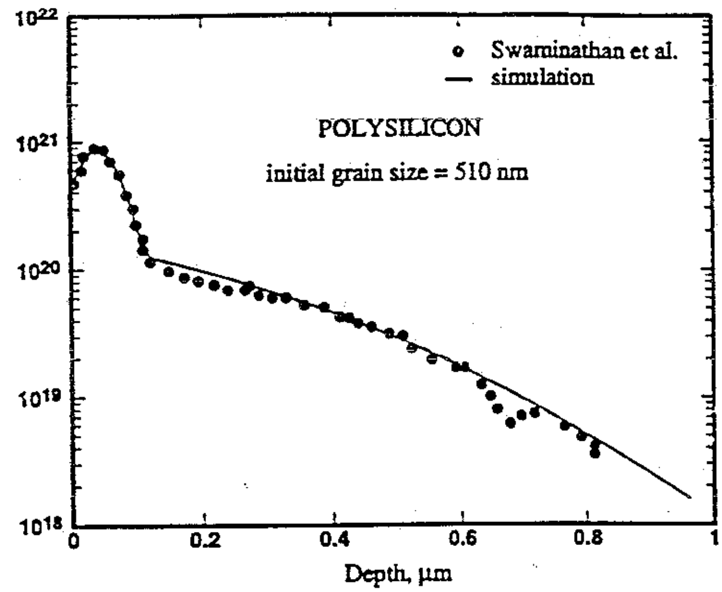
- Grain growth:

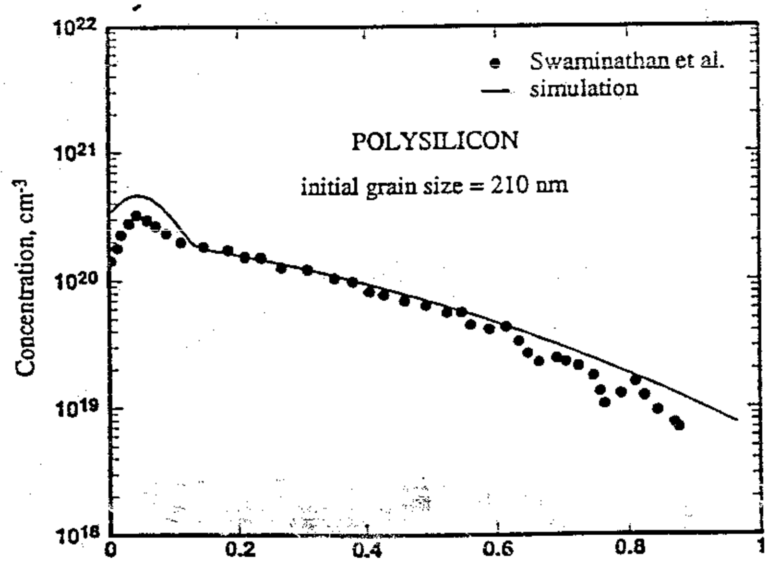
$$L_g(t) = \left[L_{go}^2 + 2\sigma t \right]^{\frac{1}{2}}$$

Diffusion Within Poly
– Two Stream Model (continued)

- Predicts effect of grain size on doping profiles.







Diffusion Through Poly – Two Stream Model

- Two stream model also accounts for diffusion through poly.
- Dopant pileup at the polysilicon/silicon interface included via interface grain boundary.