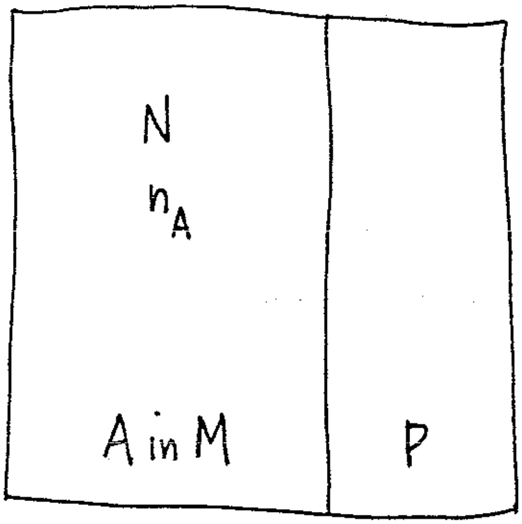
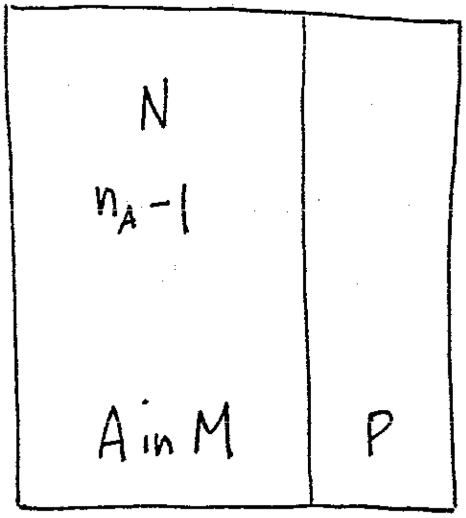
# Precipitation

The formation of a precipitates or other extended defect is a phase transformation.

Consider a system with solute species A in matrix material M.

- If the concentration of A is large enough, the system may be able to lower it's free energy by forming a separate solute-rich phase. The result is a two-phase system of A in M and P, the precipitated solute-rich phase.
- In general, precipitates form because there is a reduction in enthalpy on forming the second phase, while entropy tends to be larger for the dissolved solute.
- To consider if precipitation can be expected, consider the change in energy on a solute atom becoming part of the precipitate phase in the two-phase system.





The change in enthalpy is just $\Delta H_p$, while as for defects, we will divide up the entropy change into that due to mixing and the rest.

The change in entropy of mixing is:

$$\Delta S_{\mathrm{A}}^{\mathrm{mix}} = k\ln\left[\frac{w(n_{\mathrm{A}}-1)}{w(n_{\mathrm{A}})}\right] = k\ln\frac{n_{\mathrm{A}}}{N-n_{\mathrm{A}}+1} = k\ln\frac{C_{\mathrm{A}}}{C_s-C_{\mathrm{A}}} \cong k\ln\frac{C_{\mathrm{A}}}{C_s} \qquad (1)$$

The change in free energy for each atom added to the precipitate is then:

$$\Delta G = \Delta H_p - T\Delta S_p - T\Delta S_{\mathrm{A}}^{\mathrm{mix}} = \Delta G_p - kT\ln\frac{C_{\mathrm{A}}}{C_s} \qquad (2)$$

If $\Delta G < 0$, the precipitate will tend to grow; if $\Delta G > 0$, it will shrink.

As it grows, the concentration of solute decreases, until $\Delta G = 0$.

That critical concentration is called the solid solubility, the concentration of solute atoms at equilibrium with a very large precipitate.

Solving (4) for $\Delta G = 0$, the solid solubility is:

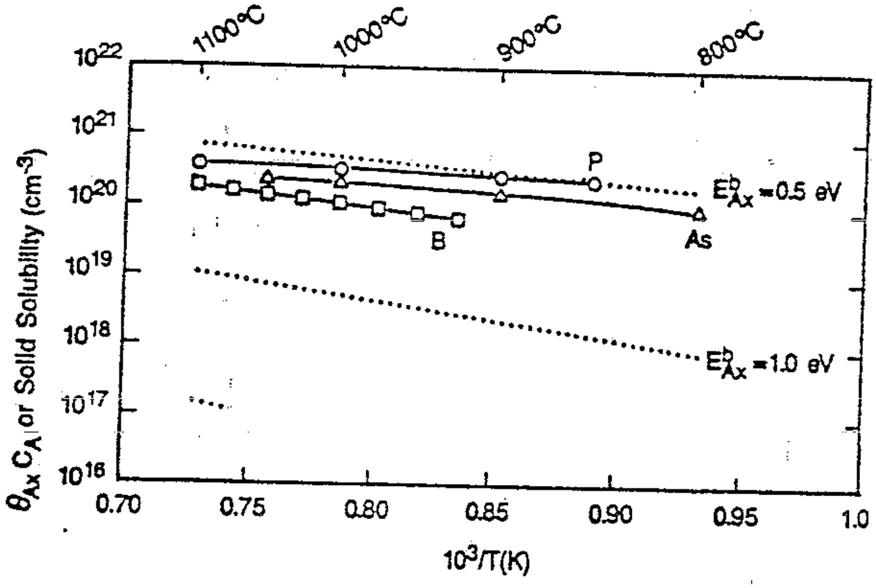
$$C_{\mathrm{A}}^{ss} = C_s\exp\left(\frac{\Delta G_p}{kT}\right) = C_s\exp\left(\frac{-\Delta S_p}{k}\right)\exp\left(\frac{\Delta H_p}{kT}\right) \qquad (3)$$

and

$$\Delta G^{\infty} = kT\ln\frac{C_{\mathrm{A}}^{ss}}{C_s} - kT\ln\frac{C_{\mathrm{A}}}{C_s} = -kT\ln\frac{C_{\mathrm{A}}}{C_{\mathrm{A}}^{ss}} \qquad (4)$$

The solid-solubility is the largest concentration of solute atoms that can be present in equilibrium. If $C_{\mathrm{A}} > C_{\mathrm{A}}^{ss}$, then a second precipitate phase will eventually form.

The solid solubilities for the common substitutional dopants are shown below.

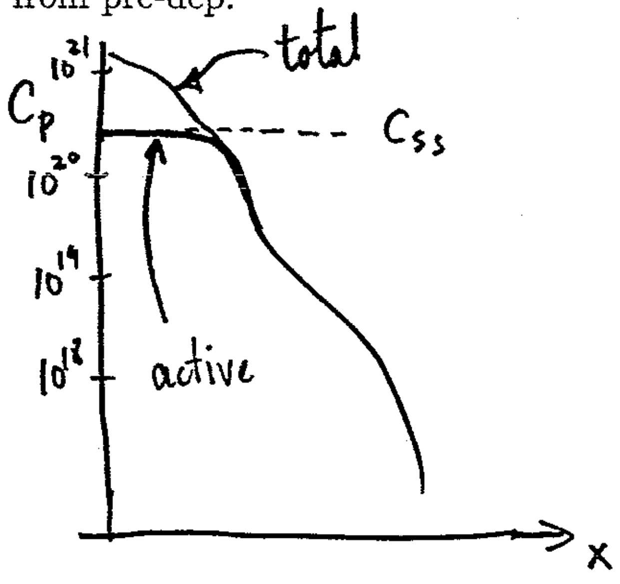


Despite the fact that solute supersaturations cannot exist at equilibrium, they may be present due to the finite kinetics of the precipitation process.

However, currently SUPREM IV assumes that all precipitation processes are instantaneous during high temperature steps, but nonexistent during cool-down.

Experimental observations have shown that this is often not a good assumption.

- Activation depends on ramp-down rate.
- Concentrations above solid-solubility from pre-dep.



## Precipitation Kinetics

To understand and model precipitation kinetics, it is essential to recognize that before we can have a large precipitate, we must first have a small one.

In considering small precipitates, there is an additional energy cost due to the interface between the matrix and the precipitate.

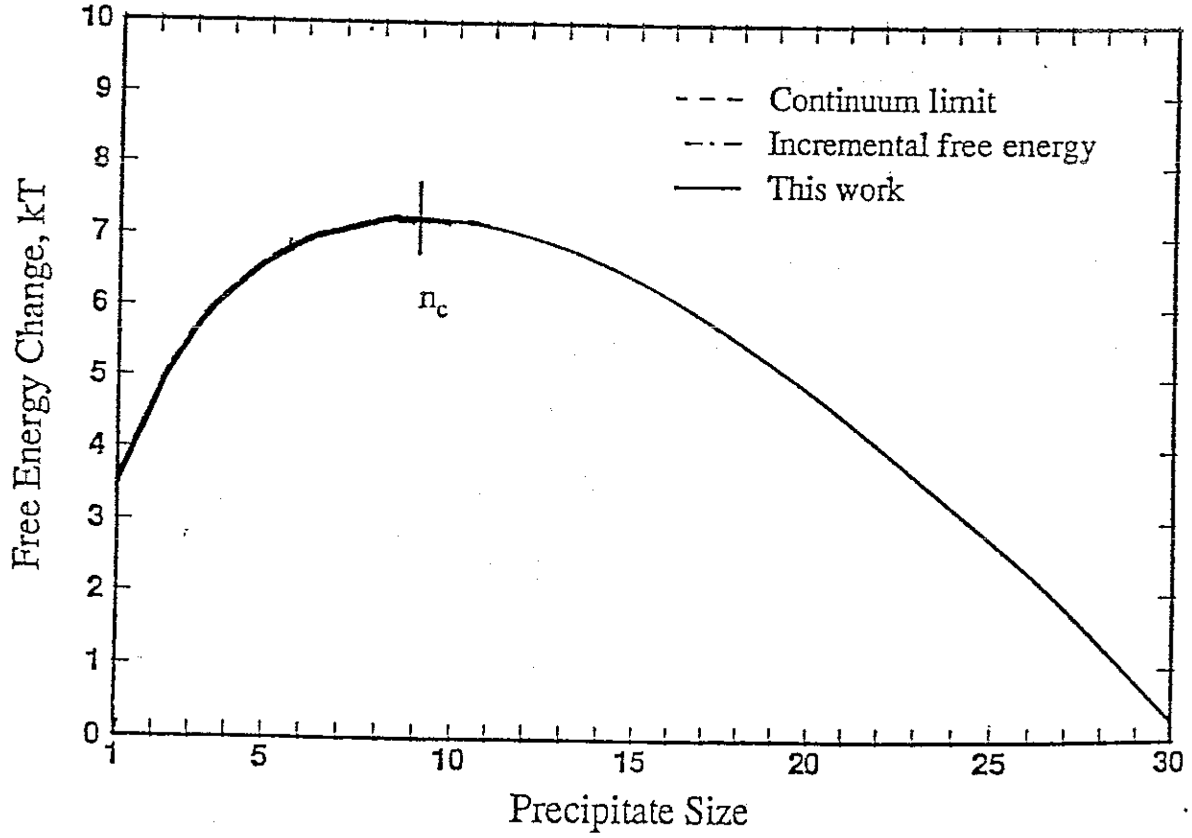
This term is proportional to the surface area so that the change in free energy on forming a precipitate of size $n$ is $n$ times the energy change on adding an atom to a very large (infinite) precipitate, plus the energy cost due to the interface.

$$\Delta G_n = n\Delta G^{\infty} + A_n\sigma = -nkT \ln \frac{C_{\mathrm{A}}}{C_{\mathrm{A}}^{ss}} + A_n\sigma \tag{5}$$

where $A_n$ is the interface area and $\sigma$ is the interface energy per unit area.

If we plot the energy as a function of $n$ we will find that the free energy will at first increase and then decrease.

An example is shown for a spherical precipitate, where $A_n \propto n^{2/3}$



If $C_{\mathrm{A}} > C_{\mathrm{A}}^{css}$, then the energy of a large precipitate will be less than for the dissolved atoms, but there is an activation barrier to overcome as the interface energy dominates for small precipitate sizes.

- Small precipitates ($n < n_c$) tend to shrink.
- Large precipitates ($n > n_c$) tend to grow.
- As in any nucleation process from metastable state, some small precipitates are able to reach critical size and continue to grow.
- Precipitate free energy depends on supersaturation.

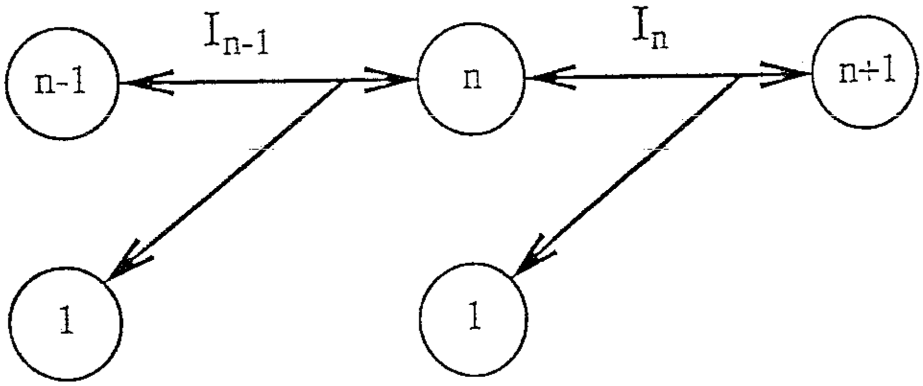
Precipitation processes have several differences from diffusion/reaction processes studied so far:

- Unlike diffusion/reaction processes, all precipitates cannot be considered equivalent.
  - Properties and interactions are functions of size.
- Assume precipitate properties depend only on precipitate size ($n$).
- The state of the system can then be described in terms of a distribution function over size at each location in space ($f(n)$).
- For a nonhomogeneous system, concentrations are replaced with distributions over size, which adds an extra dimension to analysis ($f(\vec{x}) \Rightarrow f(n, \vec{x})$).

To describe precipitation kinetics, model the time evolution of the size distribution of the precipitate density ($f_n$).

The evolution of the system over time depends on:

- Diffusion: Only single atoms ($n = 1$) diffuse.
- Growth and Dissolution: Precipitates grow/shrink by adding/releasing single atoms (fundamentally discrete).



Growth and dissolution rates are strong functions of precipitate size (larger precipitates grow faster) so kinetics depends strongly on distribution function (thermal history).

The net flux of precipitates growing from size $n$ to $n+1$ is difference between the flux of growing precipitates and the flux of dissolving precipitates.

$$I_n = g_n f_n - d_{n+1} f_{n+1} \tag{6}$$

The growth rate depends on the concentration of solute atoms near the precipitate:

$$g_n = kA_n C^i \tag{7}$$

However, a growing precipitate will tend to capture any solute atoms in its neighborhood, locally reducing the solute concentration.

For any precipitate, there is a solute concentration such that the precipitate will tend to neither shrink nor grow. That is, there is no change in free energy on growing ($\partial \Delta G_n / \partial n = 0$).

$$C_n^* = C_{\mathrm{A}}^{ss} \exp\left[\left(\frac{\partial A_n}{\partial n}\right)\sigma\right] \tag{8}$$

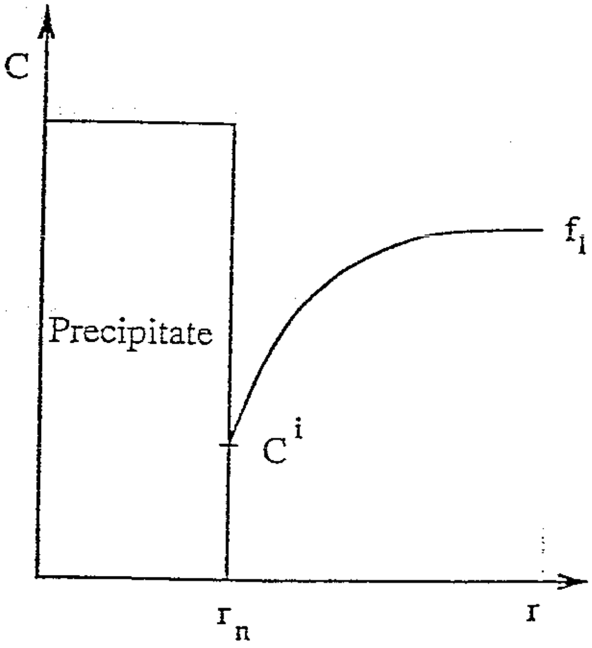
Thus the net rate of growth of any single precipitate is

$$g_n = kA_n(C^i - C_n^*) \tag{9}$$

Assuming steady state and considering a spherical precipitate, balancing the diffusion flux to the precipitate with the rate of reaction at the precipitate/matrix interface,

$$C^i = C_n^* + (C^\infty - C_n^*)\left(\frac{D}{D + kr_n}\right) \tag{10}$$

where $r_n$ is the precipitate radius.



In equilibrium, $I_n = 0$, so dissolution rates are given by

$$d_{n+1} = g_n \frac{f_n^{\mathrm{eq}}}{f_{n+1}^{\mathrm{eq}}} = g_n \exp\left(\frac{\Delta G_{n+1} - \Delta G_n}{kT}\right) \tag{11}$$

where the equilibrium distribution is

$$f_n^{\mathrm{eq}} = C_{\mathrm{Si}} \exp\left(-\frac{\Delta G_n}{kT}\right) \tag{12}$$

Use discrete rate equations for evolution of precipitate size distribution:

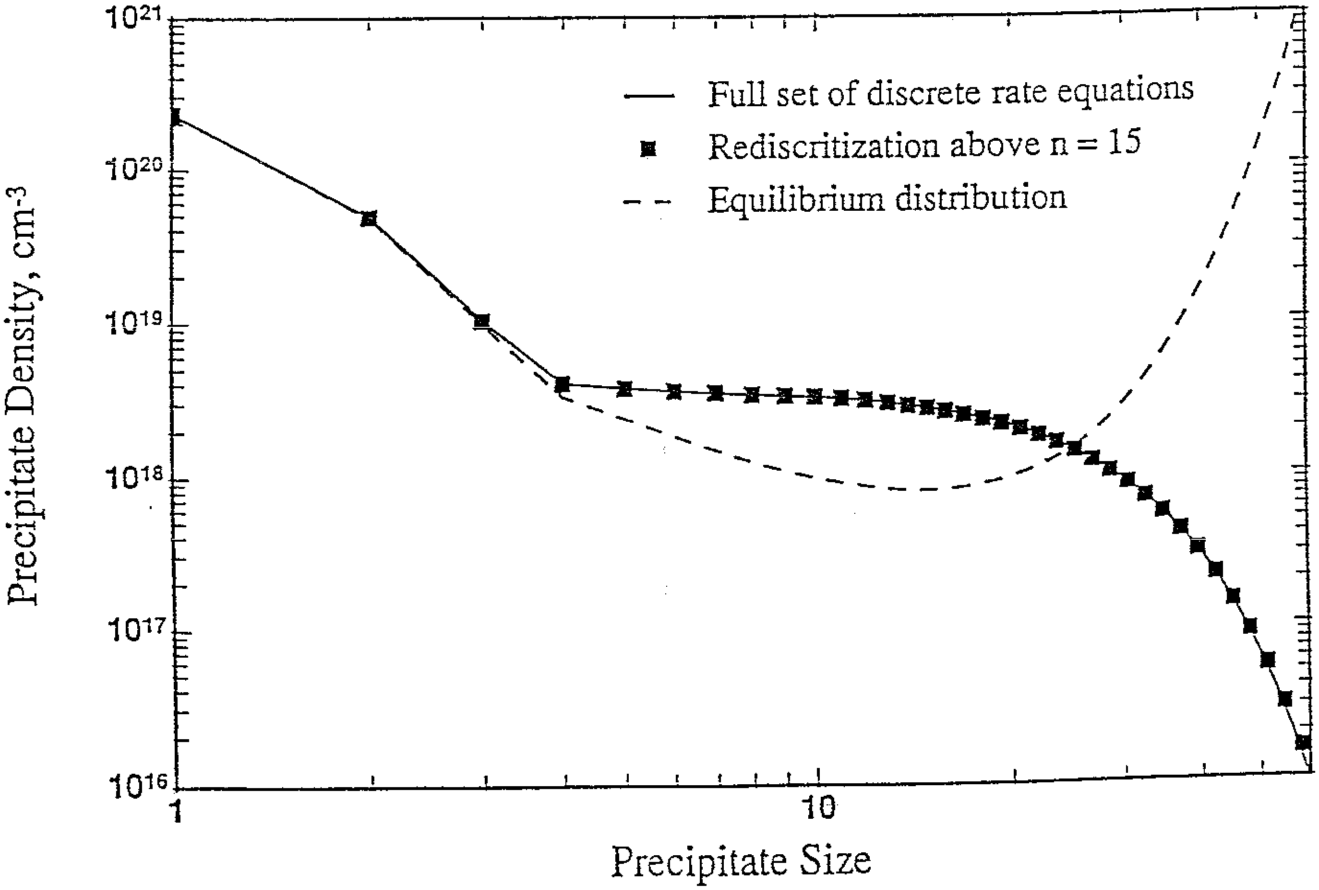
$$\frac{df_n}{dt} = I_{n-1} - I_n, \quad n \geq 2 \tag{13}$$

Must account for solute atom used in each growth step.

$$\frac{df_1}{dt} = -I_1 - \sum_{n=1}^{\infty} I_n \tag{14}$$

Example: Dopant Deactivation

Distribution Function:



# Comparison to Experiment – Dopant Activation (Nobili et al.)

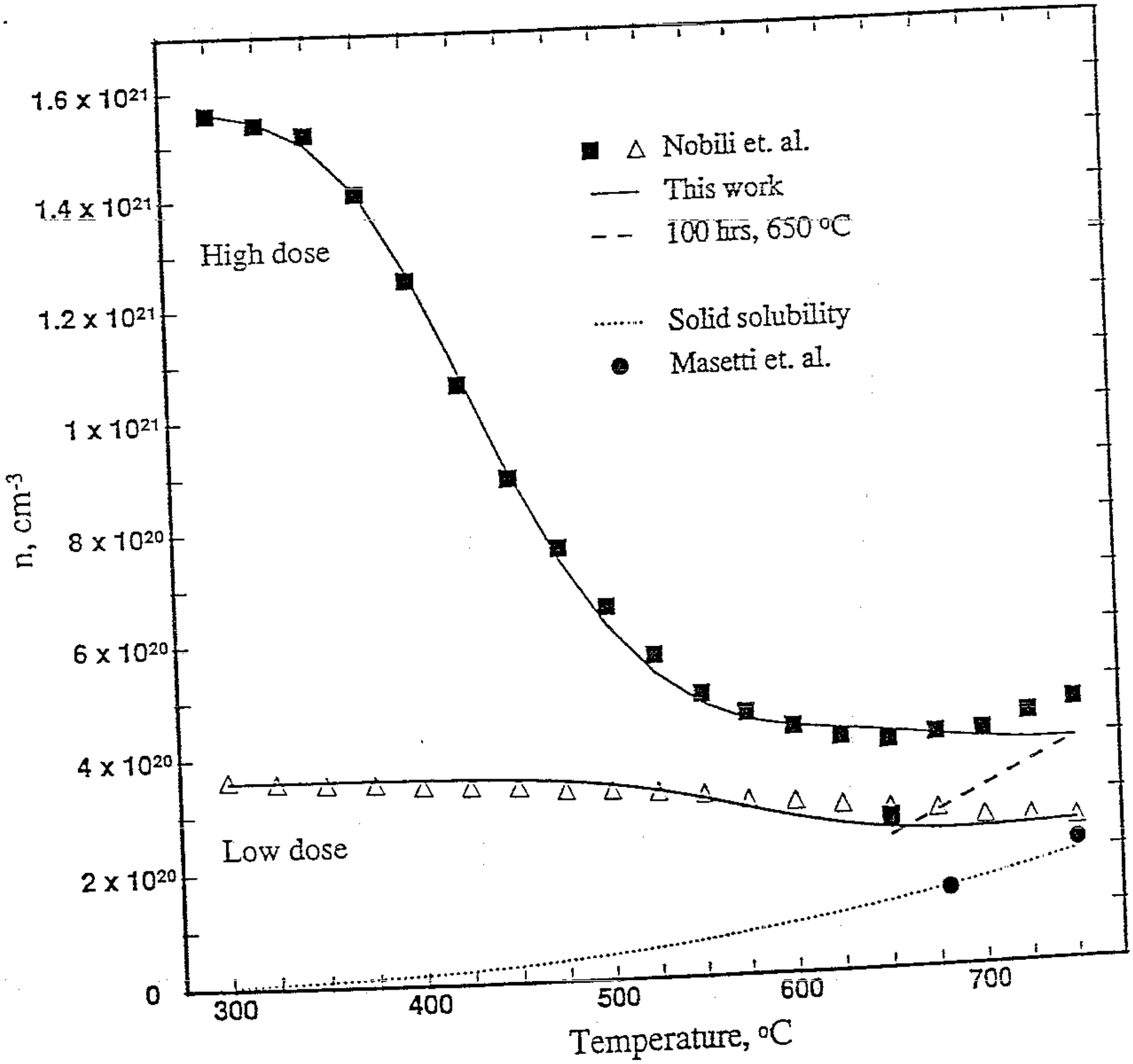
- Initial implant and laser anneal.
- Active dopant concentration measured by sheet resistance and Hall measurements.
- Two types of annealing schedules:
  - Isochronal anneals, one hour at each T.
    - 300 - 750 °C, 25°C steps for P.
    - 300 - 800 °C, 50°C steps for As.
  - Two-step anneal:
    - 550°C then 650°C.

- Solid solubility data from Masetti *et al.*

# Model Assumptions

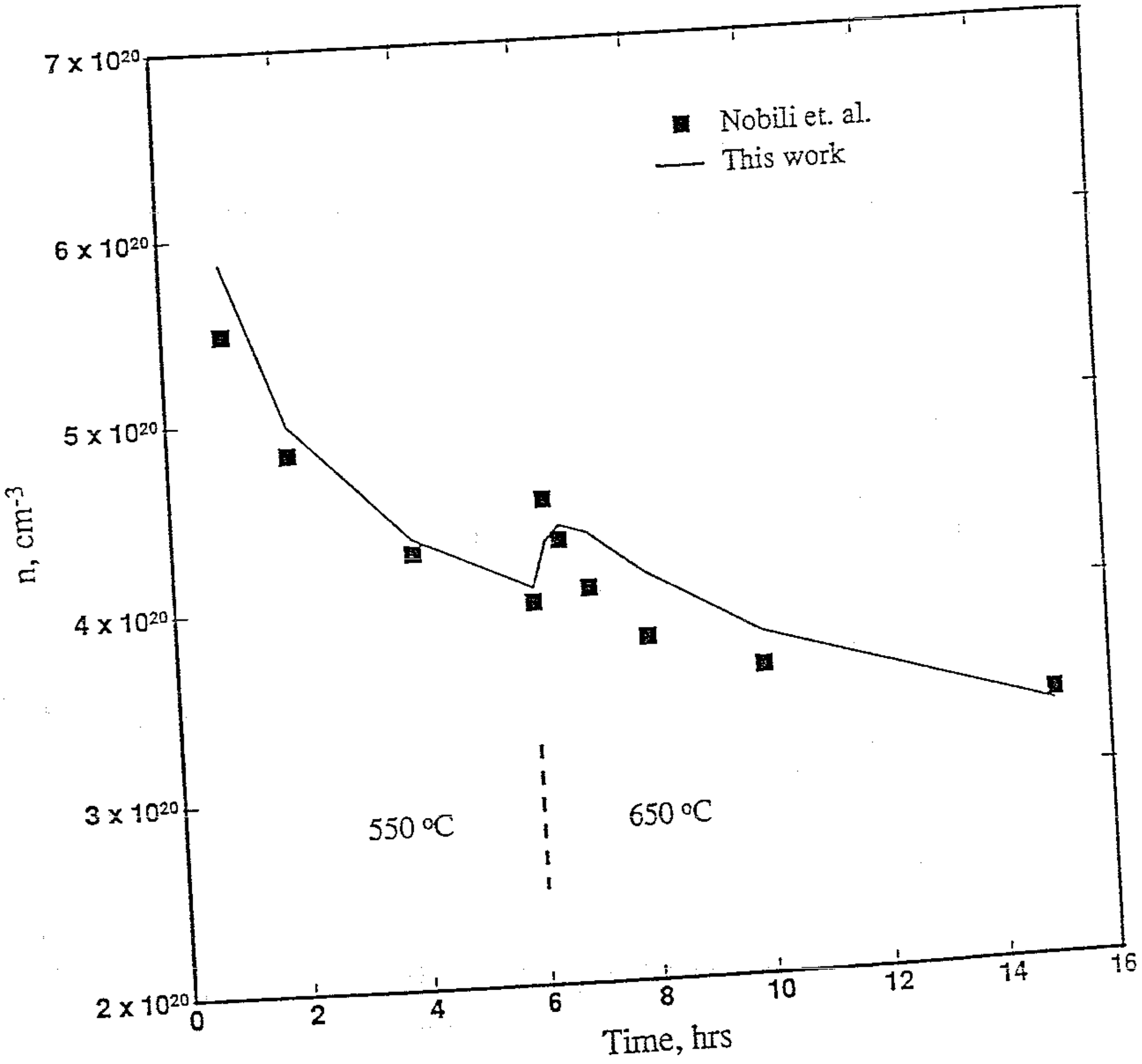
- Assume uniform concentration for finite depth.
- Neglect spreading of profile during anneals.
- High concentration, so assume $D \propto (f_1/n_i)^2$.
- Consider precipitates to be spherical.
- Fitting Parameters:
  - Surface energy ($\sigma$)
  - Pair binding energy ($E_b$)
  - Diffusivity ($D = D_0 \exp(-E_0/kT)$)

# Comparison to Experiment – Isochronal Anneals (Phosphorus)



- Good match between simulation and data
- Much faster precipitation for high dose
- Final 100 hour anneal at 650°C

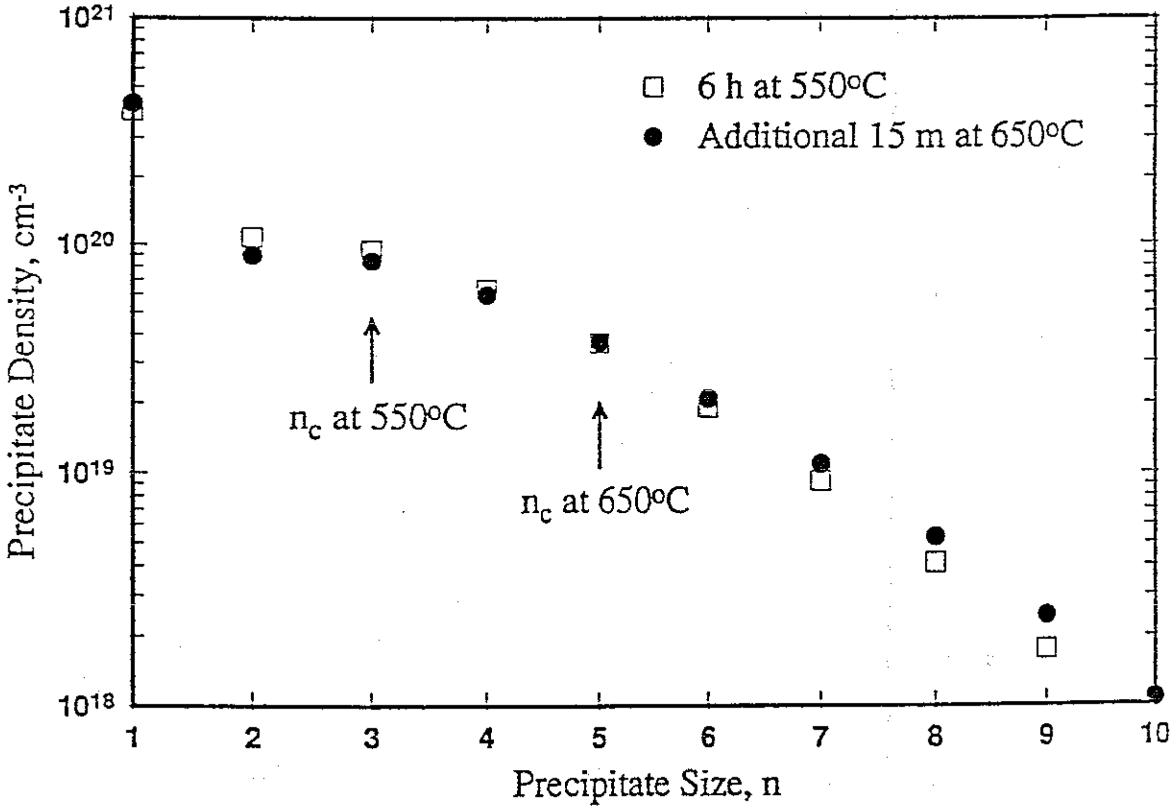
# Comparison to Experiment – Two-Step Anneal (Phosphorus)



- Reverse annealing following temperature step.
- Slower response of simulation due to steady-state growth rate assumption.

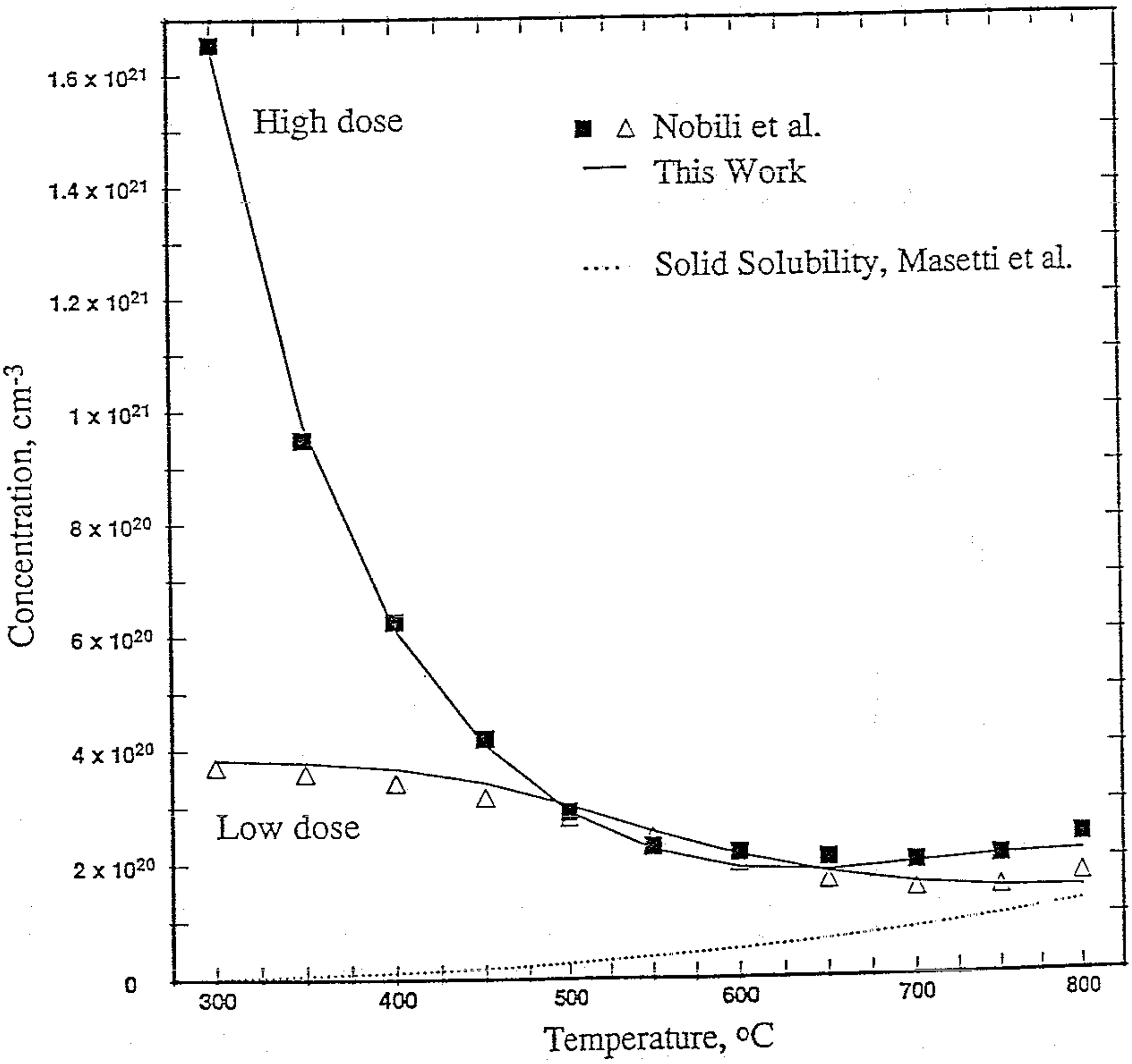
# Discussion – Two-Step Anneal

- Reverse annealing due to change in critical precipitate size ($n_c(550°\text{C}) = 3 \Rightarrow n_c(650°\text{C}) = 5$).
  - Increased solid solubility with T reduces supersaturation.



- Following temperature step, precipitates below critical size shrink, larger precipitates continue to grow.
- Only by considering distribution of precipitate sizes can this phenomena be accounted for.

# Comparison to Experiment – Isochronal Anneals (Arsenic)



- Qualitatively similar to phosphorus.
- Less active dopant for high dose under some conditions.