Final Presentation
Predicting Macroscopic Phenomena with Density-Functional Theory

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Outline

Density-Functional Theory (DFT)

- Motivation
- Introduction to DFT (Hartree-Fock $\Rightarrow$ Kohn-Sham)
- DFT implementation in VASP
- Sample applications of DFT (formation energies, transition barriers, band structure, bulk properties)

Anomalous F diffusion modeled via DFT

- Full F_nV_m model
- Continuum model based on DFT results
- Simplified F_3V model
- Calibration of simplified F model to SIMS data

Summary and conclusion

Motivation

Goal: Study N electron quantum systems

Requires: N particle wave function

$$\Psi(r_1,\ldots,r_N)$$

Exact treatment is numerical challenging:

(m # of sampling points in one direction)

$$\text{memory} \propto m^{3N}$$

Example: bulk Si (2 atoms in primitive cell, 14 electrons per Si atom)

$$\text{memory} = 8\text{Byte}\cdot 10^{3\cdot 2\cdot 14} \approx 10^{73}\text{TB}$$

$\Rightarrow$ **"currently" impossible**

Remember: Solving single particle Schrödinger equation is relative easy and fast

Need to find a way out !!!

Hartree-Fock Method

Idea: Find effective one particle Hamiltonian for N electron system and treat remaining N-1 electrons as an effective potential.

Approximation: $\Psi(r_1,\ldots,r_N) = \mathrm{A}\prod_{i=1}^{N}\phi_i(r_i)$ (Slater determinant)

Minimize: $E = \left\langle \Psi \middle| H_0 + V_{ext} \middle| \Psi \right\rangle =$ **Density:** $n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2$

$$\ldots = \underbrace{\sum_i \int d^3r \frac{\hbar^2}{2m} |\vec{\nabla}\phi_i|^2}_{T} + \underbrace{\frac{1}{2}e^2 \iint d^3r d^3r \frac{n(r)n(r')}{|r-r'|}}_{E_{direct}} - \underbrace{e^2 \sum_{i<j} \left\langle \phi_i\phi_j \middle| \frac{1}{|r-r'|} \middle| \phi_j\phi_i \right\rangle}_{E_{xc}} + \underbrace{\int d^3r V_{ext}(r)n(r)}_{E_{ext}}$$

Variational principle:

$$\frac{\delta\left(E[\phi_i,\phi_i^*] + \lambda\langle\psi|\psi\rangle\right)}{\delta\phi_a^*} = 0 \qquad \Rightarrow \text{N Hartree-Fock-Equation}$$

Hohenberg-Kohn Theorem

Theorem: "There is a variational functional for the ground state energy E[n] of the many electron problem in which the varied quantity is the electron density."

Hamiltonian: $H = T + U + V_{ext} = H_0 + V_{ext}$

N particle density: $n(r) \equiv \left\langle \Psi \left| \Psi^{\dagger}(r)\Psi(r) \right| \Psi \right\rangle$

Universal functional: $F[n(r)] \equiv \left\langle \Psi \left| T + U \right| \Psi \right\rangle$

$$E_{V_{ext}}[n(r)] \equiv \int dr V_{ext}(r) n(r) + F[n(r)]$$

P. Hohenberg and W. Kohn,Phys. Rev. **136**, B864 (1964)

Free Electron Gas

Fermi gas (non-interacting electron gas): DOS $d^3n = 2 \cdot \frac{V}{(2\pi)^3} d^3k$

$$\left.\begin{aligned} N &= \frac{V}{3\pi^2} k_F^3 \\ T &= \frac{V\hbar^2}{10m} k_F^5 \end{aligned}\right\} \qquad t = \frac{T}{V} = \frac{3}{10} \frac{\hbar^2 (3\pi^2)^{2/3}}{m} n^{5/3}$$

Interacting electron gas: $E_{HF} = T + E_{direct} + E_{XC} + E_{ext}$

$\Rightarrow$ exchange term $\qquad e_{XC} = \frac{E_{XC}}{V} = -\frac{3}{4\pi} e^2 (3\pi^2)^{1/3} n^{4/3}$

Simplest DFT: Thomas-Fermi theory

- Positive backgroud field (jellium model)
- T of Fermi gas
- Drop exchange term

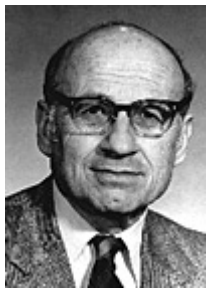
$\Rightarrow E_{TF} = E[n]$

Kohn-Sham Theory

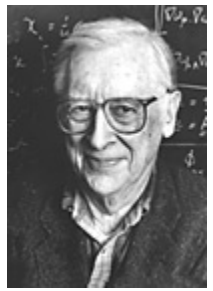
The Nobel Prize in Chemistry 1998

Kohn: "for development of density-functional theory"

Pople: "for development of comput. methods in quant. chemistry"



Walter Kohn



John A. Pople

Kohn-Sham functional:

$$E_{KS}[\phi_1,..,\phi_N] = \underbrace{\sum_i \int d^3r \frac{\hbar^2}{2m} |\vec{\nabla}\phi_i|^2}_{T} + \underbrace{\frac{1}{2} e^2 \iint d^3r d^3r \frac{n(r)n(r')}{|r-r'|}}_{E_{direct}} + E_{XC}[n] + \underbrace{\int d^3r V_{ext}(r)n(r)}_{E_{ext}}$$

Different exchange functionals:

Local Density Approx. (LDA)	$E_{XC}[n] \propto n^{4/3}$
Local Spin Density Approx. (LSD)	$E_{XC}[n] \propto (n_\uparrow^{4/3} + n_\downarrow^{4/3})$
General Gradient Approx. (GGA)	adding term $f(\vec{\nabla}n)$

Other: PW91, B3LYP

W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965)

Predictions of DFT

Atomization energy:

Method	Li_2	C_2H_2	20 simple molecules (mean absolute error)
Experiment	1.04 eV	17.6 eV	-
Theoretical errors:			
Hartree-Fock	-0.94 eV	-4.9 eV	3.1 eV
LDA	-0.05 eV	2.4 eV	1.4 eV
GGA	-0.20 eV	0.4 eV	0.35 eV

Si properties:

Property	Experiment	LDA	GGA
Lattice constant	2.35 Å	2.34 Å	2.36 Å
Bulk modulus	99 GPa	96 GPa	92 GPa
Band gap	1.17 eV	0.52 eV	0.7 eV

Summary of DFT Properties

Features:

- Ground-state theory (excitations can be treated with TDFT)
- Zero temperature theory (T=0^{o} K)
- High quality predictions for non-correlation effects

Justification:

"Justification of DFT is given through the quality of its predictions. However it is an *ab-initio* Method, since all parameters are determined *a priori* by general considerations."

Limitations:

- Phenomena which rely on correlation effects (superconductivity, Van der Waals, interactions) can not be predicted. Correlation effects are not built into wave functions.
- System size is limited by CPU power available.

Absolute observables are meaningless, only differences are sensitive quantities.

Implementation of DFT in VASP

VASP features:

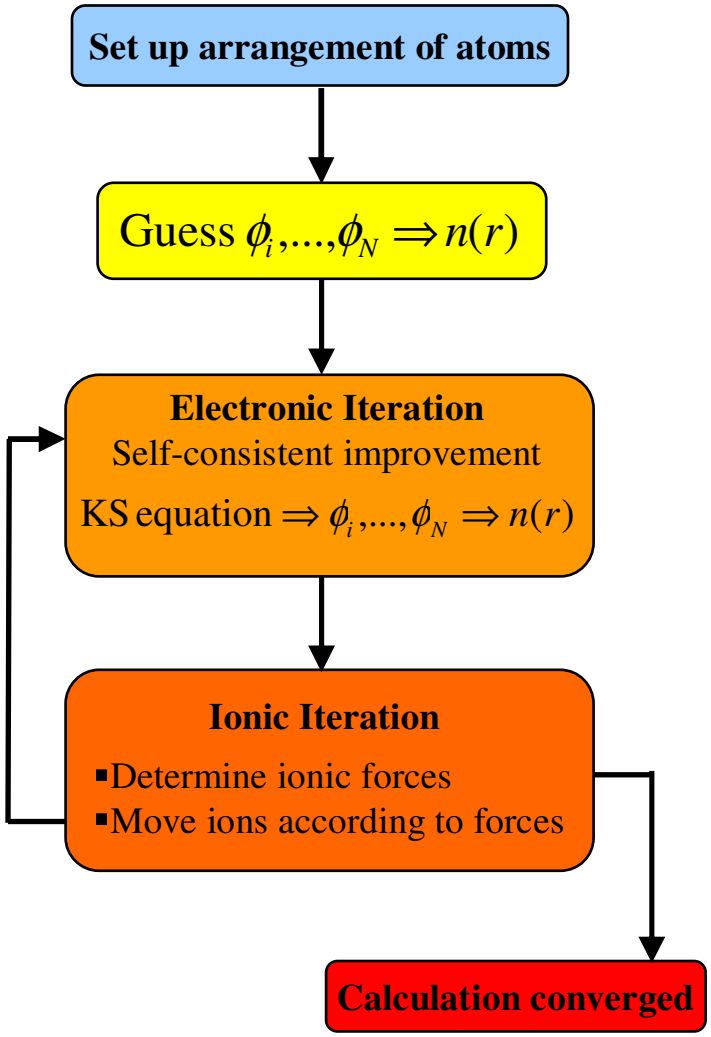
- Plane wave basis
- Ultra-soft Vanderbilt type pseudo-potentials
- Quantum-mechanical molecular dynamics (MD)

VASP output:

- Charge density and wave functions
- Relaxed ion location
- Total energy
- DOS
- …

Numerical features:

- Highly optimized serial and parallel version



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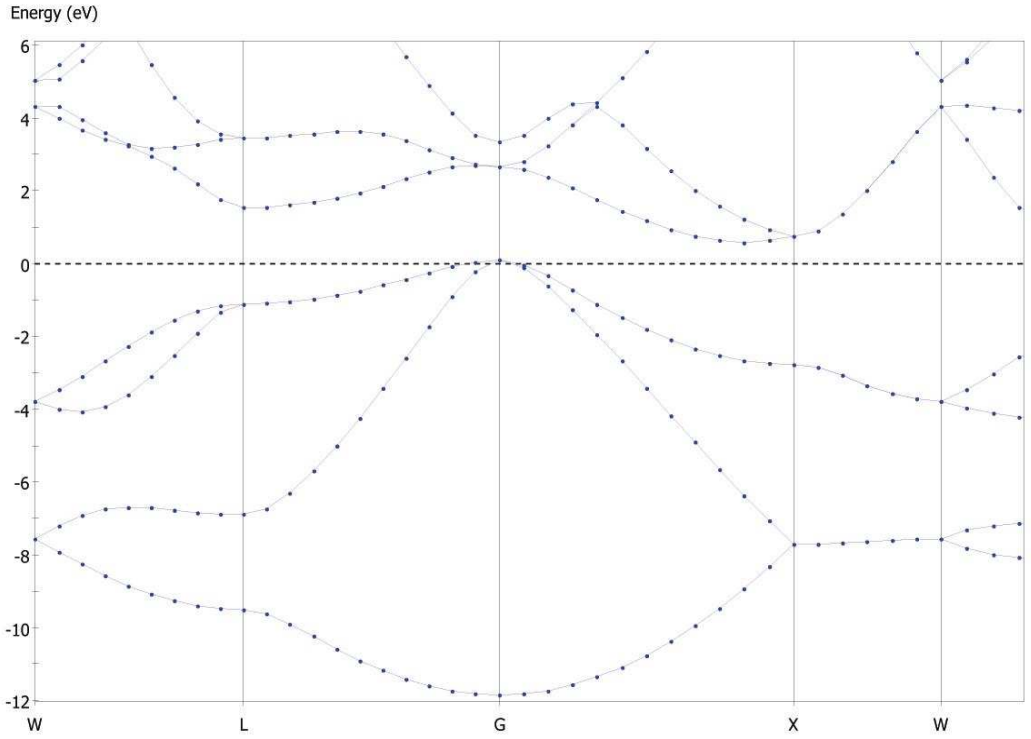
Sample Applications of DFT

- Formation energies (F model)
- Transition barriers (migration energies, diffusivities)
- Interface properties (segregation coefficients)
- Bulk properties (lattice constant, bulk modulus, strain effects)
- Band structure (effect of dopants and defects)

Band structure

- DFT band gap 0.7eV (experimental 1.12eV)
- Study band structure changes due to:
  - Dopants
  - Defects
  - Strain
  - Temperature
  - …

Si band structure

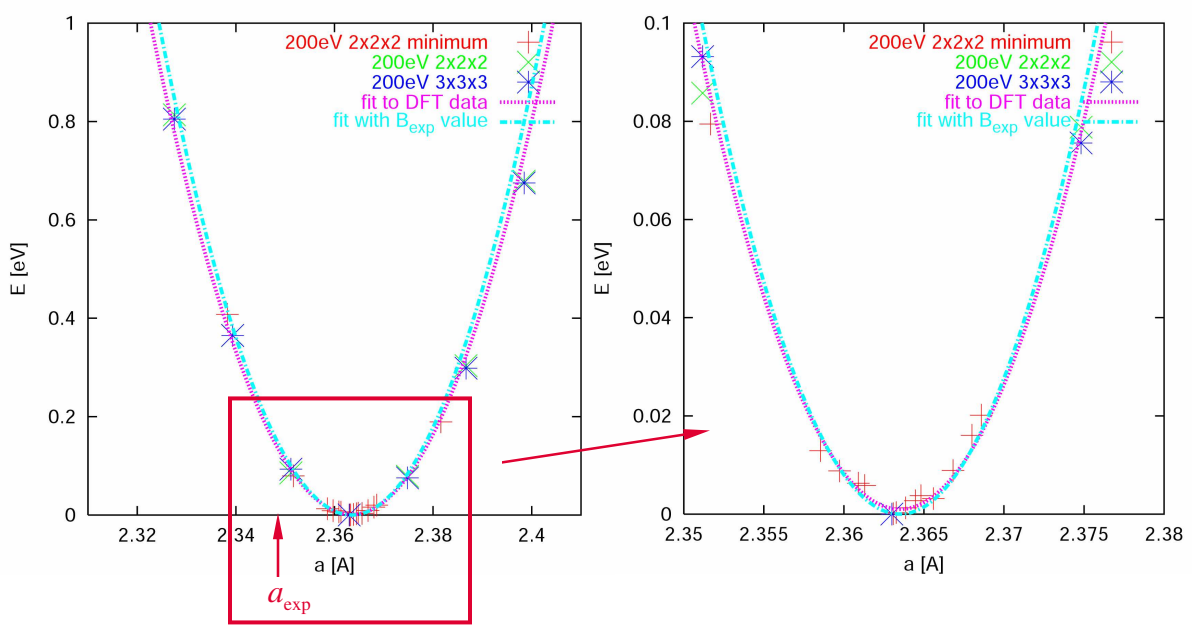


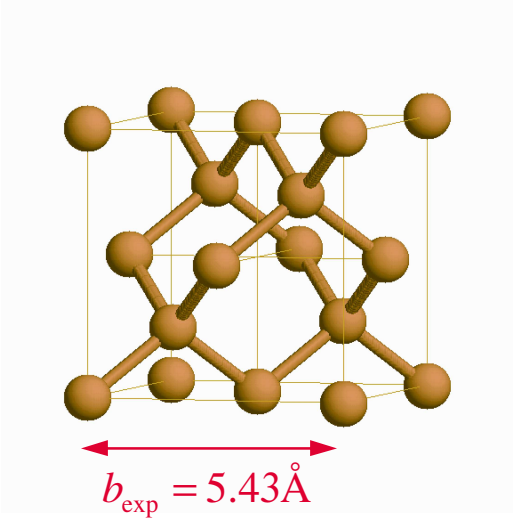
DFT calculation W. Windl

Remember: DFT predicts differences correct

Silicon Bulk Properties

Lattice Constant: Calculate E at varying box size





$$a = \frac{\sqrt{3}}{4} b$$

Bulk modulus:

$$B(V) \equiv V \frac{d^2 E(V)}{dV^2}$$

$$E(a) \Rightarrow E(V)$$

B_{exp} = 99 GPa

B_{DFT} = 92 GPa

Straining Si with Pb

Strain effect of impurities: Ge, Sn, Pb

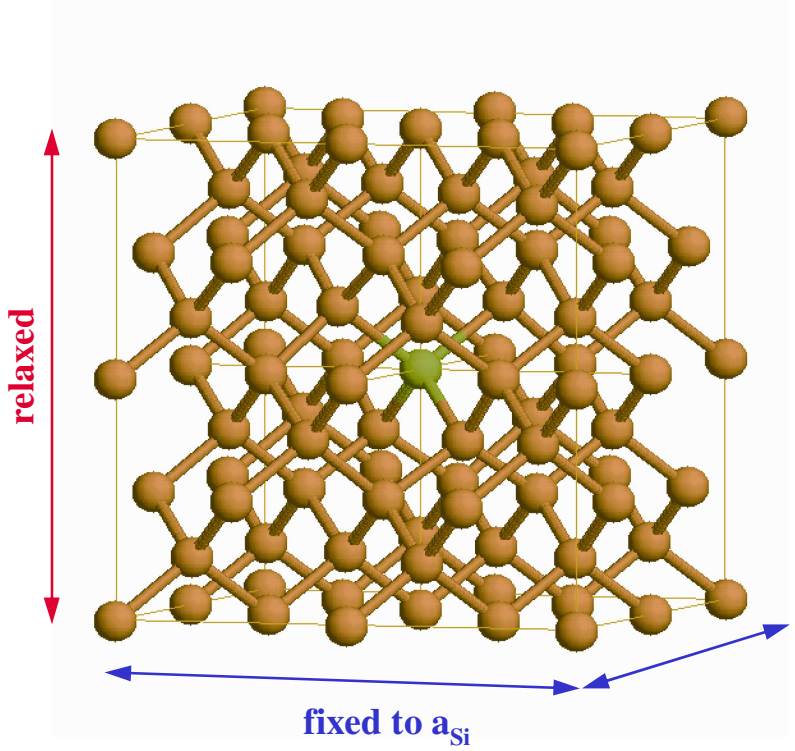
$$a_{eff} = \frac{C_{Si}}{C_S} a_{Si} + \frac{C_{Pb}}{C_S} a_{Pb}$$

Strain: $\delta = \dfrac{a_{eff} - a_{Si}}{a_{Si}}$

Simple Model: ~ 1% strain

DFT: 0.75% strain

Microscopic strain effects



64 atom supercell
(63 Si + 1 Pb) $\Rightarrow$1.56% Pb

$C_{Pb} \approx 7.8 \cdot 10^{20}\,\mathrm{cm}^{-3}$

Transition Paths and Barriers

Goal: Find transition paths and barriers

Theory: (harmonic) transition state theory (hTST)

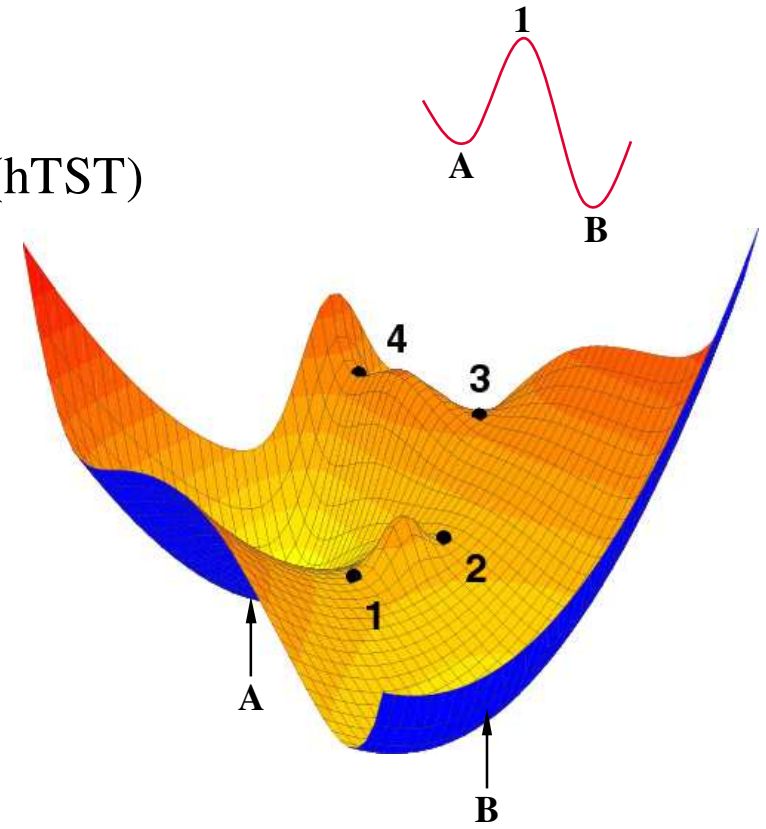
$$D = D_0 \cdot e^{-\frac{E_m}{kT}}$$

Methods:

- Nudged elastic band method (NEB)
- Dimer method

Challenging because:

- High dimensional
- Bumpy energy surface
- End up in unwanted local minimum
- Do not find all reaction paths

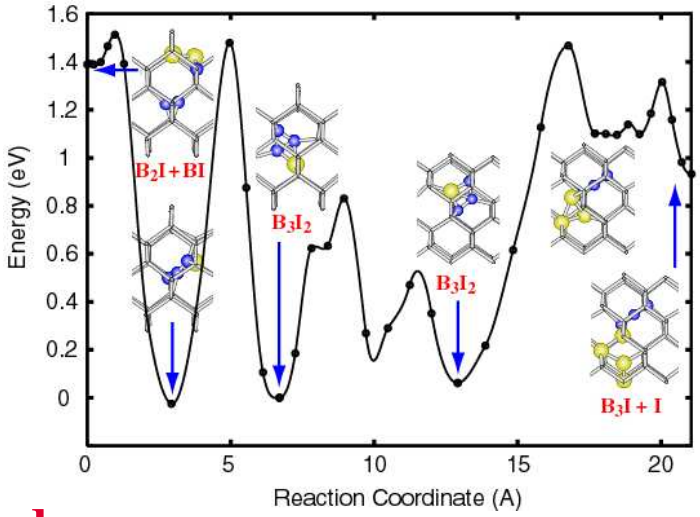


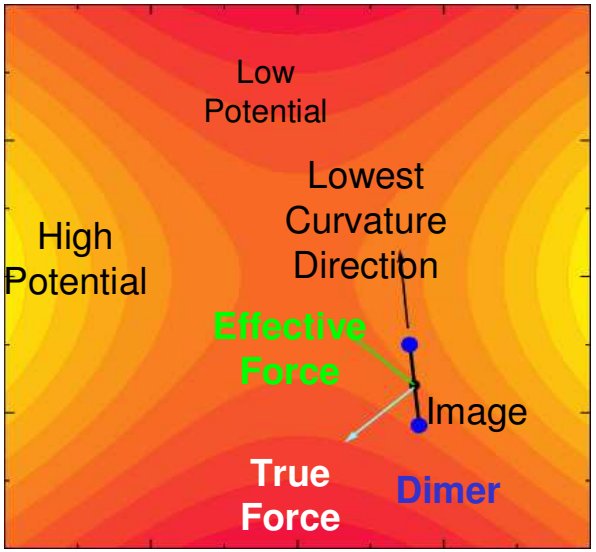
Energy surface of 3N dim. space
(N # of atoms)

NEB and Dimer Method

NEB method:

- Chain of "images" connected by springs
- Springs ensure equidistance between images
- Force minimization converges into possible reaction path
- Initial and final state need to be known





Dimer method:

- Two images form a dimer
- Dimer moves along the lowest curvature mode
- Numerically a little more expensive than NEB
- Do not need to know final state

⇒ **Possibility of exploring unknown terrain**

G. Henkelman and H. Jónsson, *J. Chem. Phys*, **111**, 7010 (1999)

Motivation: Fluorine Study

Importance of fluorine: B implantation with BF_2

Potential Advantages:

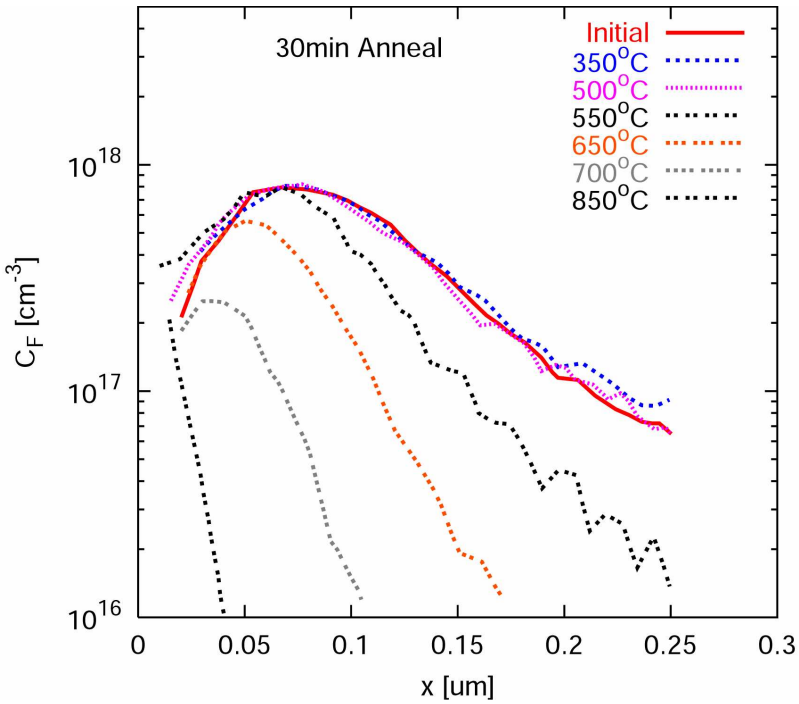
- Enhances B activation (Huang *et al.*)
- TED reduction (Park *et al.*)

Experiment:

Anomalous fluorine diffusion Behavior (Jeng *et al.*)

30keV F+ implant ⇒ anneal

QF = 1013 cm-2



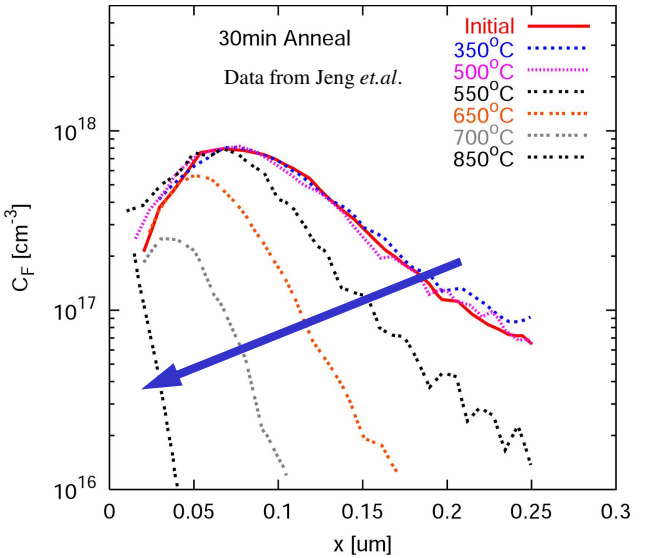
Motivation: Fluorine Study

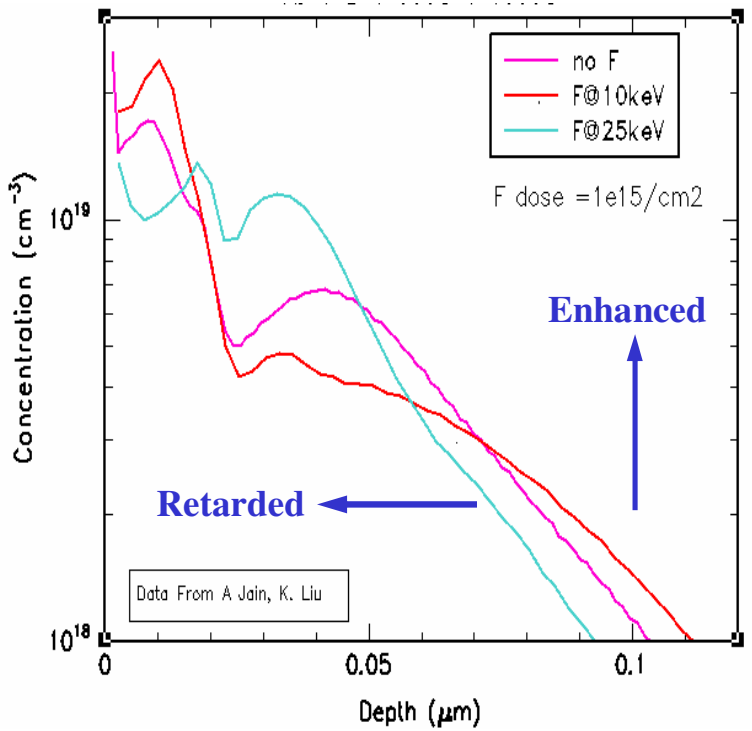
Why study F ?

- Fluorine retards/enhances B, P
- B activation

F behavior is complex:

- Exhibits anomalous diffusion
- Mechanism debatable:
  - B + F interaction ?
  - F interacts with Si point defects (I,V) ?





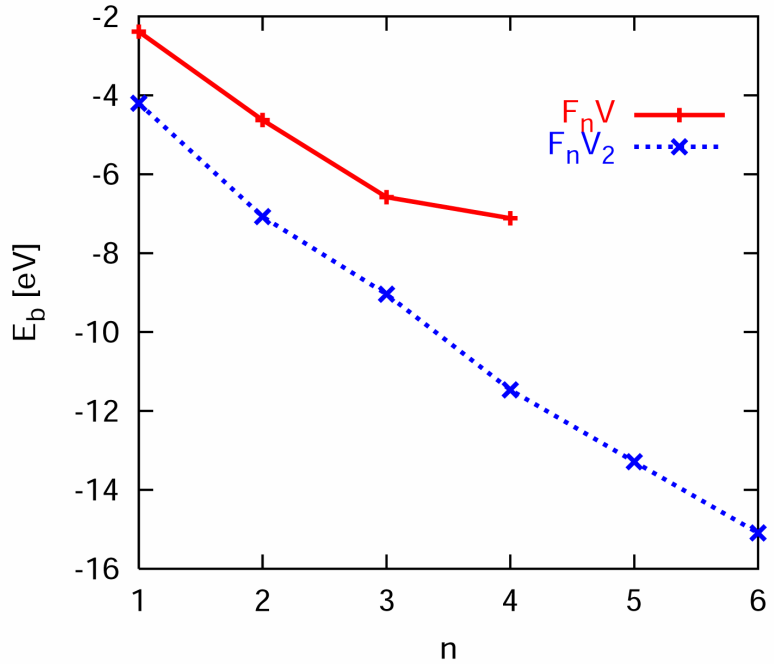
No comprehensive model available in literature

F_nV_m Clusters

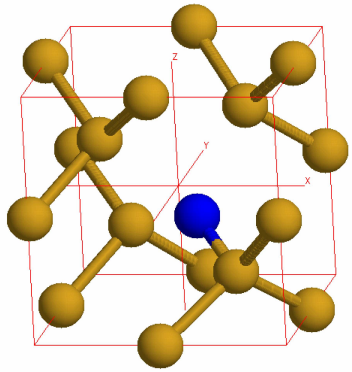
Idea: Fluorine decoration of vacancies ⇒ immobile clusters

DFT predicts

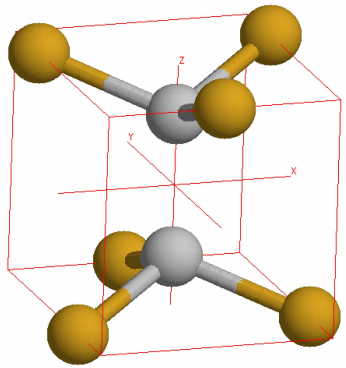
Reference:
F_i, V



FV:



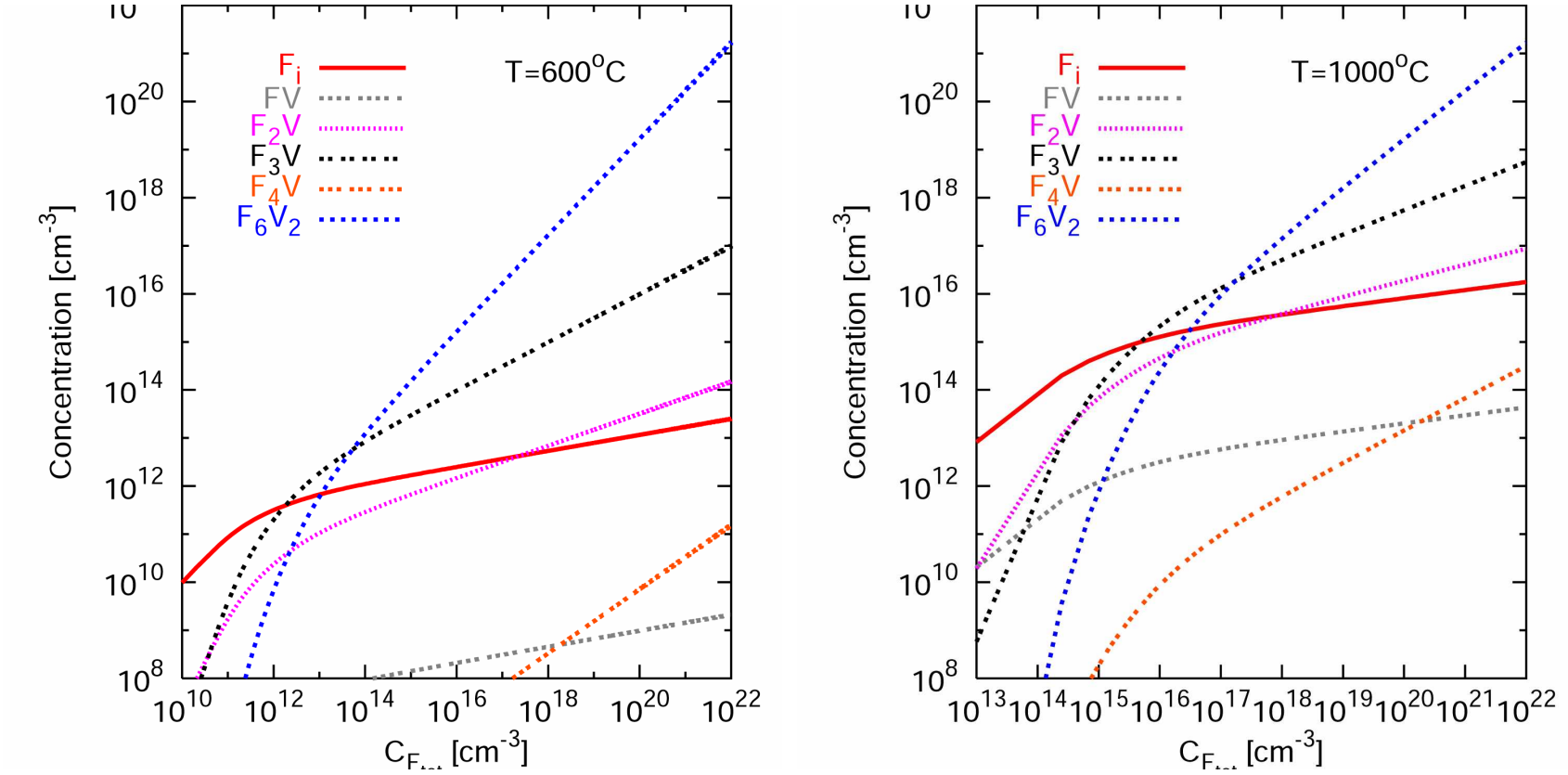
V_2:



Results:

- F_nV_m clusters have large binding energies
- E_b drop-off $F_3V \rightarrow F_4V$ (crowding)

Local Equilibrium



⇒ F_3V and F_6V_2 clusters favored for moderate/high F concentrations

Extended Fluorine Continuum Model

Formation:

$F_nV_m + F_i \leftrightarrow F_{n+1}V_m$

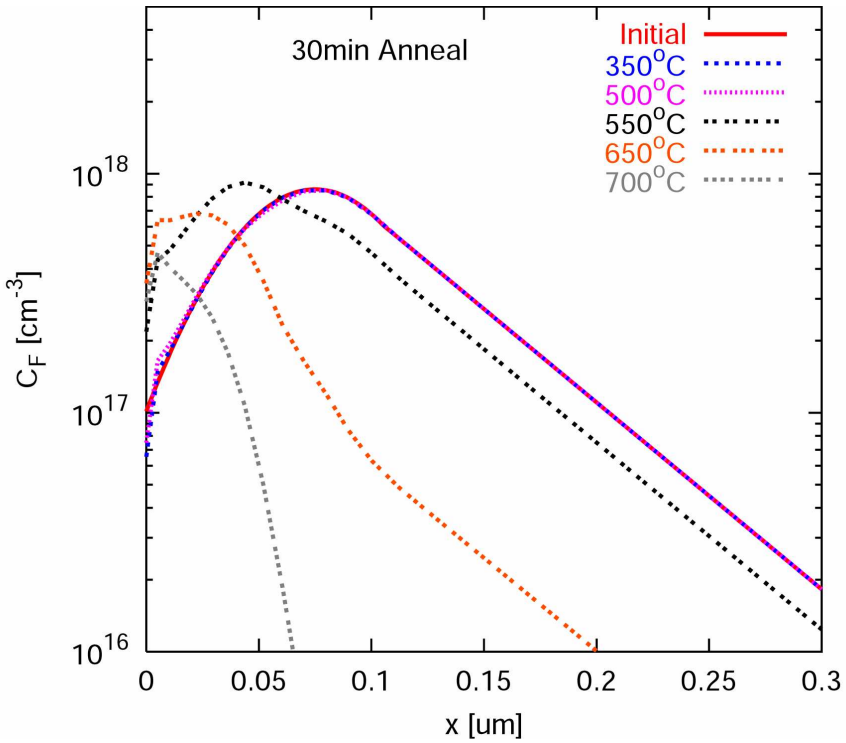
$F_i + I \leftrightarrow FI$

Dissociation:

$F_nV + I \leftrightarrow n\,F_i$

$F_nV_2 + I \leftrightarrow F_4V+(n-4)F_i$

$FI + V \leftrightarrow F_i$

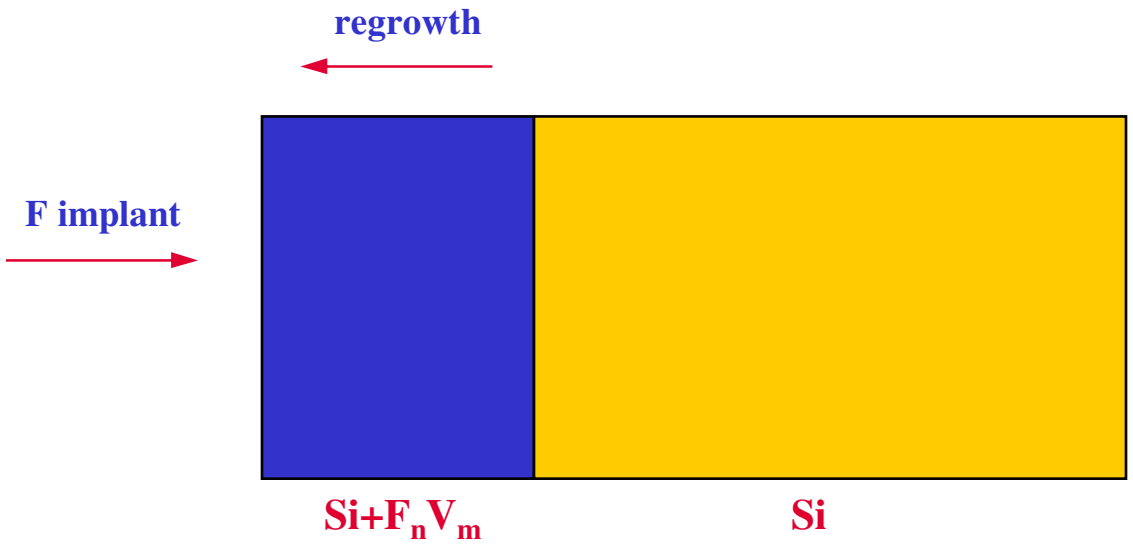


Defect Model & Boundary Conditions:

- Extended defect model including I_n, V_n, and {311} defects
- Thin oxide layer on surface (20 Å) (segregation & diffusion of F_i)

M. Diebel and S.T. Dunham, Mat. Res. Soc. Symp. Proc. **717**, Warrendale, PA, 2002

Pre-amorphizing Implant



Possible Interactions:

F causes the incorporation of excess V during regrowth

$\Rightarrow$ TED reduction due to excess V

$\Rightarrow$ B activation due to reduced B/I clusters

Both seen in pre-amorphized samples

Simplified Fluorine Model

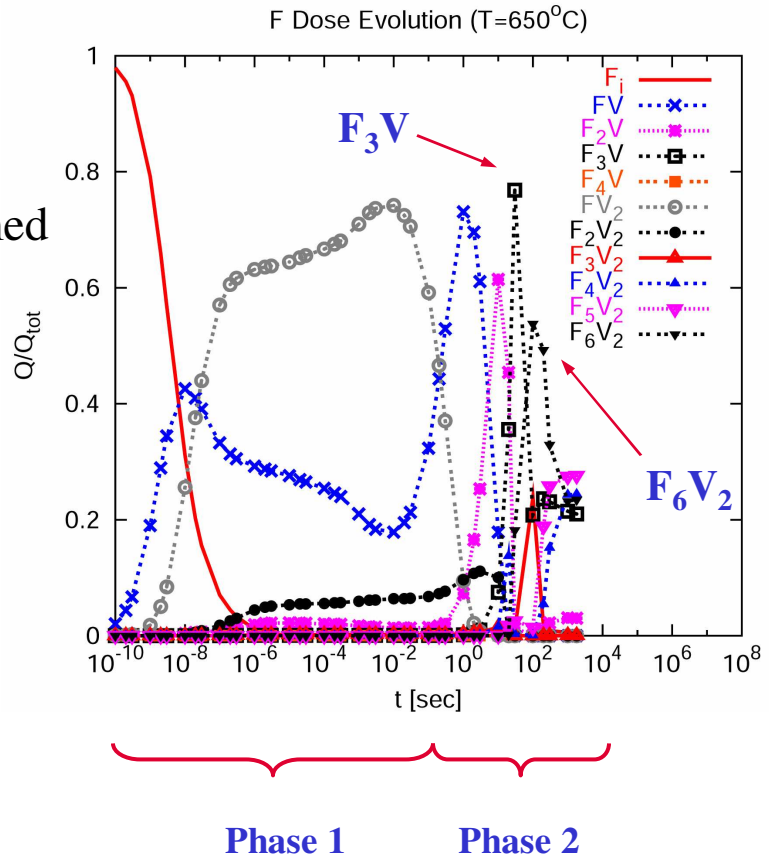
Mechanism:

- F_i diffuses fast and forms FV
- Via cascade larger F_nV_m clusters are formed
- F_nV_m dissolves in presence of I

$\Rightarrow$ assume first two steps are fast

Simplified model:

- Implant large stable F_nV_m cluster (F_3V)
- Implant additional I (shifted Rp)
- Dissolve F_3V via: $F_3V + I \leftrightarrow 3\ F_i$



Higher T will shift formation to earlier times

Model Implementation

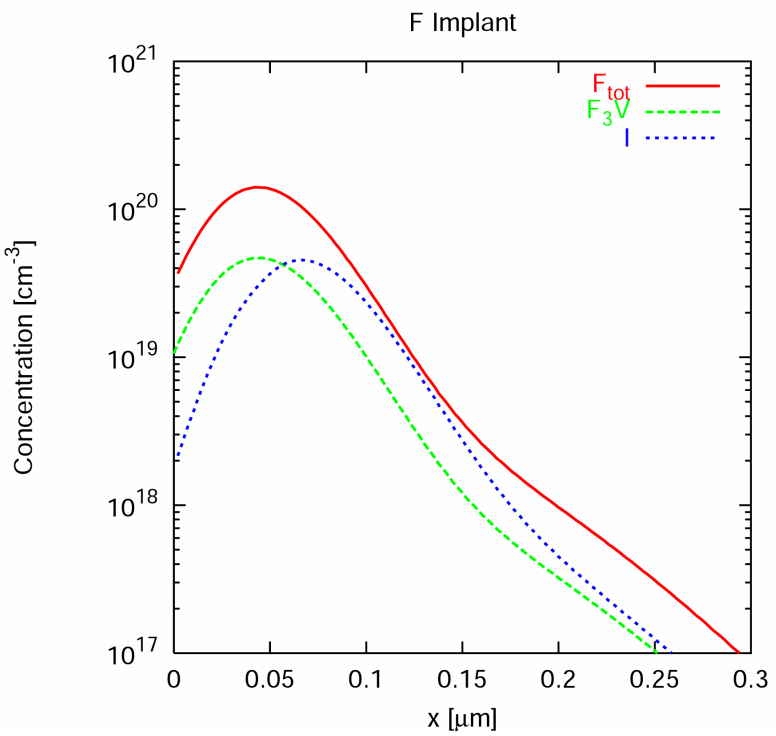
Implant:

- $F_3V \Rightarrow$ effectively +2/3 I
- Interstitials (40% shifted Rp) $\Rightarrow$ +1/3 I

Reactions: $F_3V + I \leftrightarrow 3\ F_i$

Parameters:

- F implant moments (analytic expression)
- d.scale, d.plus $\Rightarrow$ **a/c**
- F_3V dissolution rate
- F_i diffusivity



Advantage:

Model can treat sub-amorphizing and amorphizing conditions together.

Fluorine Model

Sub-amorphizing condition:

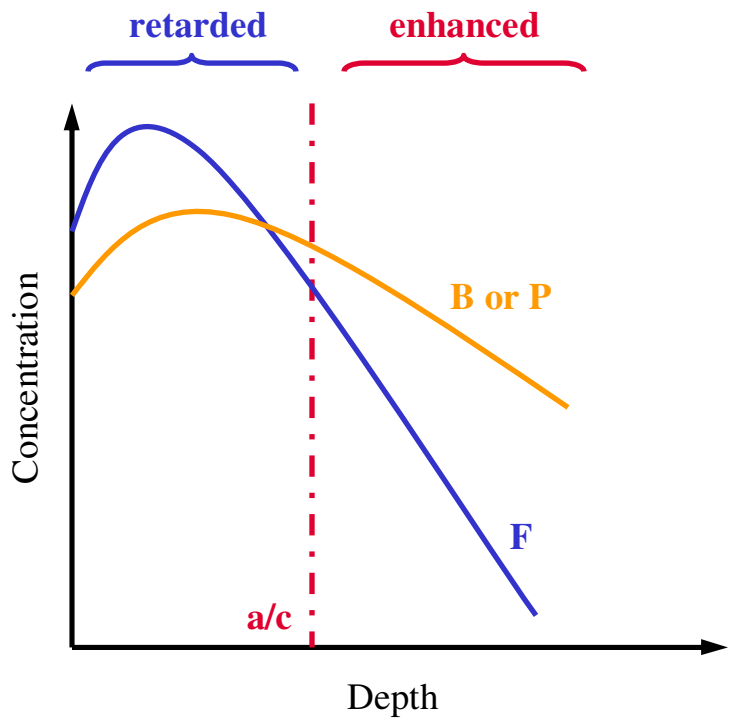
TED effect

Amorphizing condition:

Retardation effect

Effect depends on:

- F concentration
- Dopant concentration
- I concentration



Calibration to SIMS Data

Fluorine only (dose loss)

Fluorine + dopants (fluorine effect on dopants, a/c depth)

	S/D high E + high Q	**MDD** low E + high Q	**Pocket** high E + low Q
Boron (PMOS)	✓	✓	✓
Phosphorus (NMOS)	✓		✓

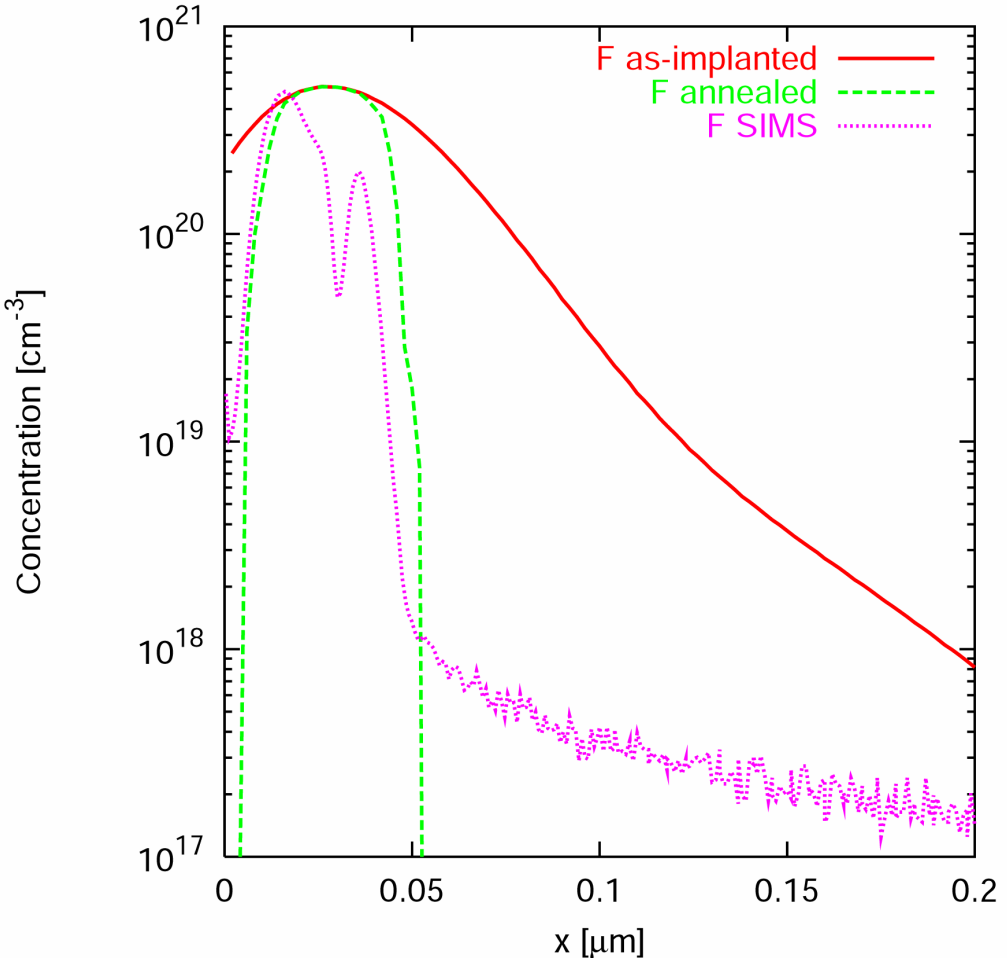
Fluorine Only

Analysis:

- General trend correct
- Underestimates dose loss

Experiment:

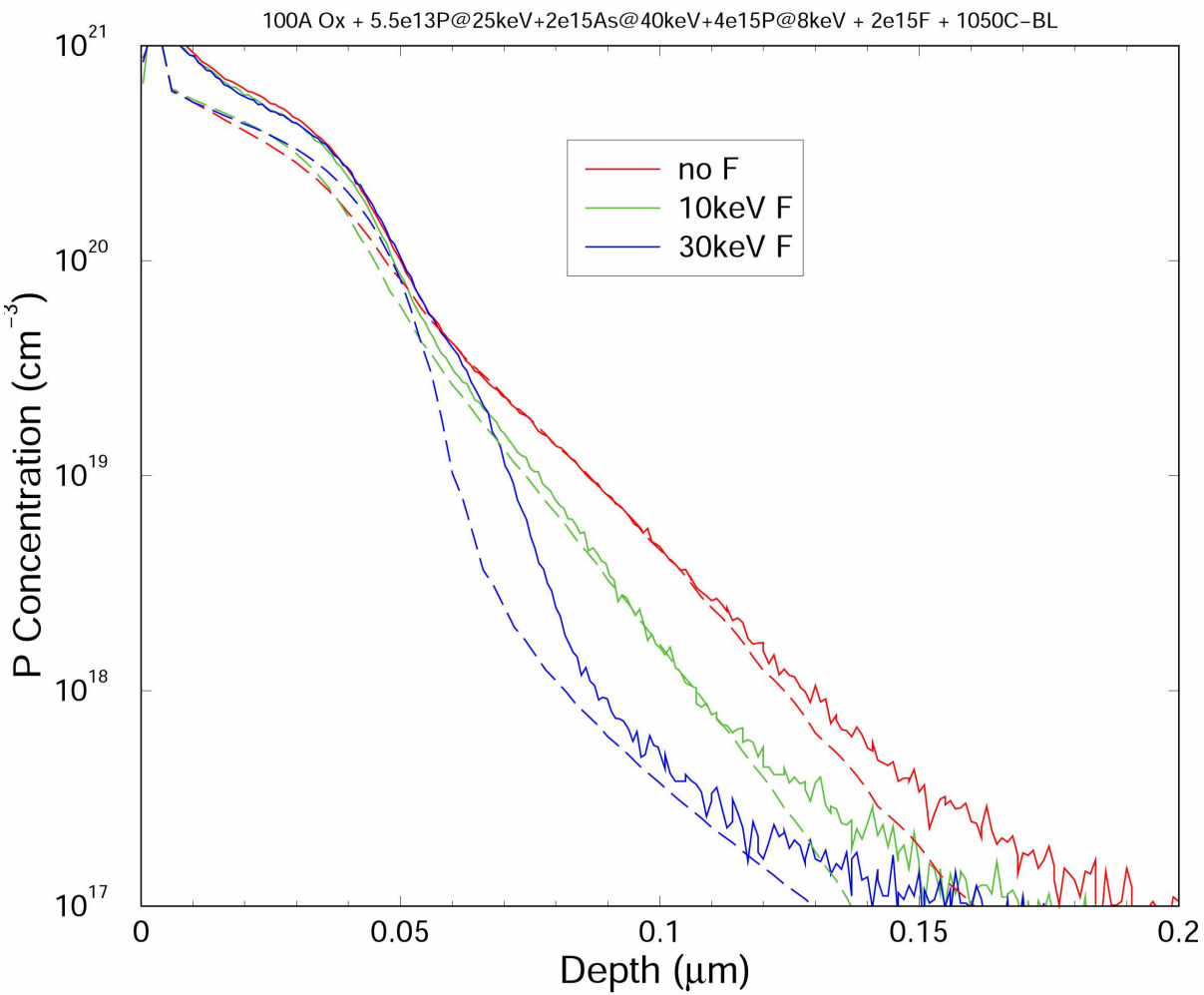
- 100A Poly Ox
- **F 20keV 3e15**
- 1050C spike anneal



Phosphorus-Fluorine S/D

Analysis:

- Trend correct
- Overestimates retardation



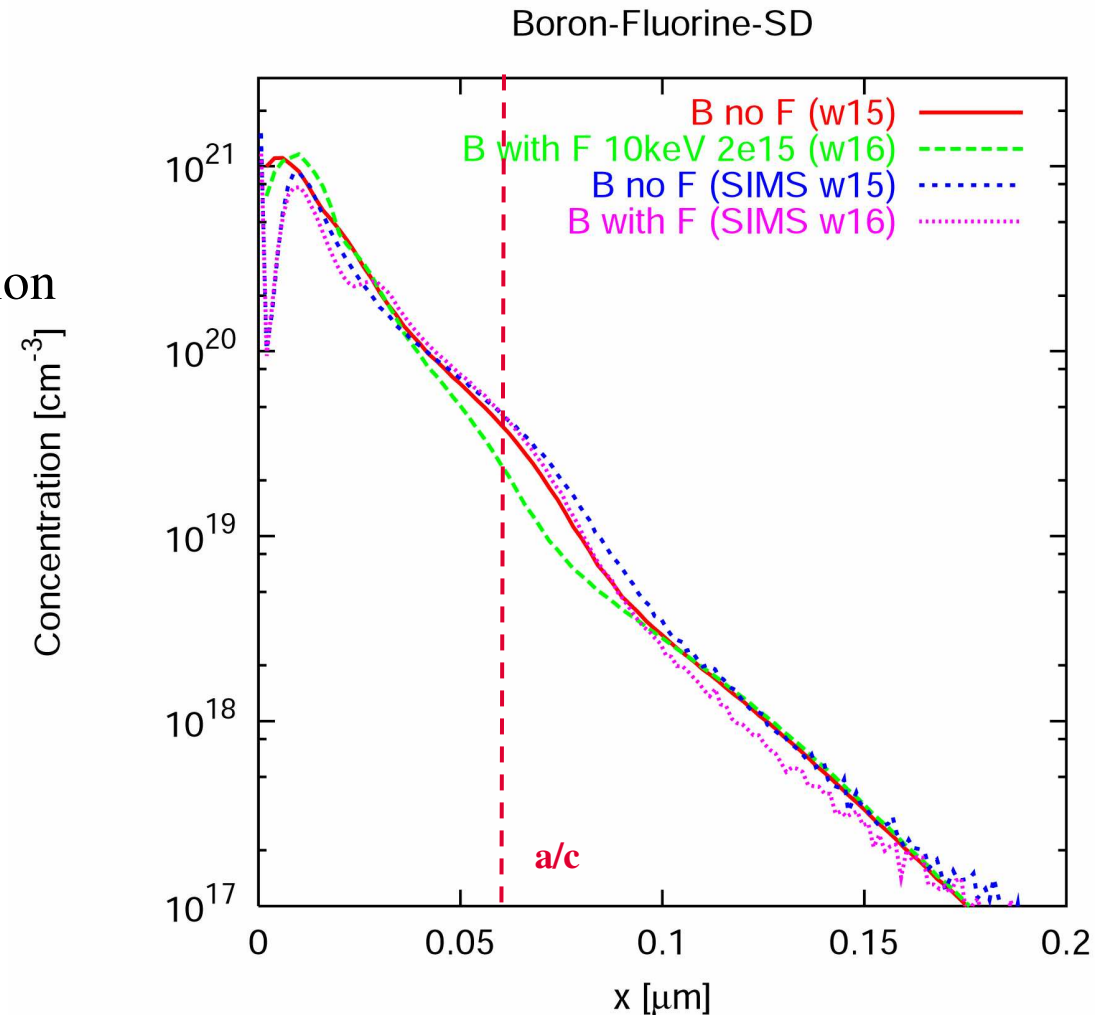
Boron-Fluorine S/D

Analysis:

- Trend correct
- Overestimates retardation

Experiment:

- P 25keV 5.5e13
- As 40keV 2e15
- P 10keV 1.5e15
- **F 10keV 2e15**
- 1050C spike anneal



Boron-Fluorine Pocket

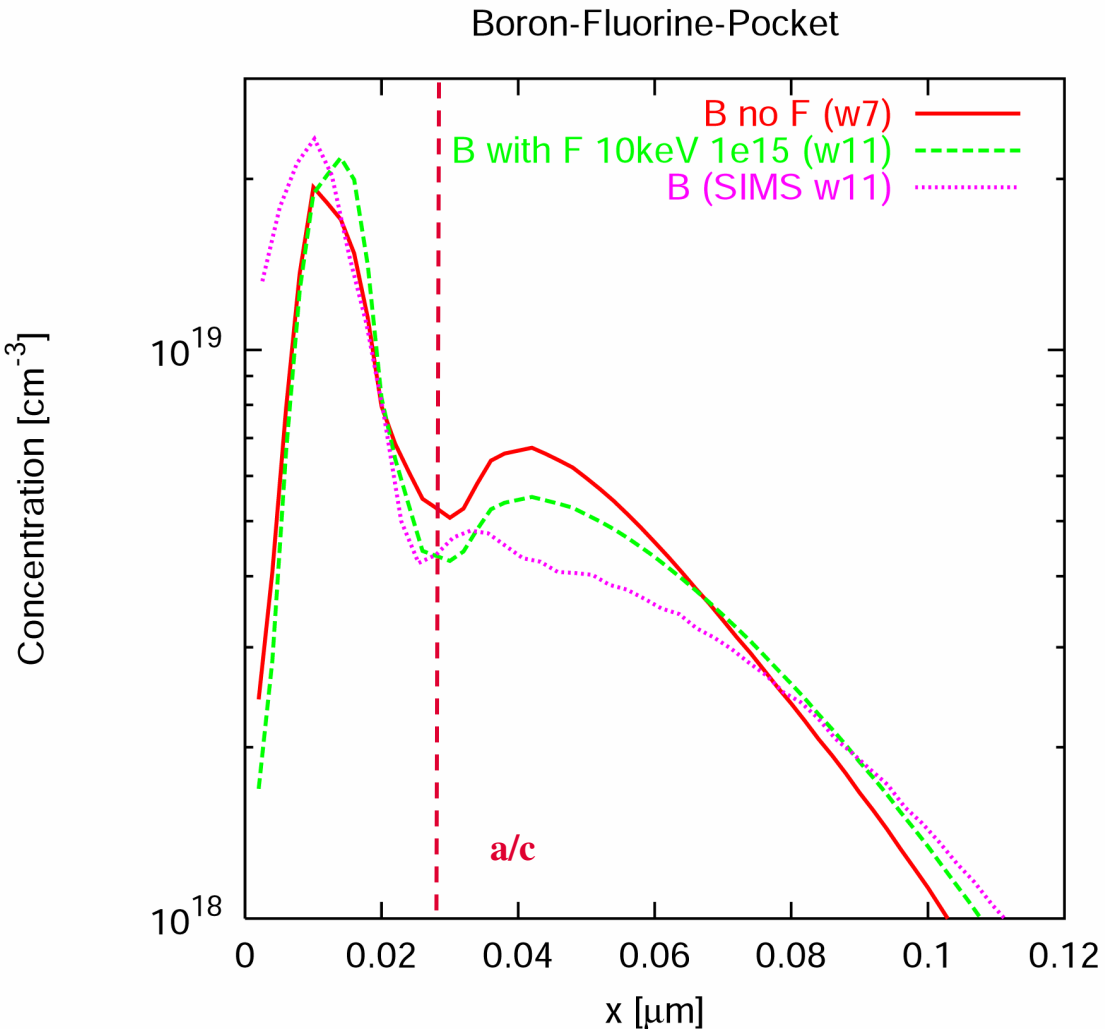
Analysis:

- Tail diffusion **enhanced**

Experiment:

- As 5keV 2e15
- B 10keV 6e13
- **F 10keV 1e15**
- 950C spike anneal
- 1050C spike anneal

Lot: Fluorine-Effects I
Amitabh Jain and Kaiping Liu



Phosphorus-Fluorine Pocket

Analysis:

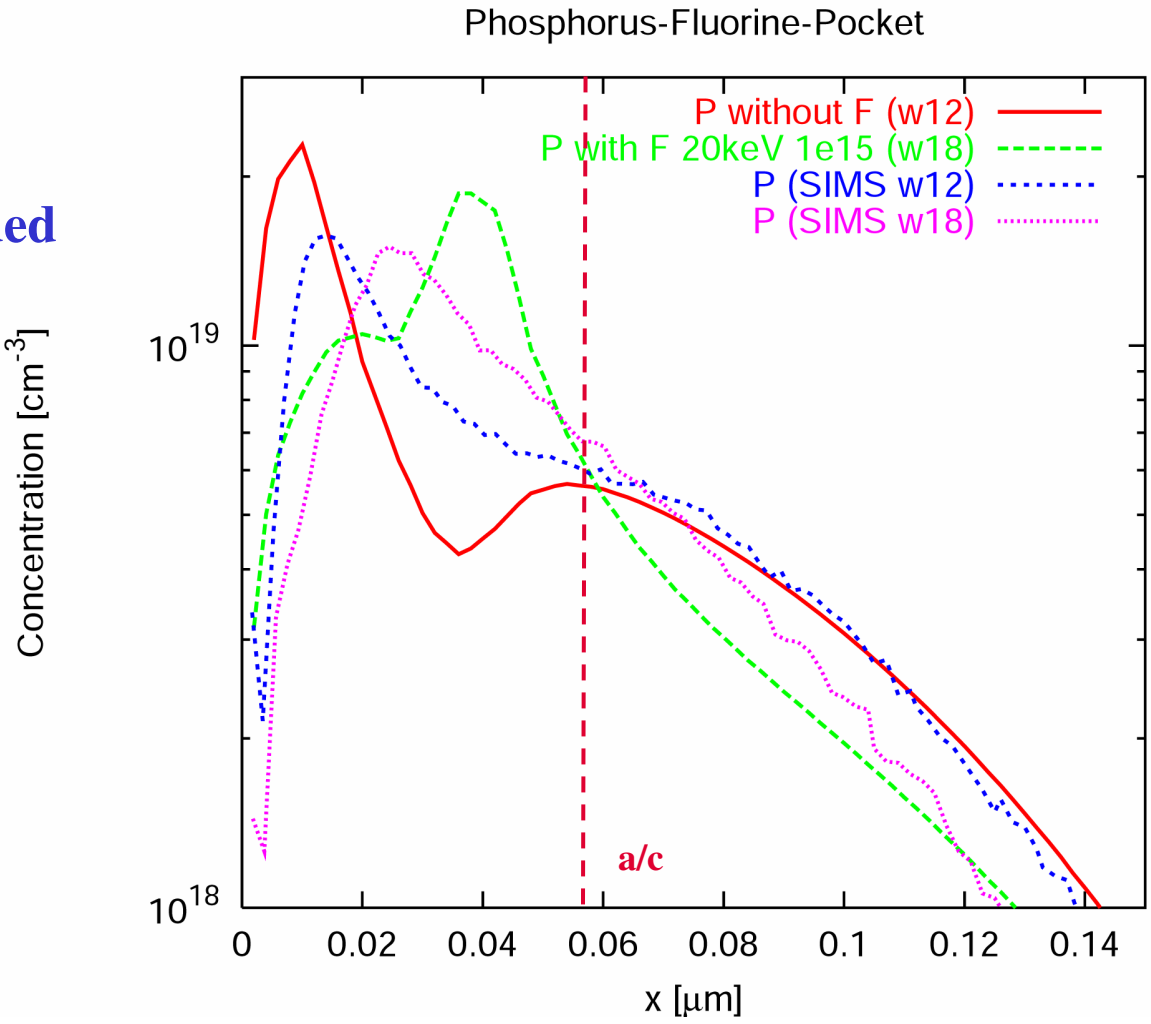
- Tail diffusion **retarded**

Experiment:

- Sb 30keV 3e13
- **F 20keV 1e15**
- BF_2 6keV 1e15
- 950C spike anneal
- 1050C spike anneal

Lot: Fluorine-Effects II

Amitabh Jain and Kaiping Liu



Summary and Conclusion

Summary: New F_3V model developed for TS4

Predicts:

	S/D high E + high Q	**MDD** low E + high Q	**Pocket** high E + low Q
Boron (PMOS)	**Ok**	**Poor**	**Ok**
Phosphorus (NMOS)	**Good**		**Ok**

Confirms DFT calculation:

F effect is primarily due to changes in I and V, not B-F or P-F binding.

Problems: F_3V model predicts stronger retardation effects

Possible improvements:

- Initial conditions (formation of F_nV_m important)
- Larger clusters (2 or more clusters)

References

Density-Functional-Theory

- G.F. Bertsch, Les Houches Lecture July 2000
- G.F. Bertsch and K. Yabana, Lecture Notes Graduiertenkolleg Rostock, Germany 2001/Summer School Trieste, Italy 2001
- http://www.nobel.se

F Diffusion Model

- M. Diebel and S.T. Dunham, Mat. Res. Soc. Symp. Proc. **717**, Warrendale, PA, 2002.

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