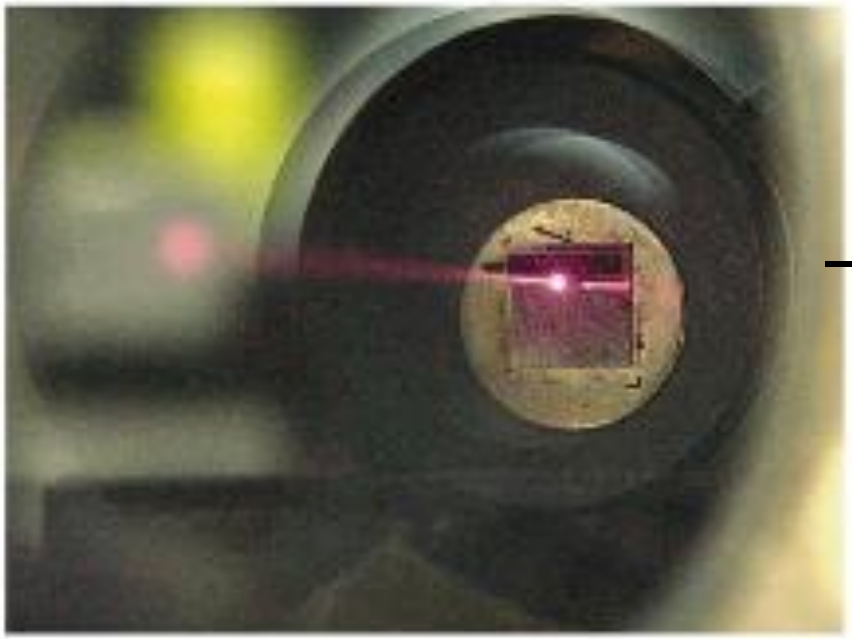
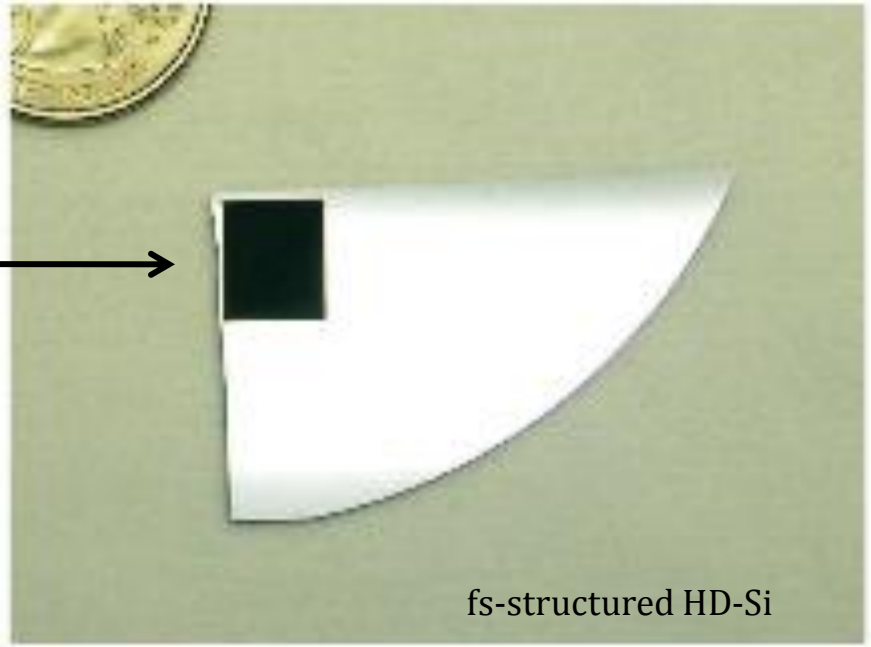
Understanding non-equilibrium structures with multi-data set fitting and component analysis

Dr. Bonna Newman
MIT Laboratory for Photovoltaic Research

NSLS XAFS Workshop
November 5, 2010

Making Hyperdoped Silicon





Pulsed laser processing

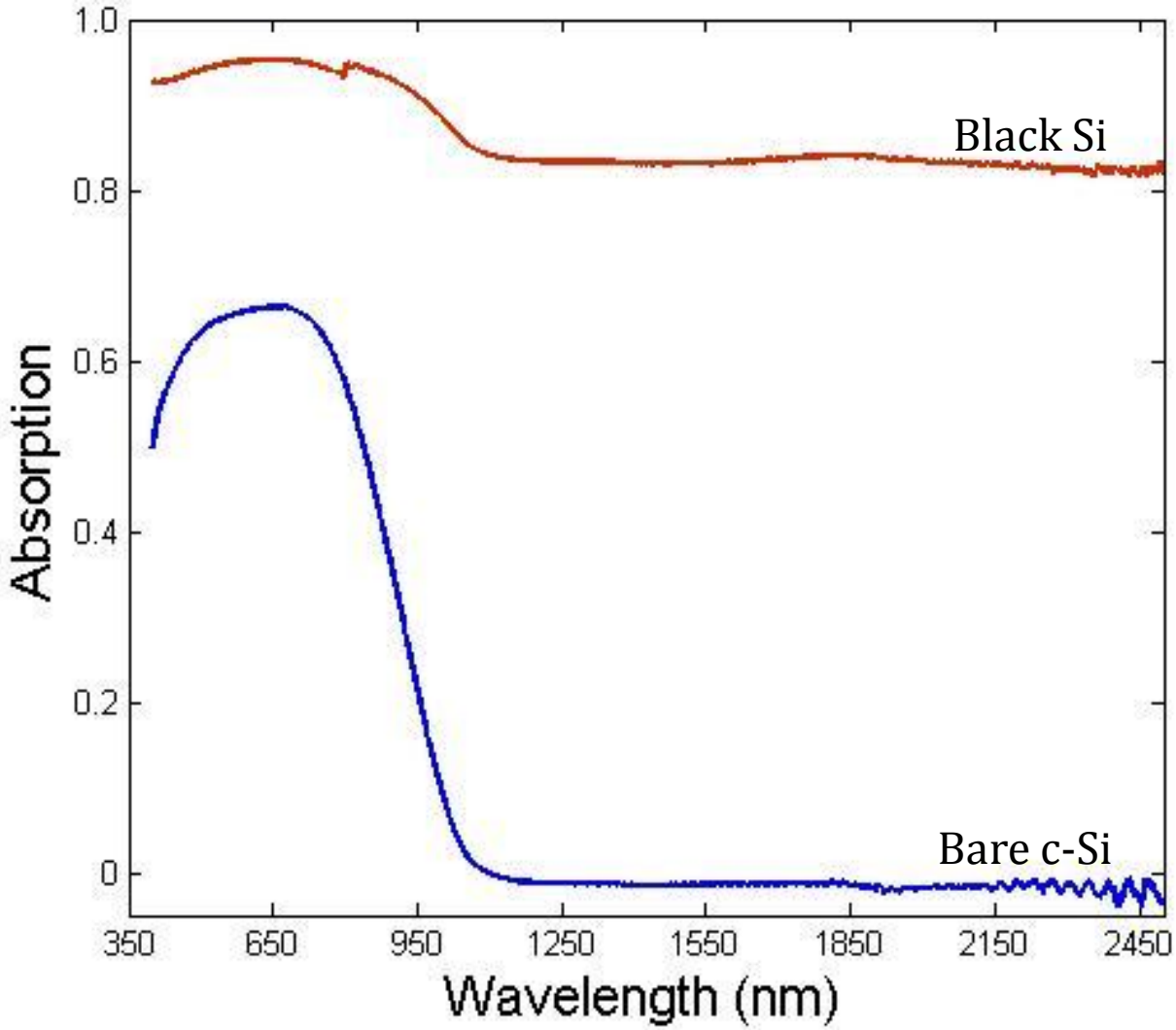
(1) fs-laser structuring, in the presence of a source of S, Se, or Te atoms

(2) ion implantation and ns-laser melting

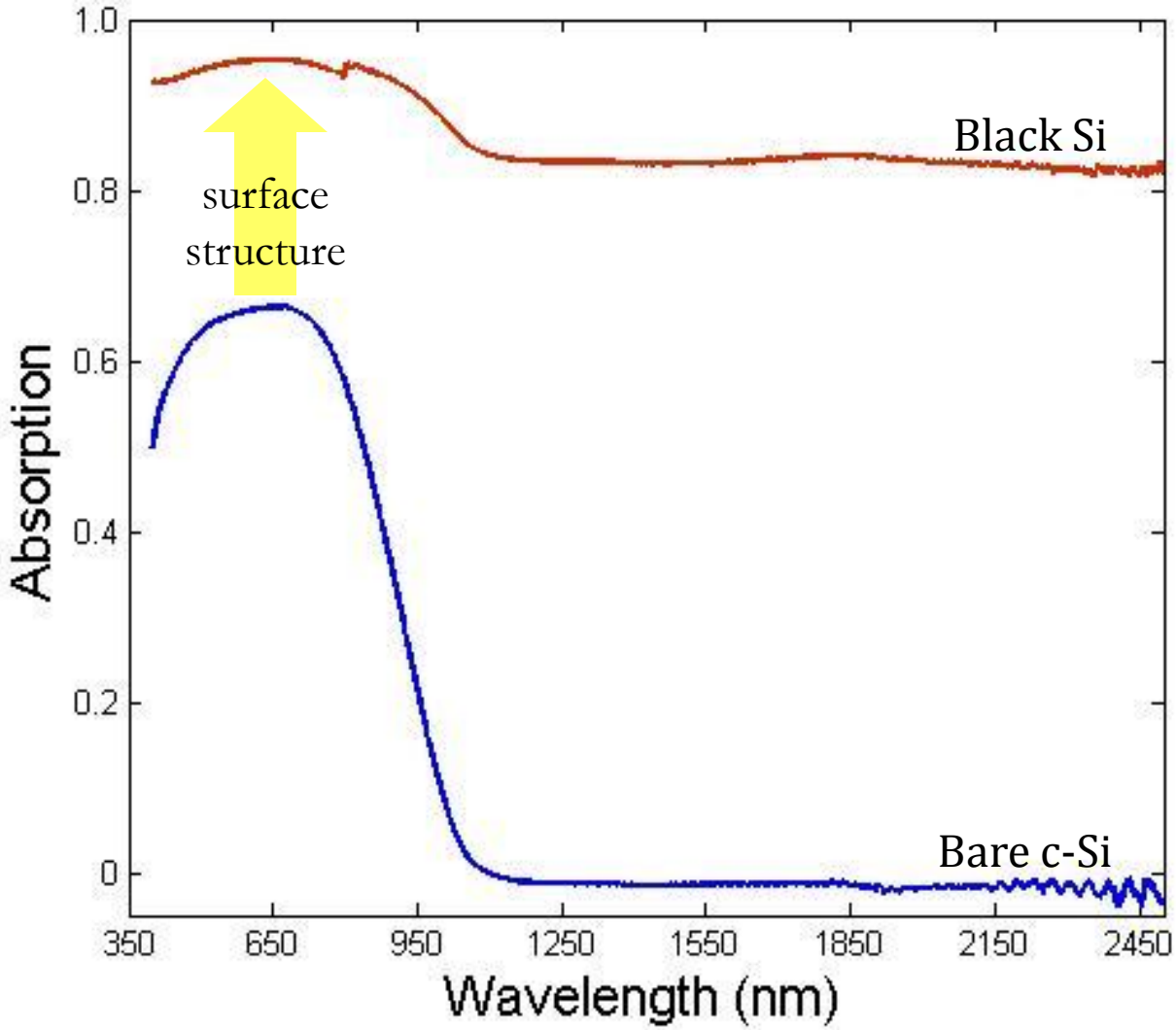
Dramatic change in optical properties!

Photos courtesy of E. Mazur

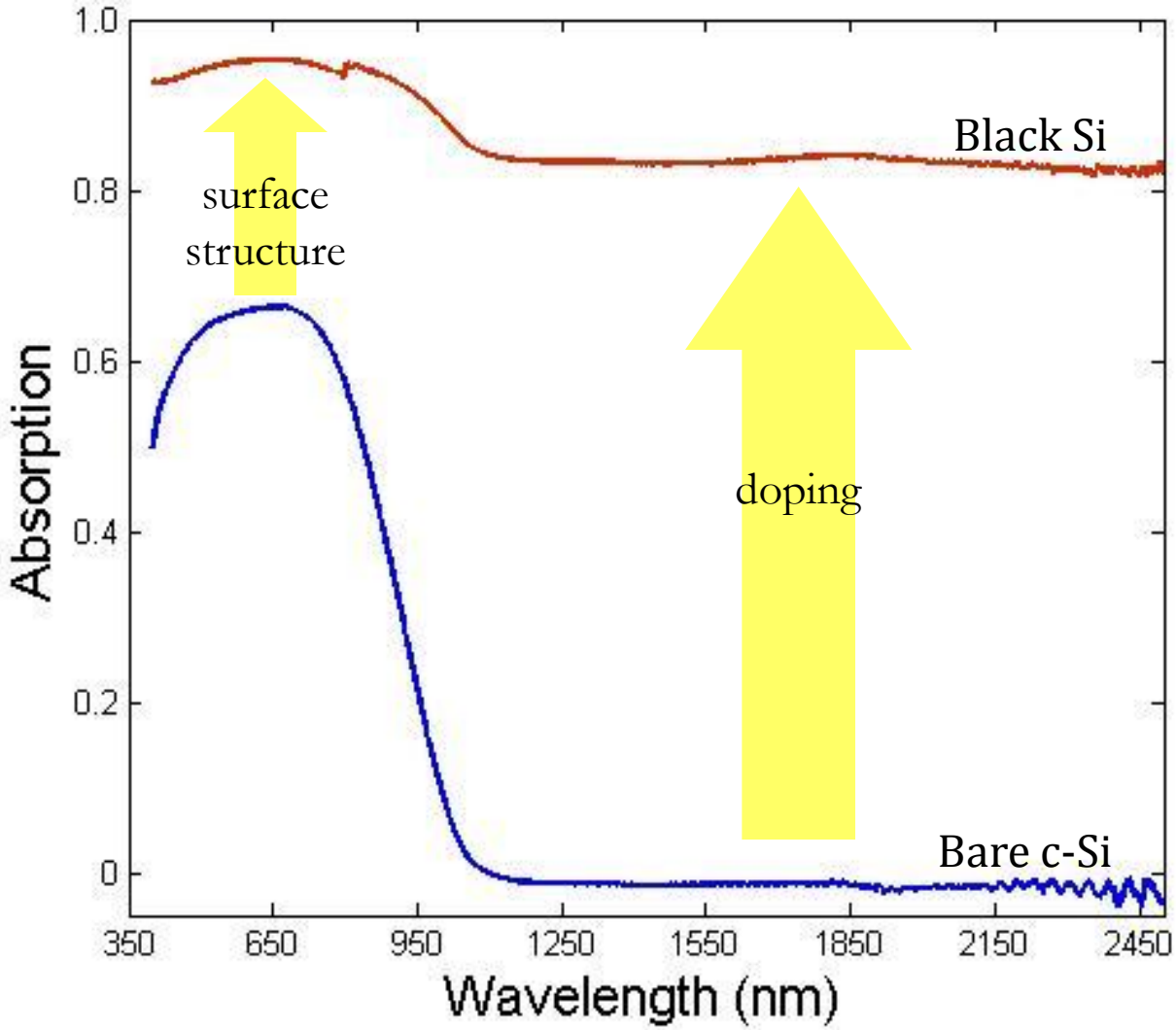
Absorption


1.0
0.8
0.6
0.4
0.2
0
Absorption
350
650
950
1250
1550
1850
2150
2450
Wavelength (nm)
Black Si
Bare c-Si

Absorption

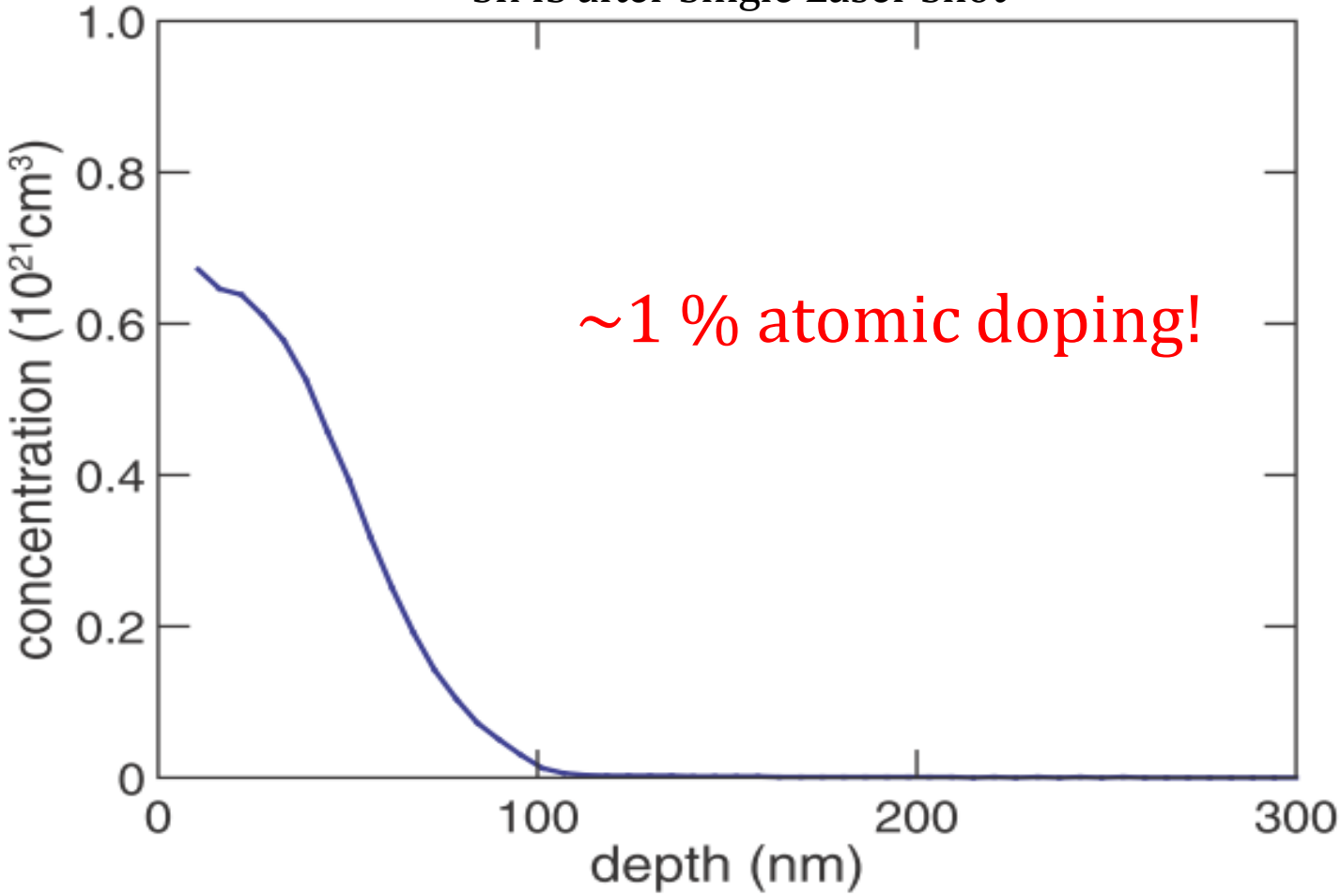

1.0
0.8
0.6
0.4
0.2
0
Absorption
350
650
950
1250
1550
1850
2150
2450
Wavelength (nm)
Black Si
surface
structure
Bare c-Si

Absorption


1.0
0.8
0.6
0.4
0.2
0
Absorption
350
650
950
1250
1550
1850
2150
2450
Wavelength (nm)
Black Si
Bare c-Si
surface
structure
doping

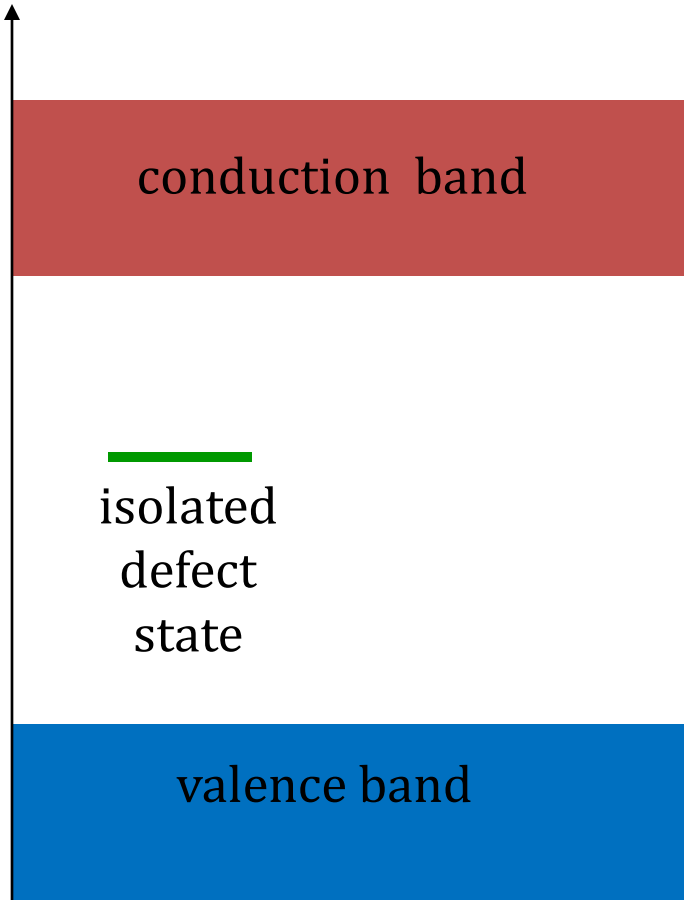
Distribution of Dopants

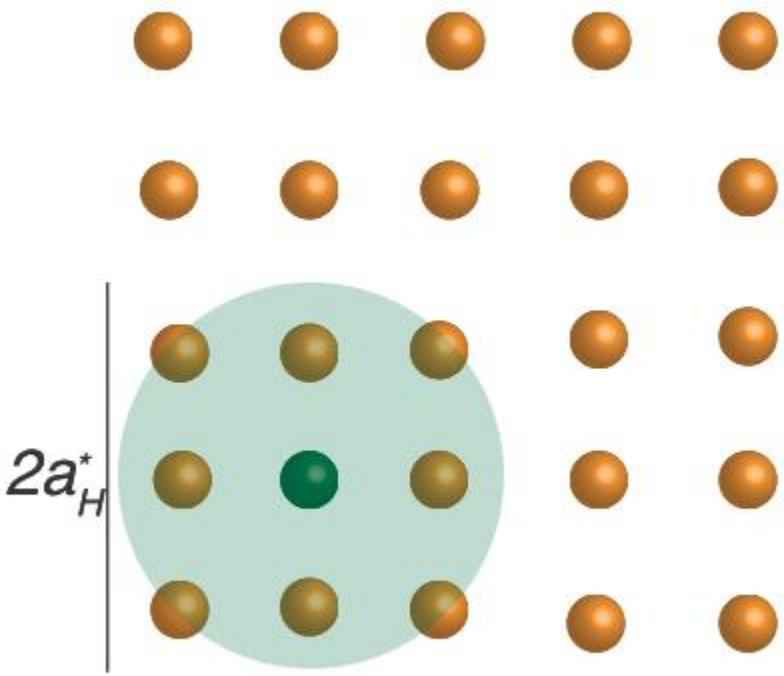
SIMS after Single Laser Shot



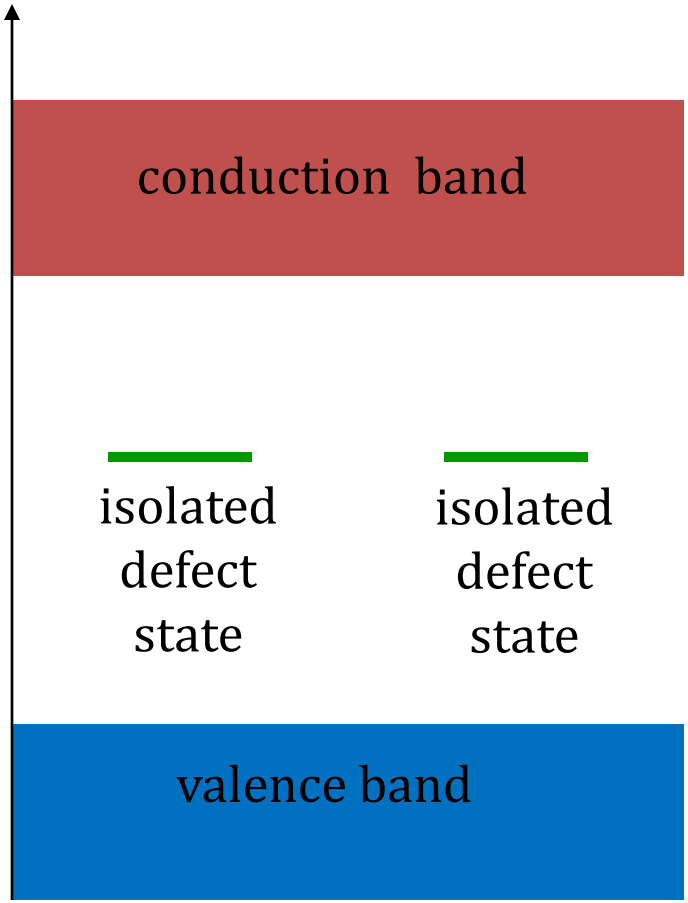
Courtesy of M. Winkler

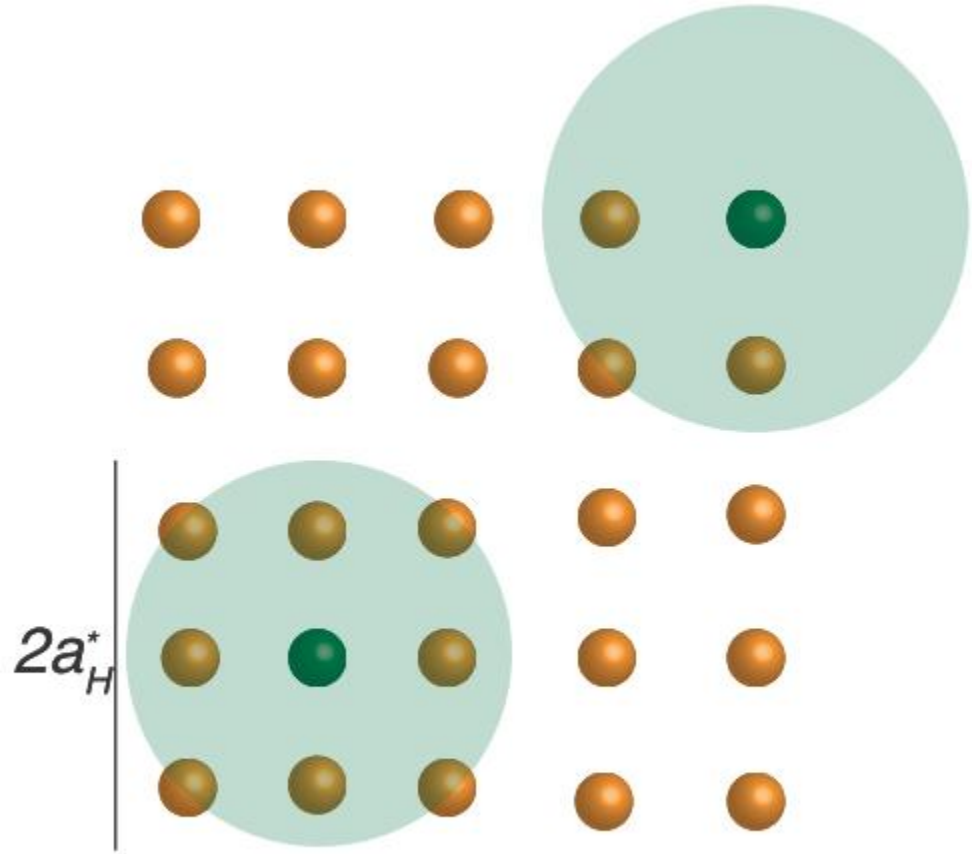
Why hyperdoping?



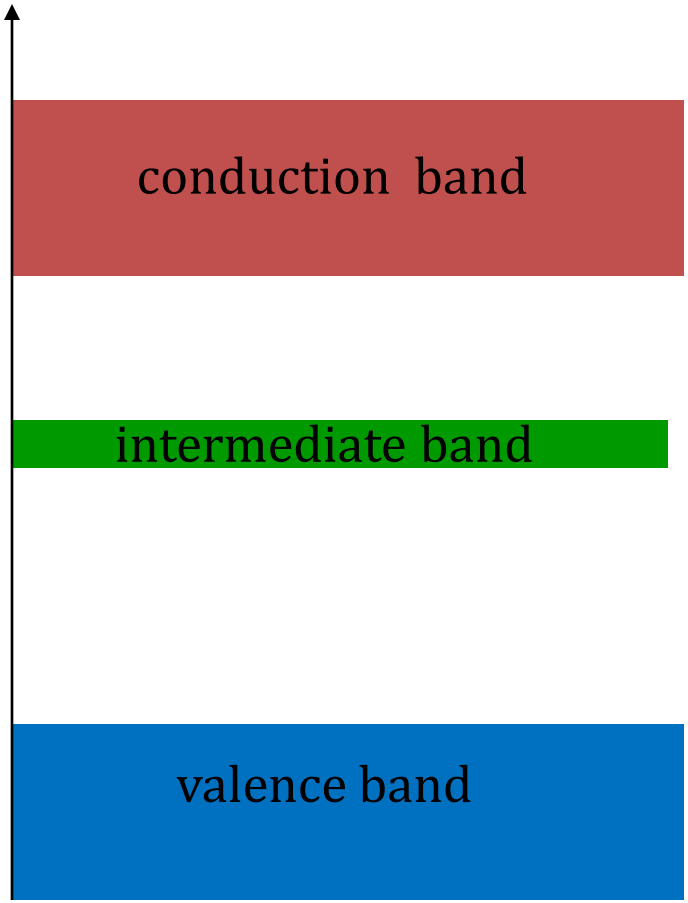


Why hyperdoping?

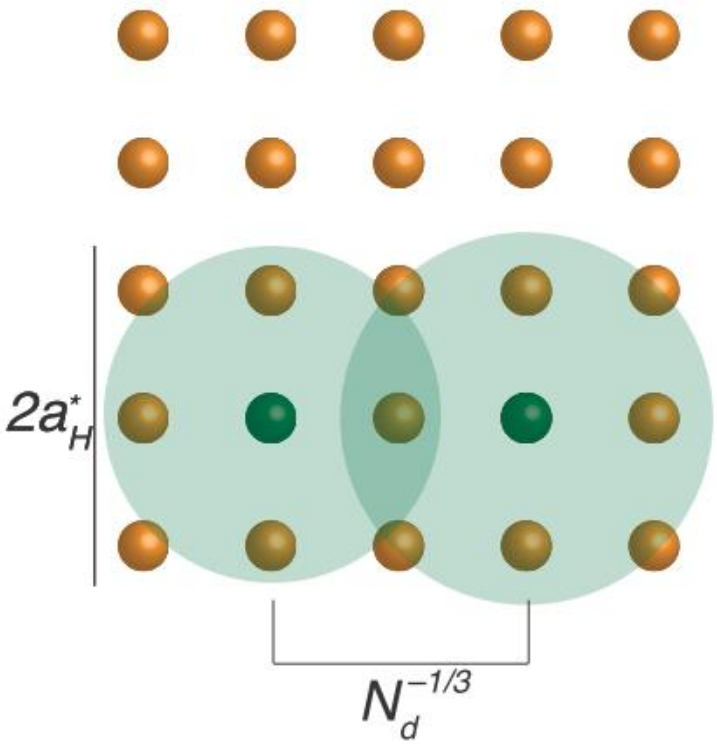




Why hyperdoping?

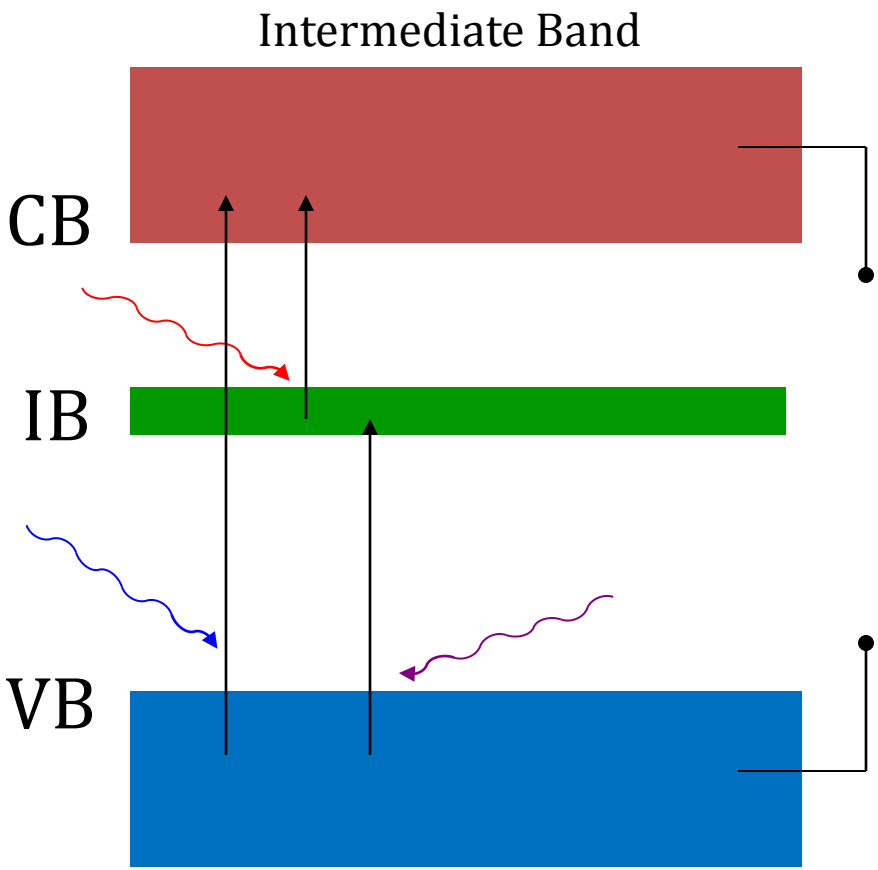


$$N_{crit}^{1/3} a_h^* = 0.26$$

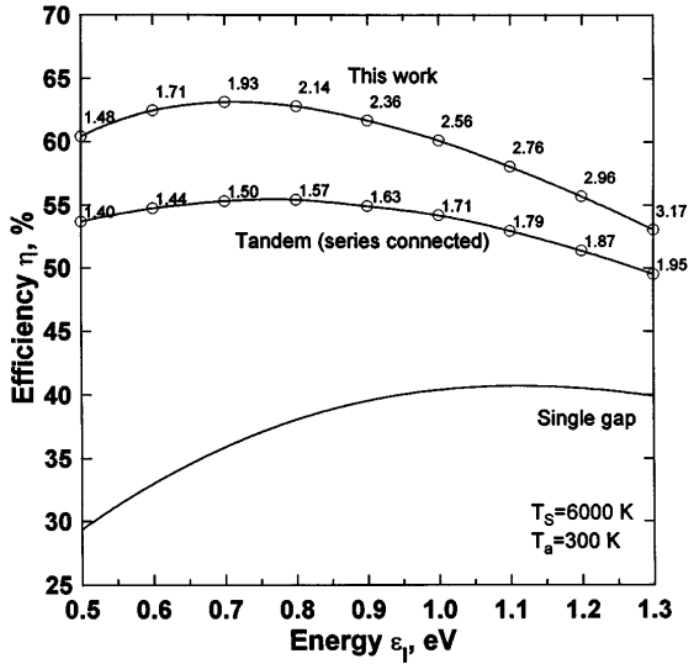


A. Luque, *et. al.*, Physica B, **354**, 320 (2006).

Advanced Solar Cells



- Absorption of lower energy photons
- Maintain output voltage



H29 7: Mark Winkler at 9:30

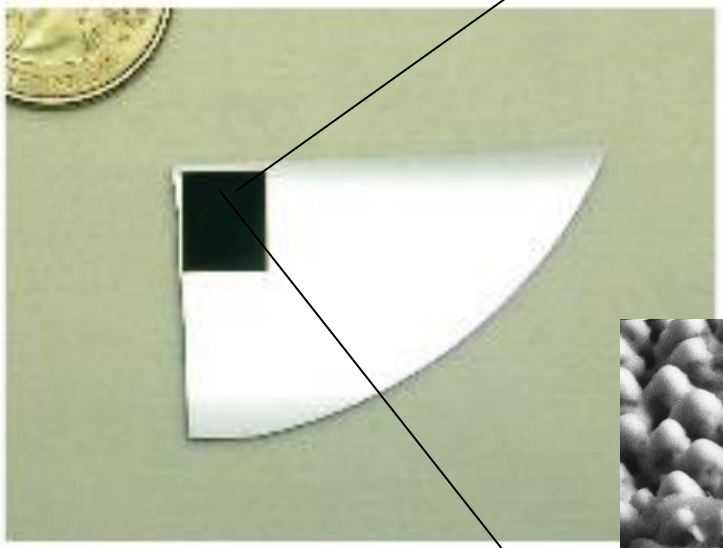
Smaller bandgap energy (eV)

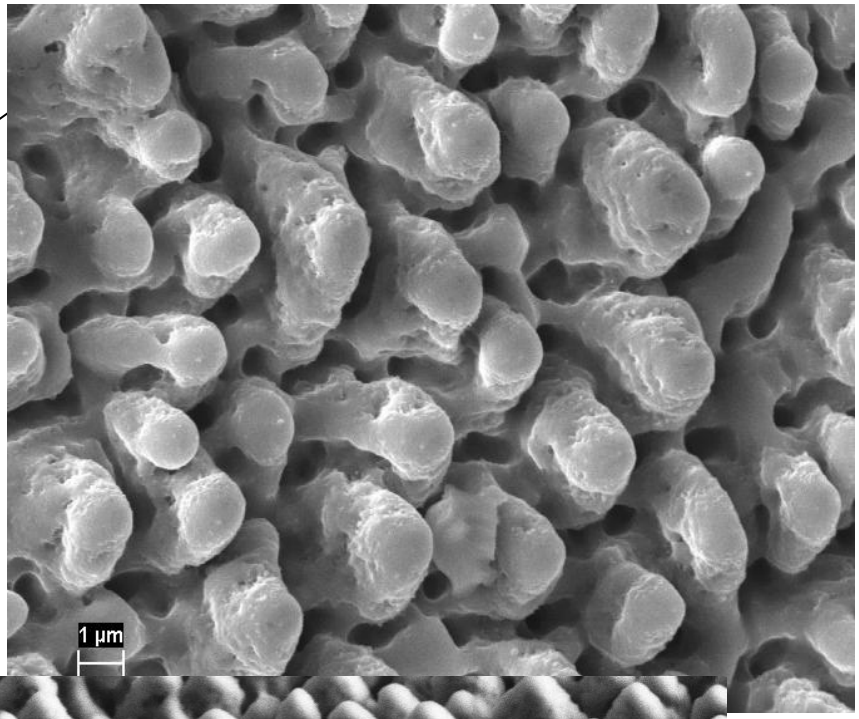
A. Luque and A. Marti, PRL **78**, 5014 (1997).

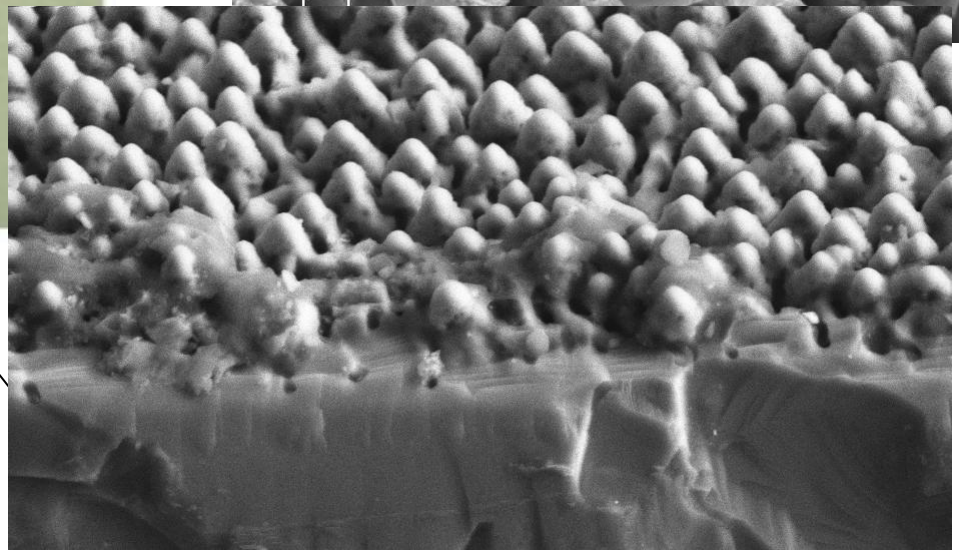
Fundamental Questions

- What role are the dopant atoms playing in sub-bandgap absorptance?
- How much order is there in the chemical structure?
- What kind of thermodynamics govern the problem?

Under the Microscope



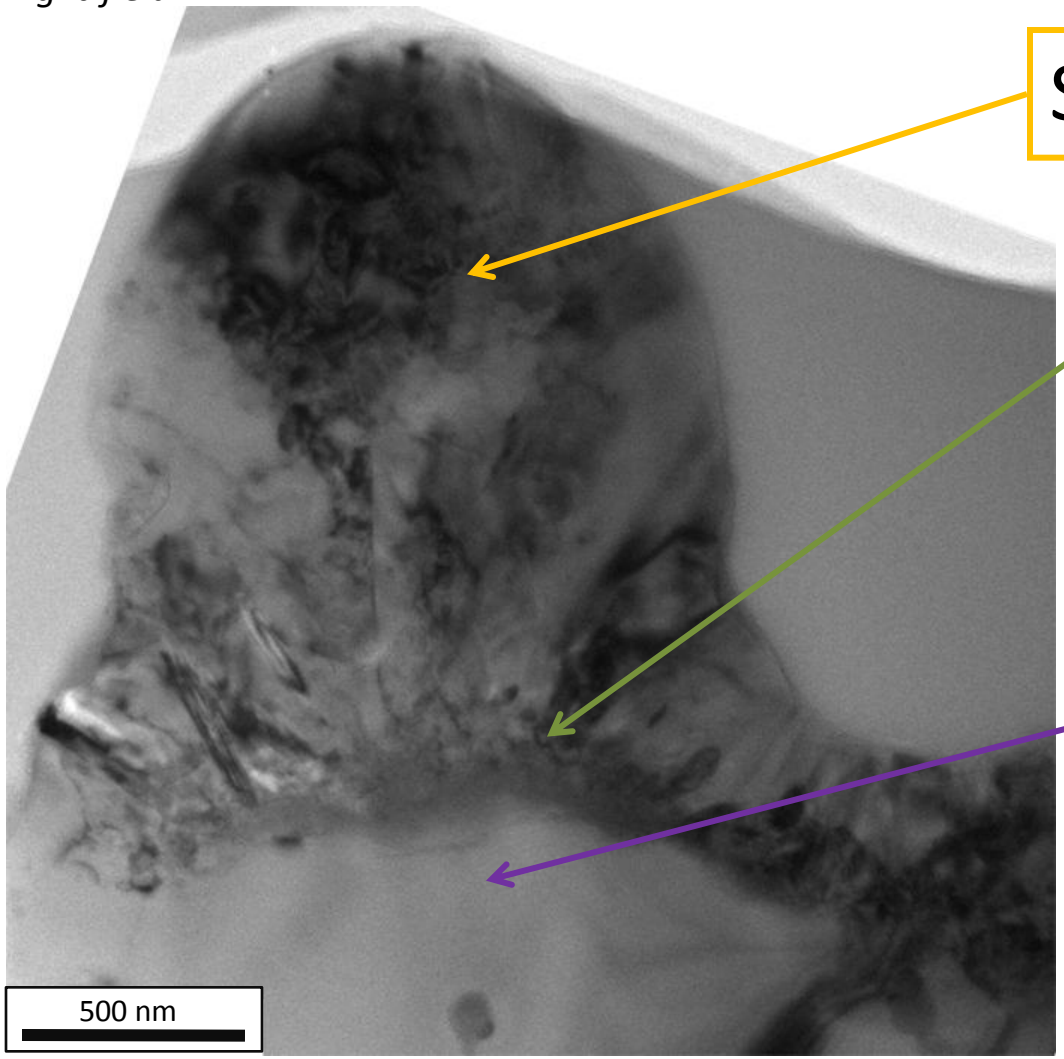




SEM images

Selenium-doped Black Silicon

Bright-field TEM



Selenium-rich peak

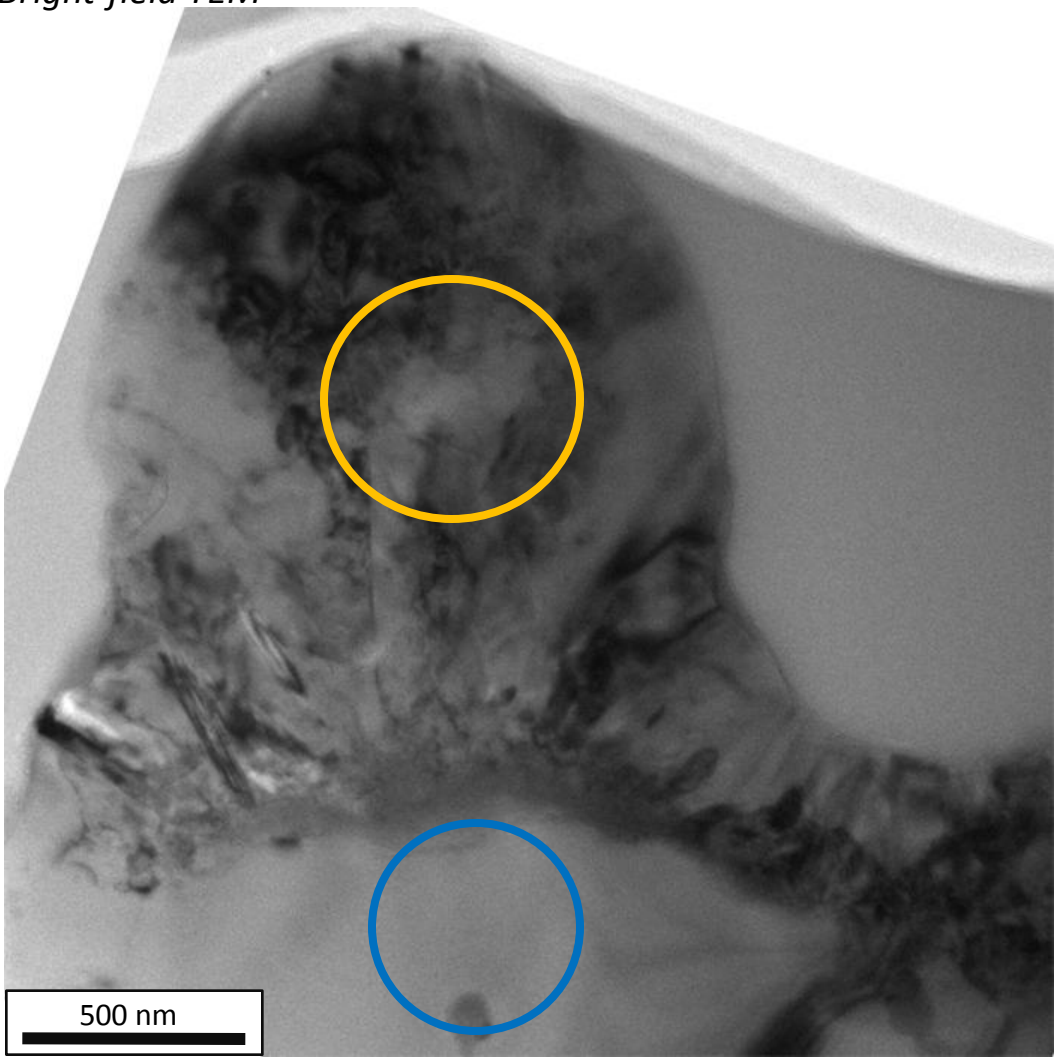
Interfacial layer

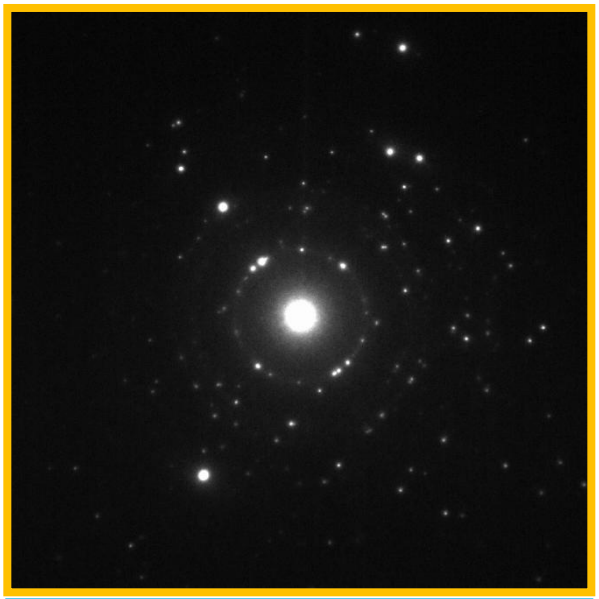
Intrinsic Si core

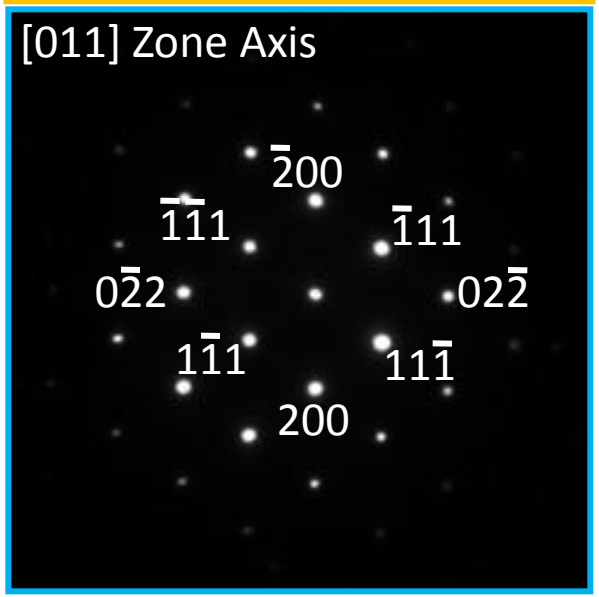
Courtesy of M. J. Smith

TEM of fs-structured Si:Se

Bright-field TEM

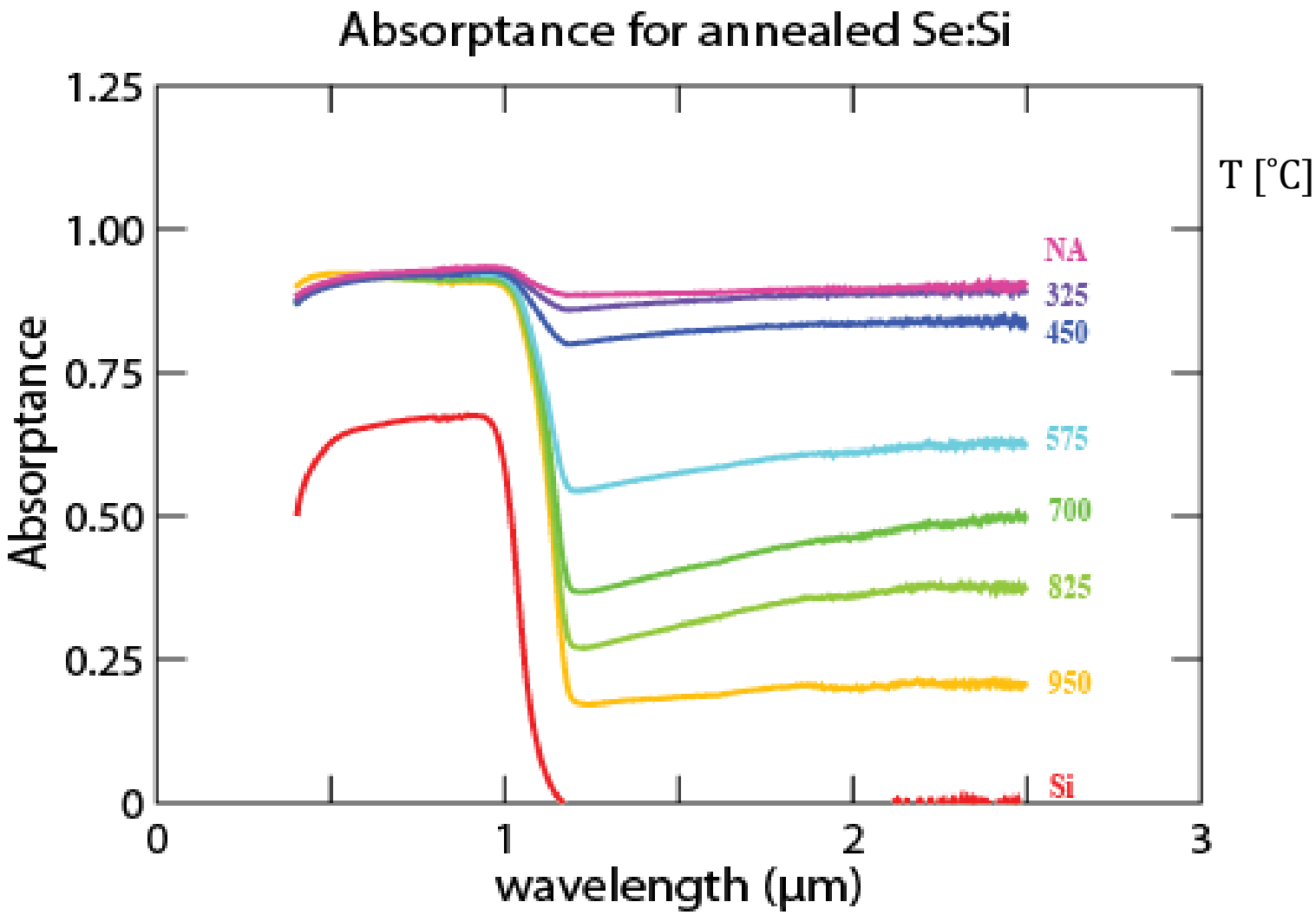






Courtesy of M. J. Smith

Reaction to Annealing



All anneals for 30 min. followed by slow cool.

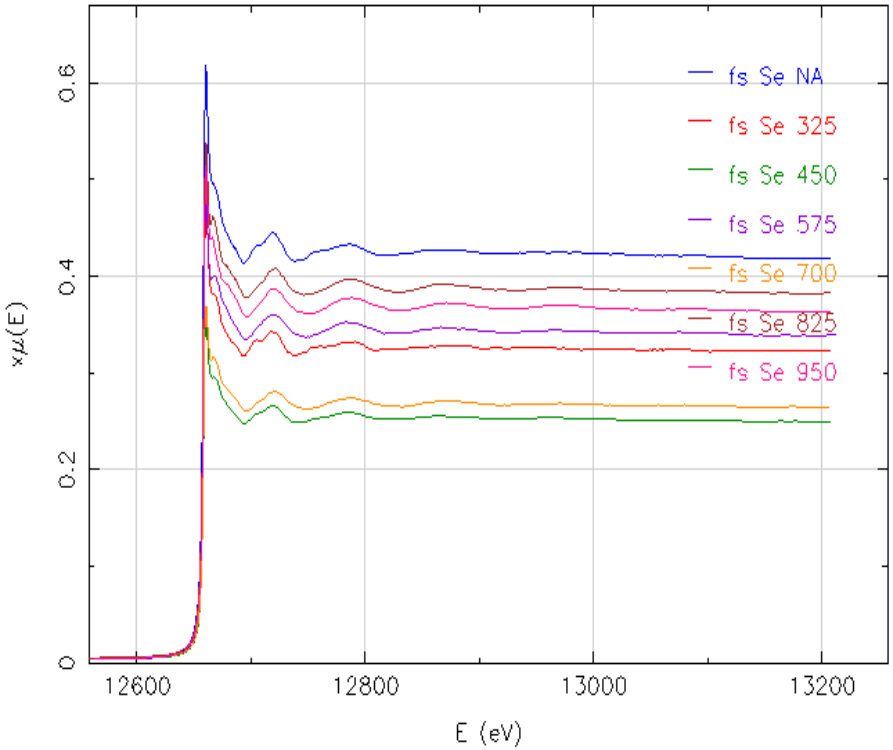
What we know…

1. Density of dopant atoms is ~10^4 x larger than equilibrium solubility
2. Some order but small grain size (~10-20 nm likely)
3. Dopant atoms play some kind of role in enhanced absorptance
4. Absorptance /annealing relationship can be modeled in terms of diffusion of the dopant

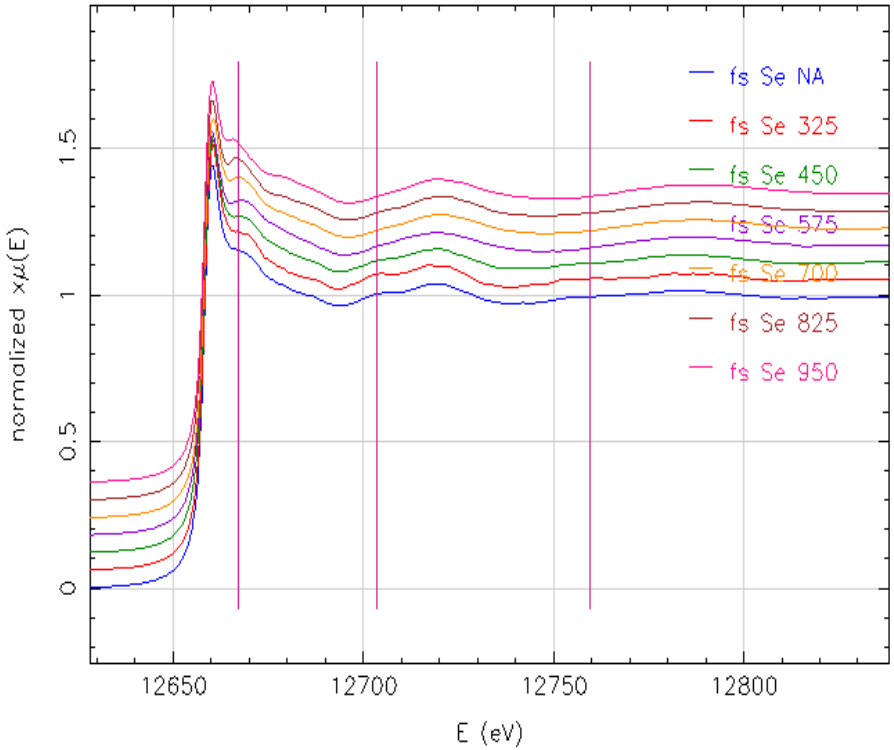
Use EXAFS to map the chemical state of Se atoms as a function of annealing temperature and sub-bandgap absorptance.

EXAFS of Si:Se

Raw



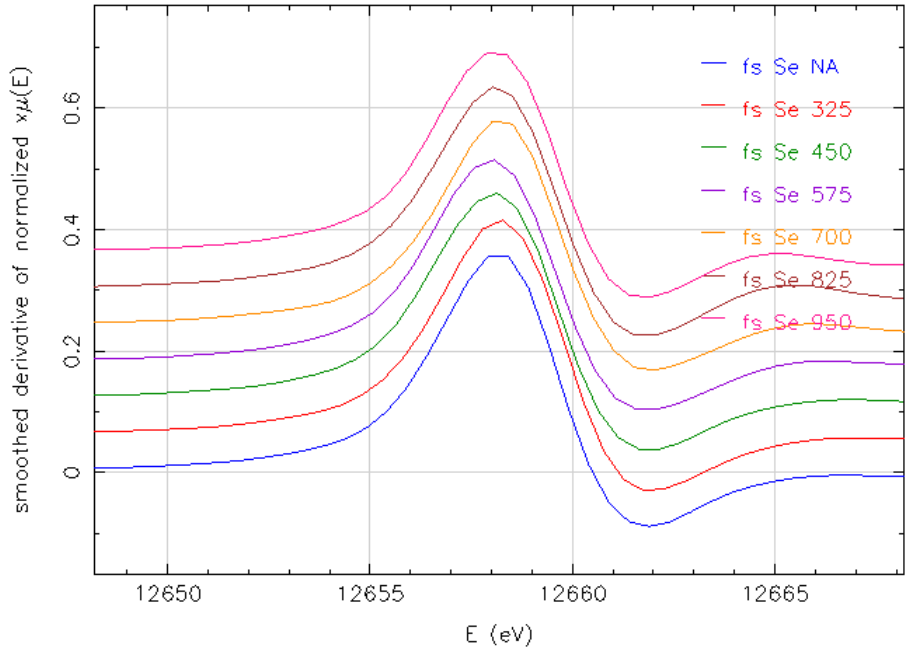
Normalized



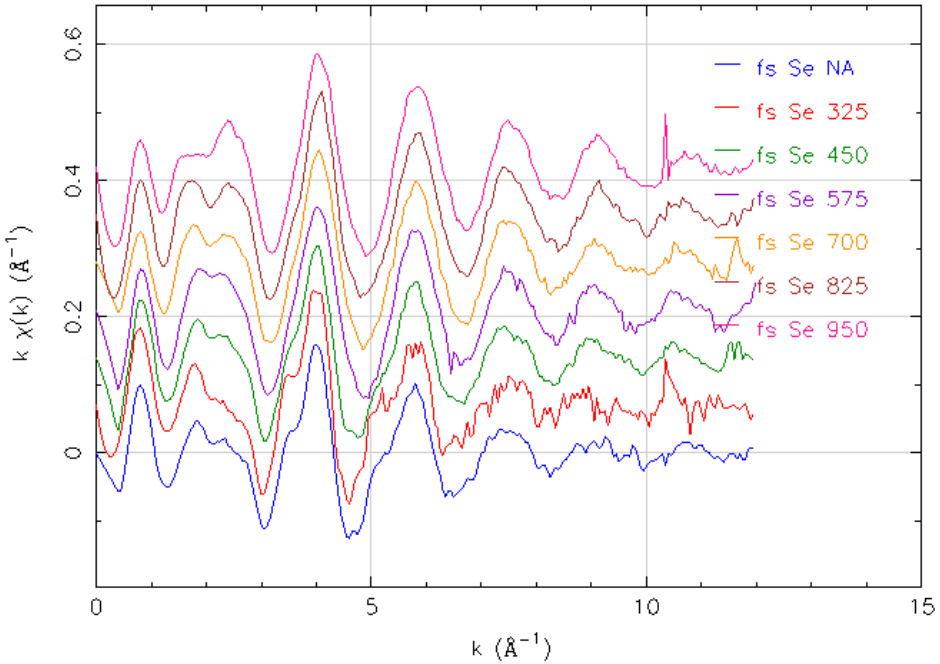
We observe a change in three features of the data as a function of annealing temperature

Processing EXAFS of Si:Se

Derivative



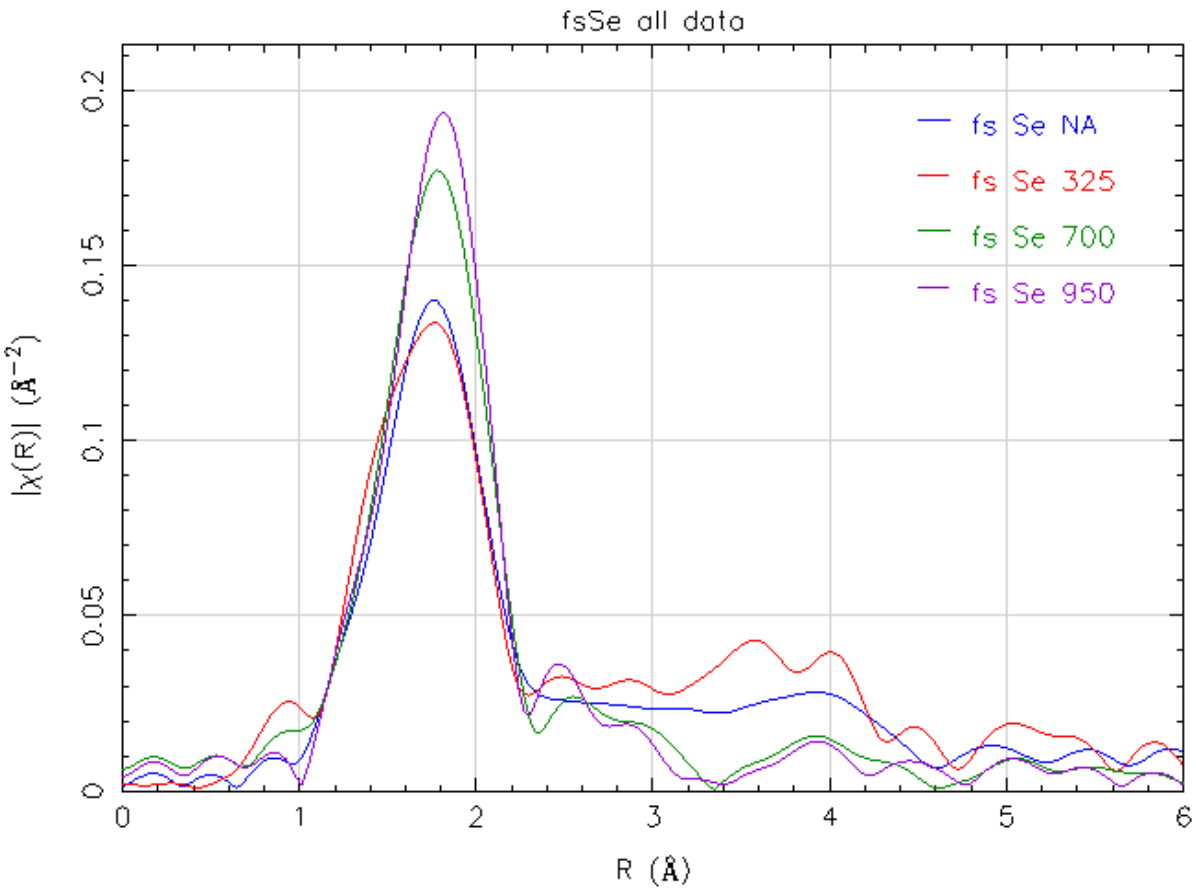
Chi(k)



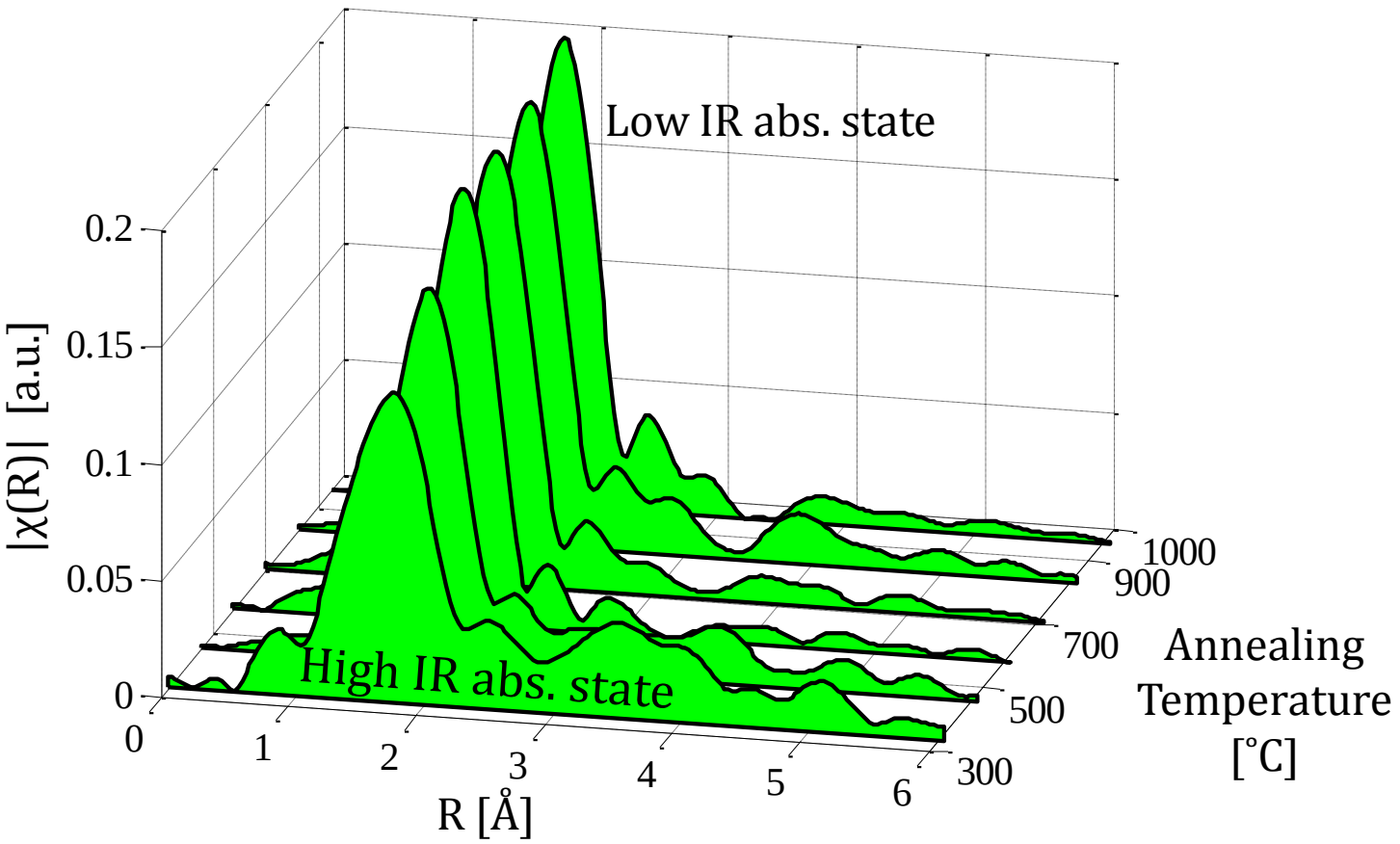
No distinct edge energy shift (< .1 eV)

- Smooth transition in features
- Use data out to k = 10 $Å^{-1}$

Processing EXAFS of Si:Se

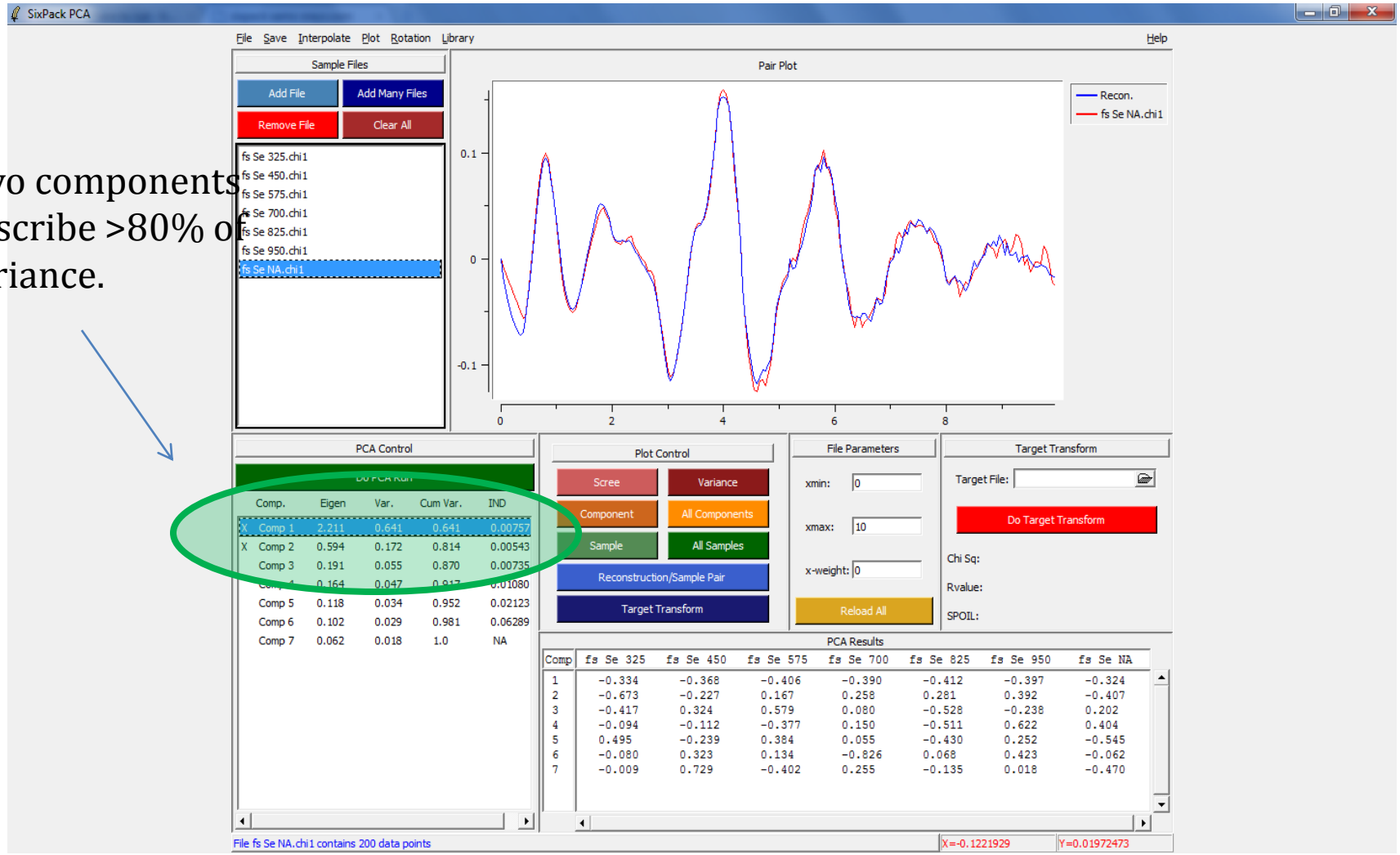


Initial Findings



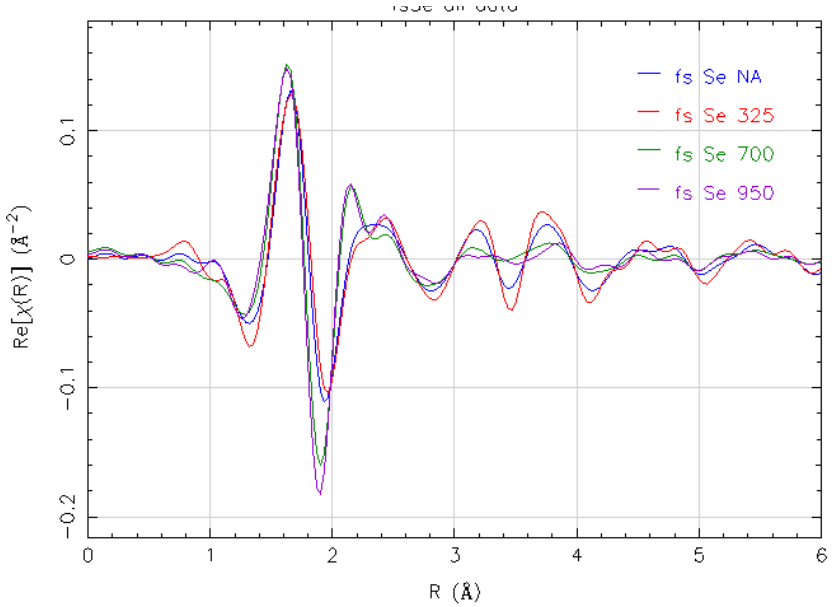
PCA in Six Pack

Two components describe >80% of variance.



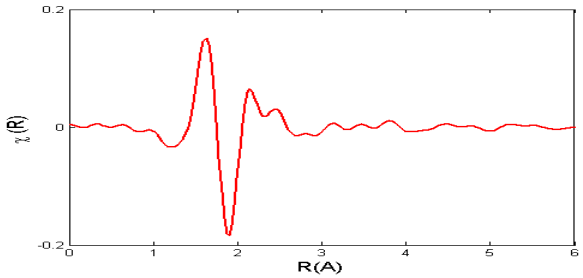
Iterative Target Factor Analysis (ITFA)

Experimental Data Set



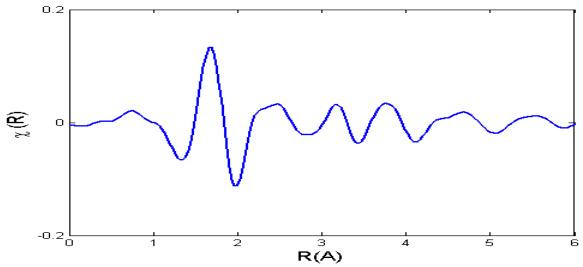
=

A x



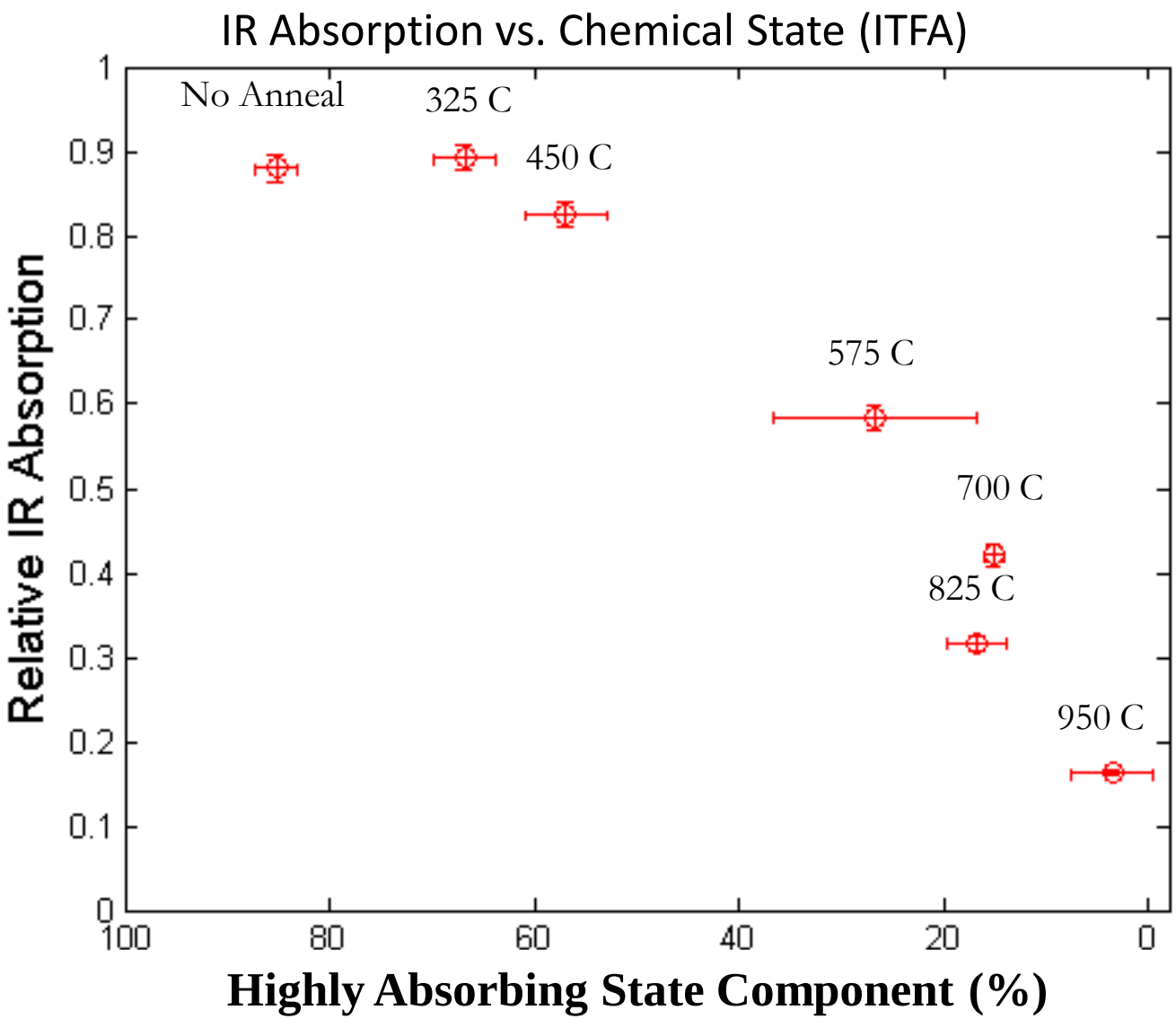
+

B x



Scheinost, et. al., Physica Scripta T115, 1038(2005)
Rossberg, et. al, Anal. Bioanal. Chem. 376, 631(2003)

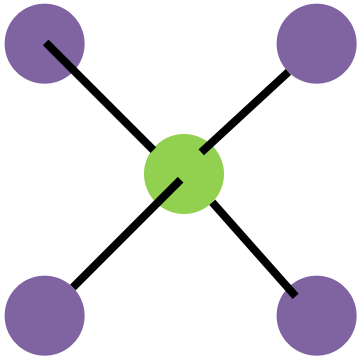
Numerical analysis: Two-state model



B. Newman, et. al., *EU-PVSEC*, Hamburg, Germany (2009).

Hypothetical model

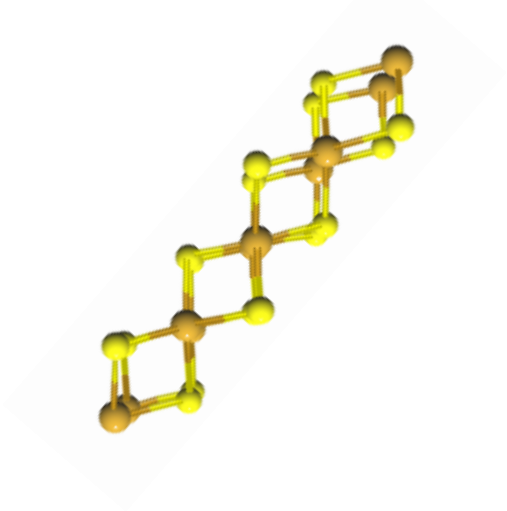
Point defect



Absorbing

Annealing

Precipitated state

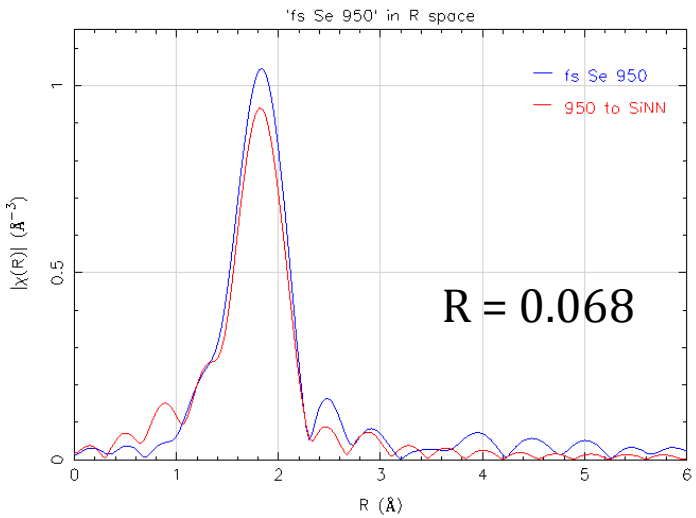


Non-Absorbing

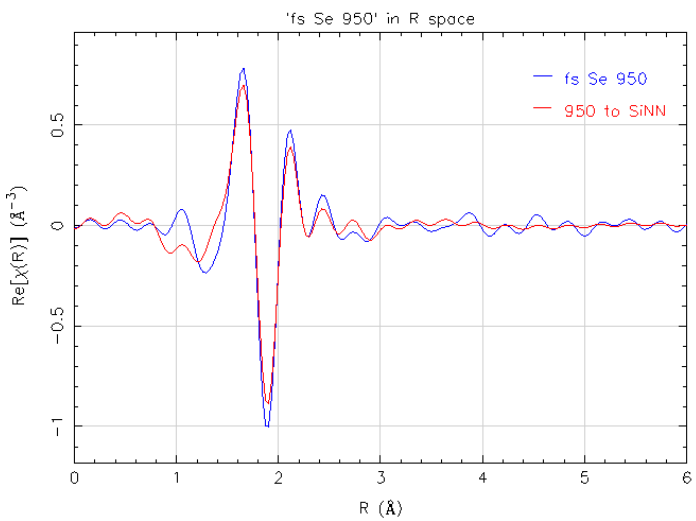
Artemis: Fitting 950C to Si NN

Fitting Parameters (range R = 1 – 2.8 Å)

path= Se<->Si
r = 2.304 (.02) Å
s02 = 1.611 (amp = 0.75, N = 2.1)
e0 = 5.99 (2.31) eV
dr = 0.0295 Å
ss2 = 0.0024 (0.001) Å^2



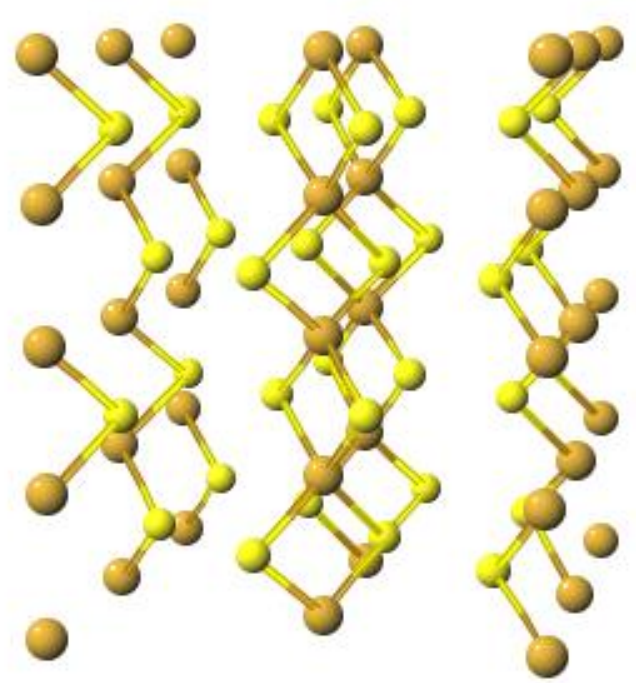
Independent points = 9.005859375
Number of variables = 3.000000000
Chi-square = 2156.080470096
Reduced Chi-square = 358.996162826
R-factor = 0.068000700
Measurement uncertainty (k) = 0.001005133
Measurement uncertainty (R) = 0.001630473
Number of data sets = 1.000000000



Silicon Diselenide ($SiSe_2$)

- *Ibam* structure
- Composed of chains held together with Van der Waals forces

Atom	N	R_{eff} [Å]	
Si	2	2.28	Same Chain
Se	1	3.48	
Se	2	3.78	
Se	2	3.84	Neighboring Chain
Se	2	3.87	



J. Peters and B. Krebs. Acta. Cryst. **B38,** (1992)

Previous EXAFS on $SiSe_2$

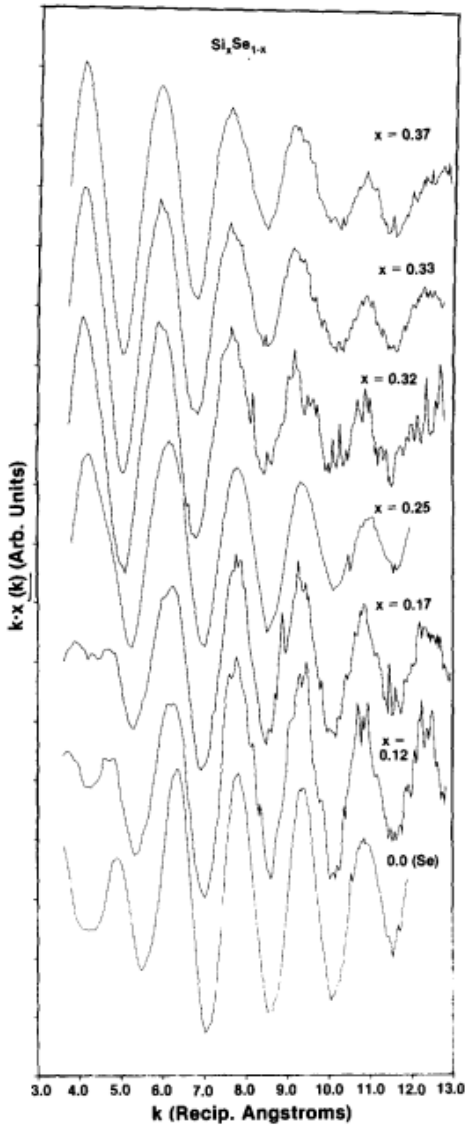


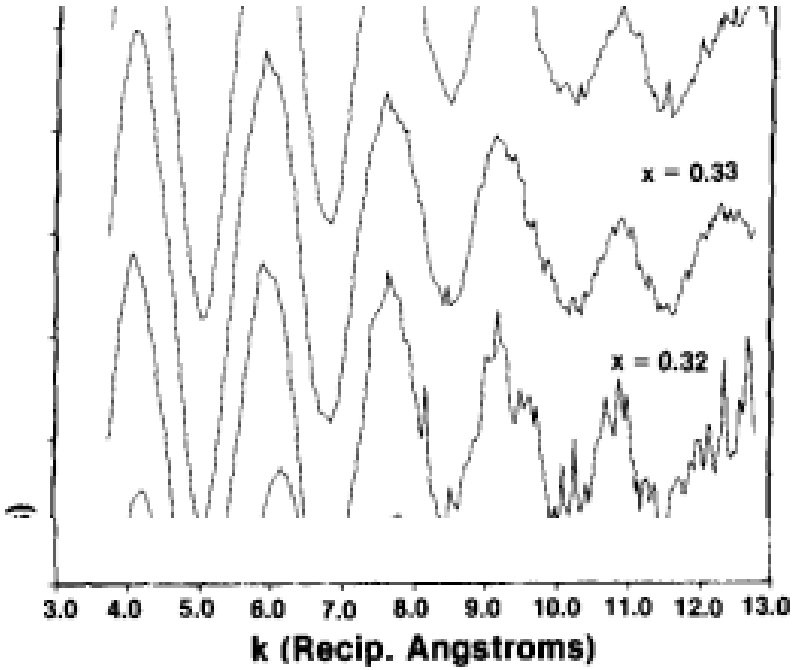
Table 3
Experimental values for the positions r_{Sei}, thermal parameters σ_i and amplitudes A_i for i = Si and Se derived from the Se K-edge EXAFS data by fittng to the point-scattering expression; R is the ratio $N_{SeSe}/(N_{SeSe} + N_{SeSi})$ (see text)

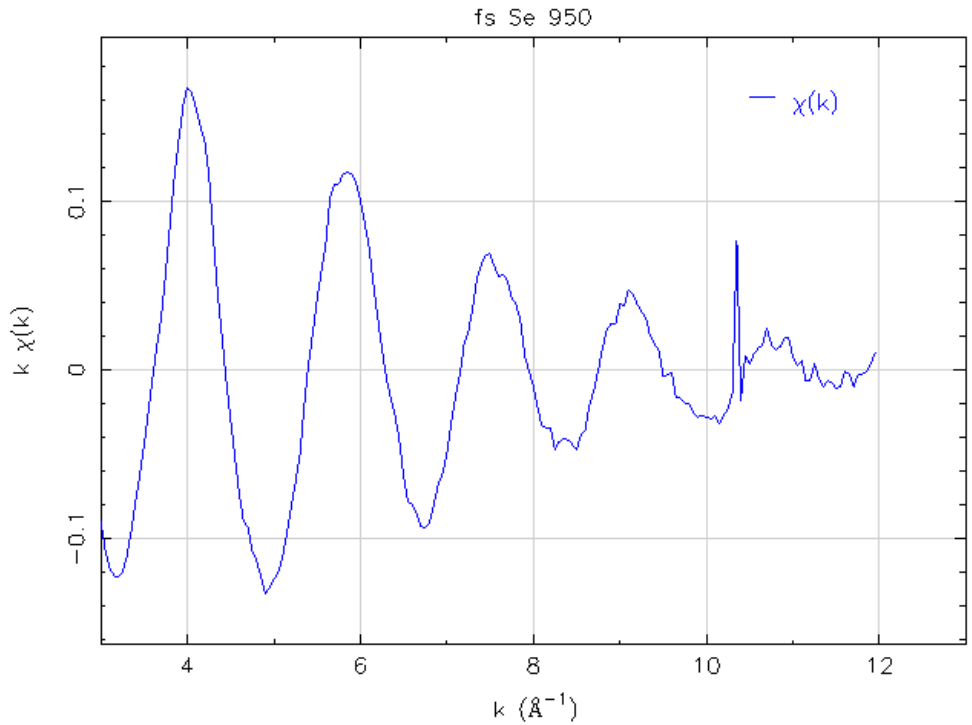
Compostion	r_{SeSi}	A_{Si}	σ_{Si}	r_{SeSe}	A_{Se}	σ_{Se}	R
Se	–	–	–	2.346 ±0.012	0.206 ±0.028	0.040 ±0.013	1
$Si_{0.12}Se_{0.88}$	2.285 ±0.011	0.092 ±0.008	0.023 ±0.013	2.362 ±0.012	0.129 ±0.006	0.040 ±0.004	0.60 ±0.06
$Si_{0.17}Se_{0.83}$	2.272 ±0.023	0.094 ±0.019	0.035 ±0.021	2.365 ±0.012	0.114 ±0.012	0.045 ±0.009	0.57 ±0.06
$Si_{0.25}Se_{0.75}$	2.226 ±0.011	0.156 ±0.024	0.041 ±0.016	2.369 ±0.024	0.058 ±0.015	0.045 ±0.023	0.30 ±0.08
$Si_{0.32}Se_{0.68}$	2.279 ±0.011	0.221 ±0.022	0.045 ±0.010	–	–	–	0.0 ±0.10
$Si_{0.333}Se_{0.667}$	2.280 ±0.011	0.208 ±0.026	0.045 ±0.012	–	–	–	0.0 ±0.10
$Si_{0.37}Se_{0.63}$	2.284 ±0.011	0.210 ±0.023	0.045 ±0.012	–	–	–	0.0 ±0.10

J.E. Griffiths, et. al. PRB **30** (1984).

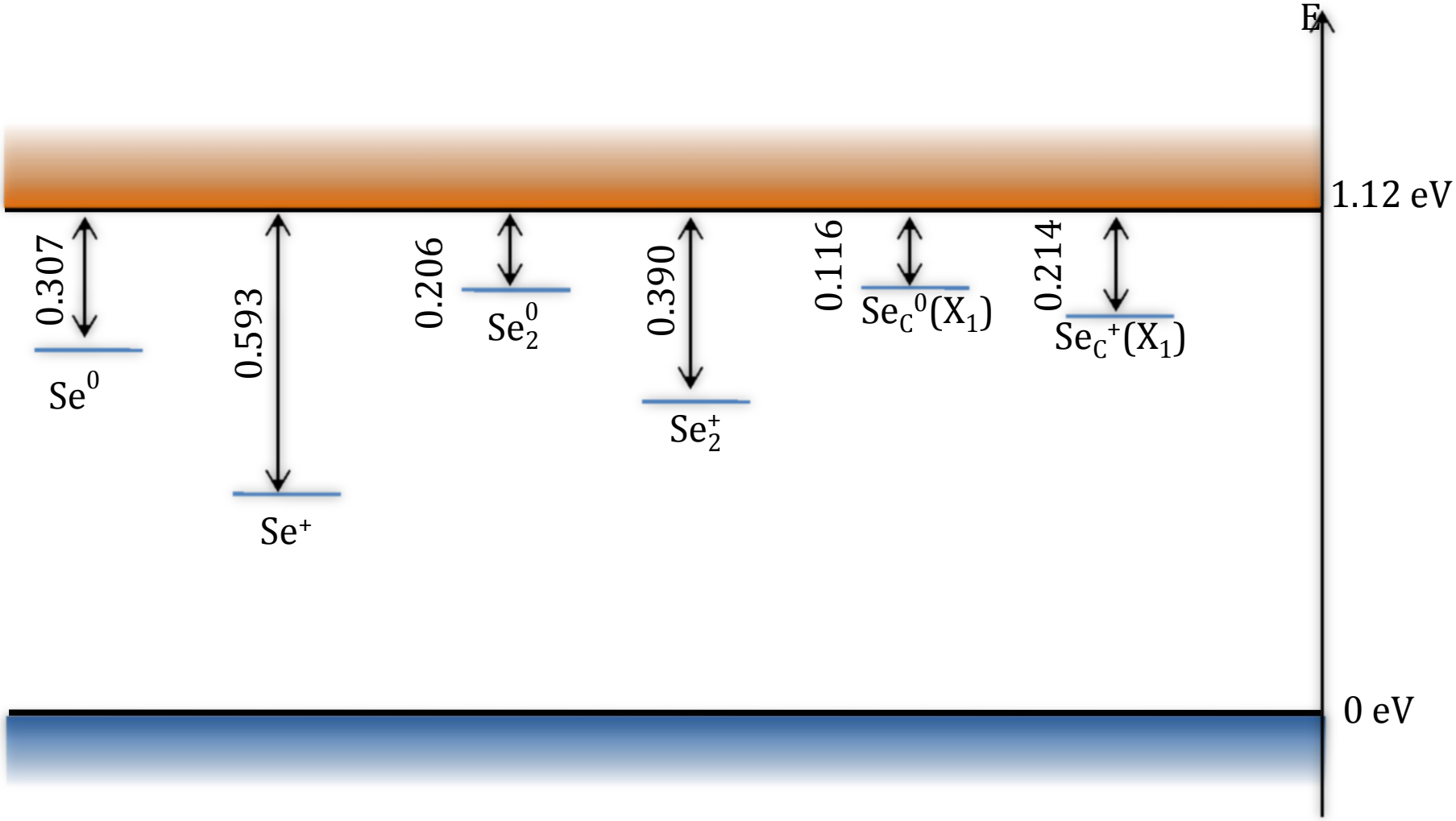
No 2nd shell information!

Comparison to previous EXAFS





Known Se Structures in Silicon



Janzen *et al.*, Phys Rev B **29**, 1907 (1984)

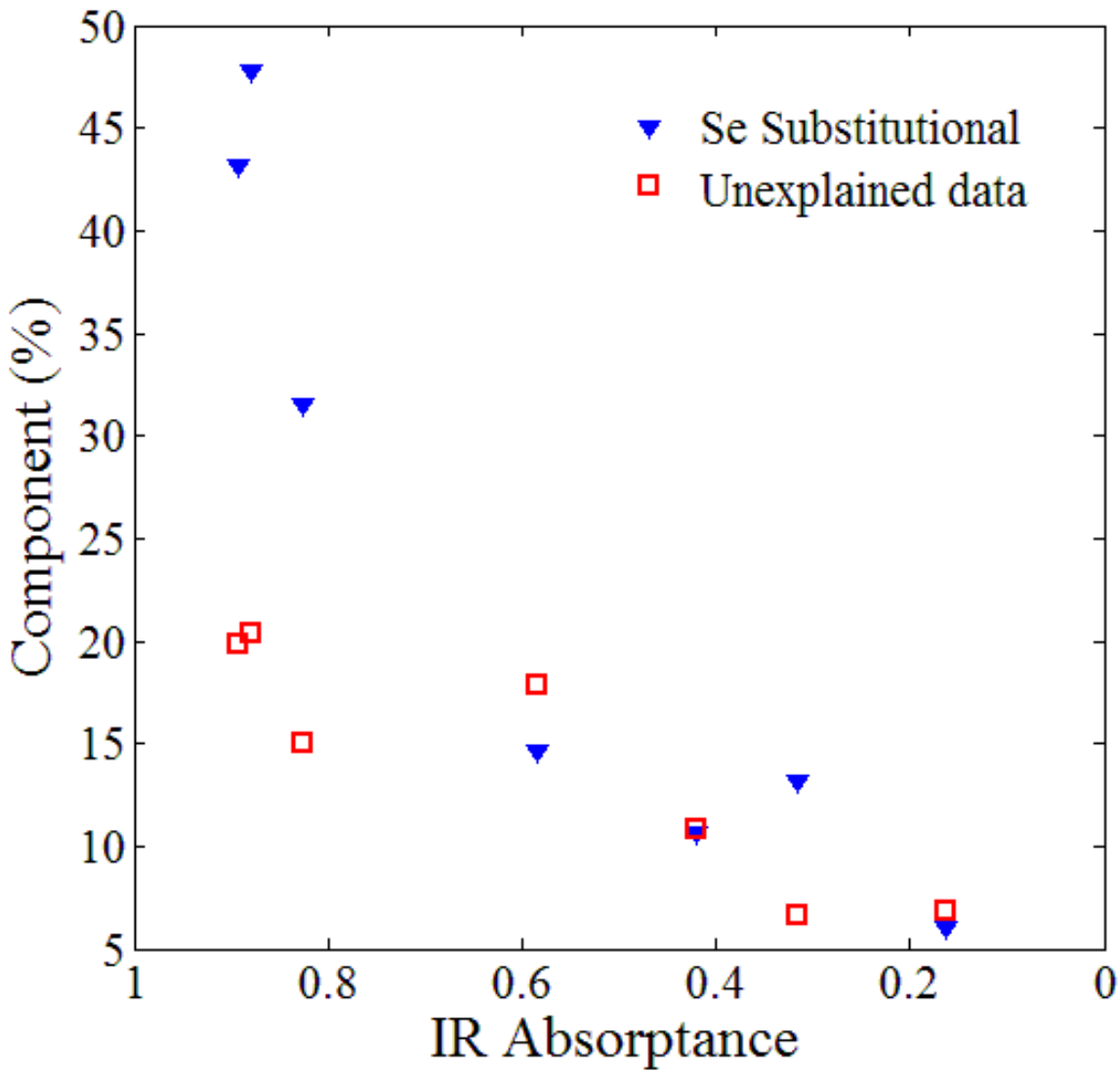
Linear Combination Analysis

UNPUBLISHED

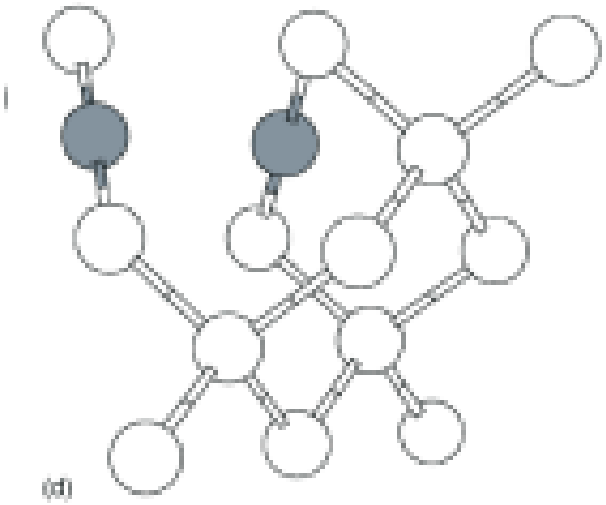
Two States:

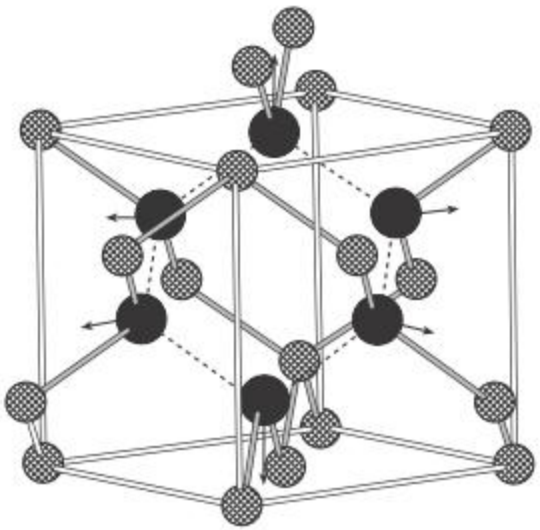
1. Se substitutional
2. 2 Si NN (possible precipitate)

Significant portions of the spectra are not explained by these two states.



What Structure?





- Pair of interstitials around vacancy
- Lowest formation energy if vacancy already exists.

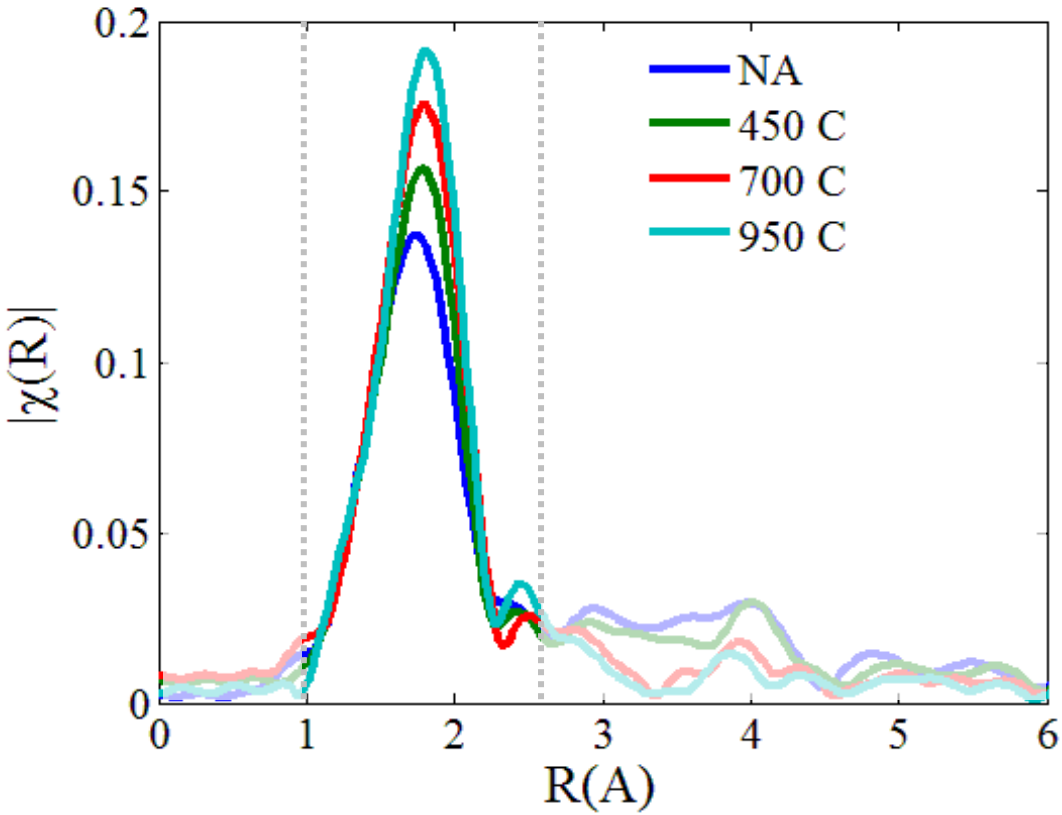
Mo, Y. *et al.* PRB, **70,** 205210, (2004).

- Substitutional configurations of multiple Se atoms
- Ring structure predicted stable

Taskin, A.A. Semiconductors, **36**, 1083 (2002).

And many many more!

First shell fitting



Procedure:

1. Pull amp and enot from the 950C fit to 2 NN Si atoms
2. Fit only R = 1 – 2.8 Å
3. Track 1st shell N and Reff

Scientific Conclusions

- Change in Se chemical neighborhood correlated to sub-bandgap absorptance
- Apparent “shorter” range order can be explained in precipitated phase
- Data does not fit to expected equilibrium states
- 2 NN Si atoms give best fit
- Distance to these neighbors changes with annealing

Lessons Learned

- Selection of initial sample set can greatly aid the problem
- Think about the dynamics of the system – can you make something change??
- Literature search – find out as much as possible about the system
- Don't be afraid to do the theory
- EXAFS has no unique solution
- Be creative about what you can learn from the data

Acknowledgments

MIT

Joe Sullivan
Matthew Smith
Dr. Elif Ertekin
Dr. Mark Winkler
Prof. Tonio Buonassisi
Prof. Silvija Gradecak
Prof. Jeff Grossman

Harvard University

Renee Sher
Daniel Recht
Dr. Aurore J. Said
Prof. Eric Mazur
Prof. Mike Aziz

Synchrotron Collaborators

Sirine Fakra (ALS,LBNL)
Dr. Matthew Marcus (ALS, LBNL)
Dr. Paul Northrup (NSLS, BNL)

Funding

Clare Boothe Luce Foundation
MIT Energy Initiative
Chesonis Family Foundation