Materials Related Problems/Solutions of the Next Generation Computer Chips

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Support: National Science Foundation, Research Corporation

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Outline

- Introduction-current status and issues
- Pulsed Laser Deposition method (synthesizing high-k dielectric thin films)
- X-ray absorption fine-structure spectroscopy (XAFS)
- Local structural information from XAFS
- Combining the synthesis and characterization in high-k and clustering problems of semiconductor industry
- Conclusions and future work

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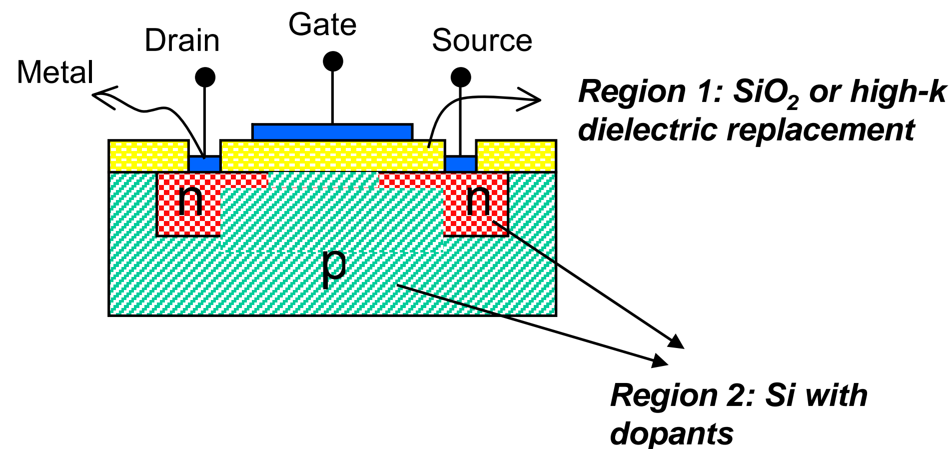
Building Blocks of Computer Chips: CMOS Devices



Current Technology

- Region 1: Silicondioxide gate
- Region 2 : Silicon with dopants to increase conductivity

The challenge is to be able to shrink these blocks as much as possible in order to put more of them into a computer chip for faster operations and greater number of calculations per second.

Problems:

1. *Dielectric region- SiO_2 must be replaced*
2. *Clustering and precipitation of dopants*

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Continuation of Moore's Law

Process Name	P856	P858	Px60	P1262	P1264	P1266	P1268	P1270
1st Production	1997	1999	2001	2003	2005	2007	2009	2011
Process Generation	0.25µm	0.18µm	0.13µm	90 nm	65 nm	45 nm	32 nm	22 nm
Wafer Size (mm)	200	200	200/300	300	300	300	300	300
Inter-connect	Al	Al	Cu	Cu	Cu	Cu	Cu	?
Channel	Si	Si	Si	Strained Si	Strained Si	Strained Si	Strained Si	Strained Si
Gate dielectric	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	High-k	High-k	High-k
Gate electrode	Poly-silicon	Poly-silicon	Poly-silicon	Poly-silicon	Poly-silicon	Metal	Metal	Metal

Introduction targeted at this time

Subject to change

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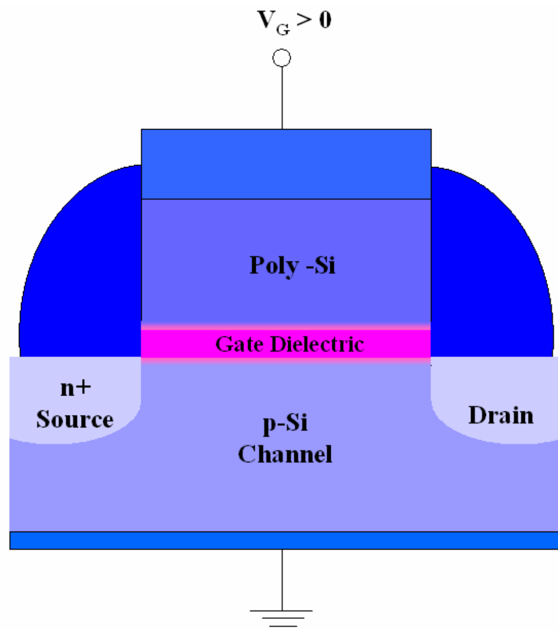
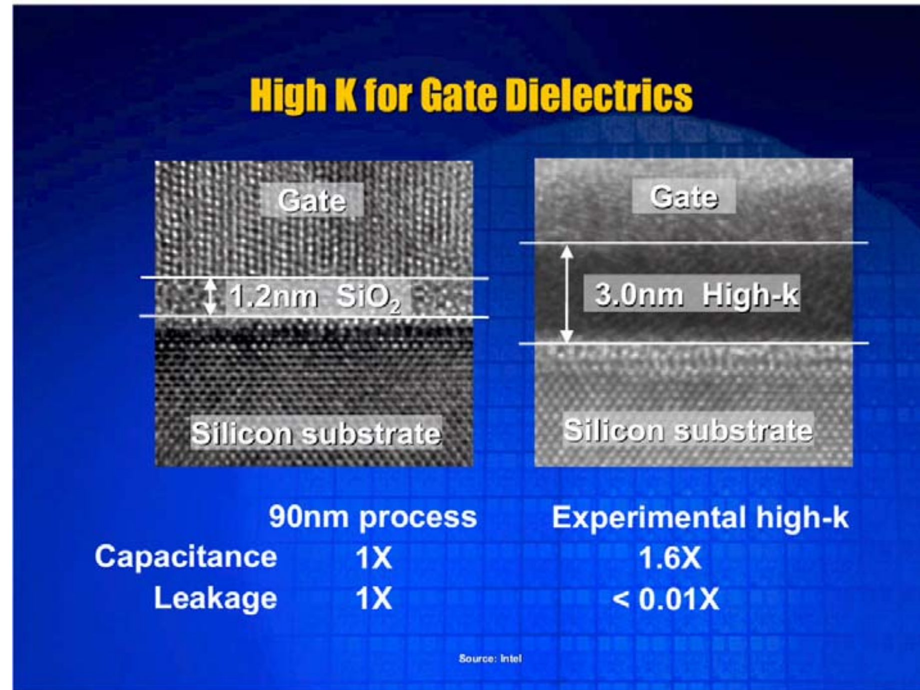
Source: Intel

The Need for High-k Dielectrics



Basic CMOS Transistor

$$C = \frac{A\kappa\varepsilon_0}{t_{ox}}$$



As thickness of SiO_2 decreases, leakage current increases exponentially due to quantum tunneling of electrons→ breakdown of the device

Challenge: is to preserve capacitance, without decreasing the oxide thickness (so no tunneling). Can't use SiO_2 anymore→ find a replacement with higher k value

Source: Intel

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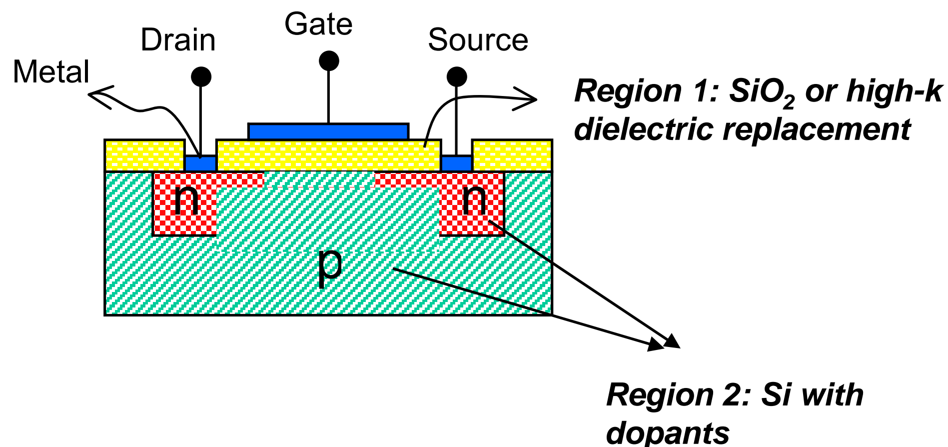
Region 1: Replacement of SiO_2 with a High-k Dielectric Material



- With the ever decreasing size of the transistors SiO_2 will reach its physical limits by 2007(8)…
- By 2007(8).. gate-SiO_2 will be too thin to block the unwanted electron tunneling so new candidates, high-k dielectric materials, are needed to replace SiO_2
- Our method is using pulsed laser deposition to synthesize novel materials (based on HfO_2, ZrO_2, Y_2O_3) on silicon crystals.
- We determine the structure and quality of the high-k dielectric thin films by x-ray methods in our lab. and Brookhaven National Laboratory.

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Problems with the High-k dielectrics

- Interface abruptness
  - SiO_2/Si interface has almost atomic layer sharpness
- Formation of interfacial oxide
- Thermal stability
  - The new materials should be stable at high-temp semiconductor processing conditions
- Crystallinity
  - In order to reduce leakage current films should preserve specific crystal structures
- Channel mobility
  - Carrier mobility in the channel should not be diminished by high-k dielectric replacement

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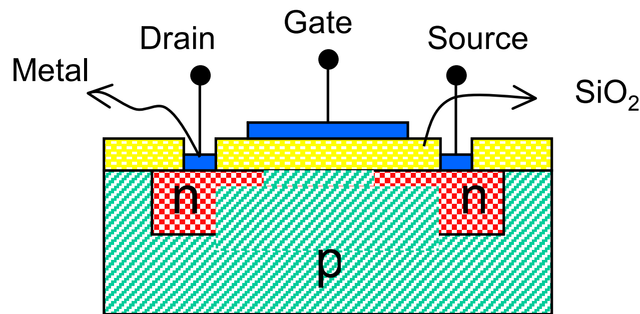
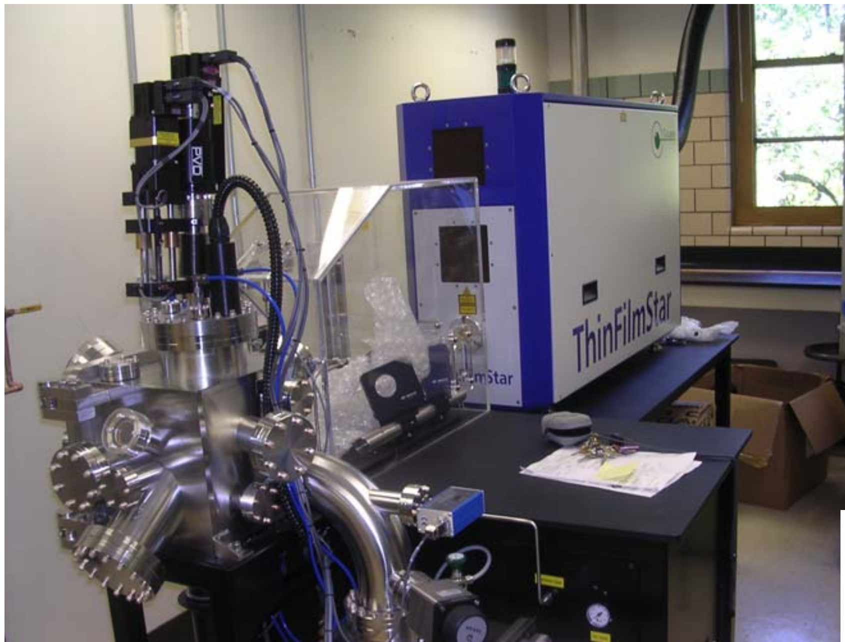
Our Approach: PLD and Local Structural Probing

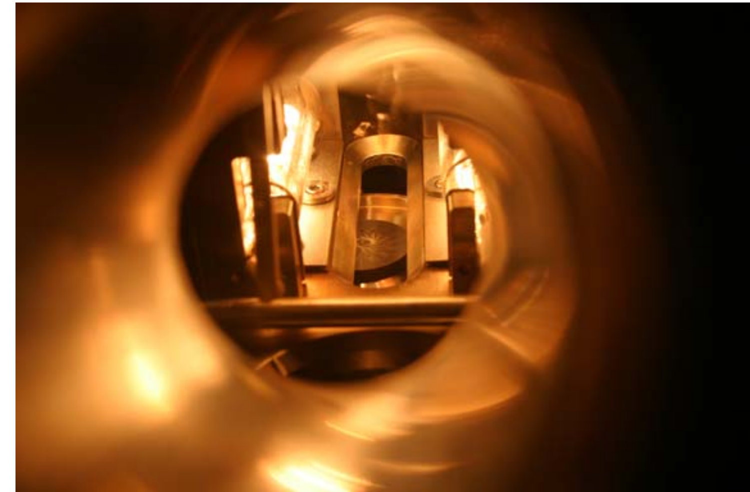


- Our approach is using pulsed laser deposition to synthesize novel materials (based on HfO_2, ZrO_2, Y_2O_3) on silicon crystals.
- Can we determine the local structural modifications caused by the variations by the deposition conditions by XAFS (even in amorphous films)?

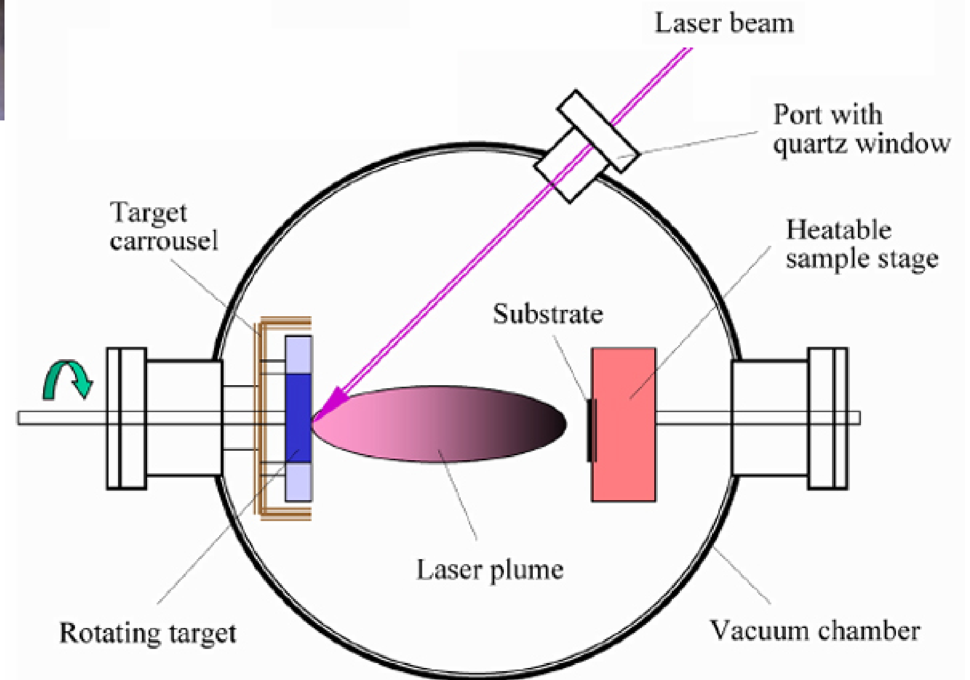
  If yes, then that means we have a powerful tool (PLD+ XAFS) controlling the thin film synthesis of these materials.

PLD System at Seton Hall





- Krf Excimer Laser, $\lambda = 248$nm
- Laser frequency up to 100Hz
- Rotating substrate and target
- Heated substrate up to 850°C



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Advantages of PLD

- High quality epitaxial thin films
- Control over the structural properties of the thin films by varying the deposition parameters
  - (e.g., oxygen partial pressure, substrate temperature, laser frequency, laser energy)

- Relatively cheaper than molecular beam epitaxy (MBE) → or as they say sometimes:

  “poor assistant professor’s MBE”

Characterization: X-ray Absorption and Fluorescence

X-ray Absorption

Incident x-ray ejects a core level electron.
Kinetic Energy (KE) of the photo-electron is:

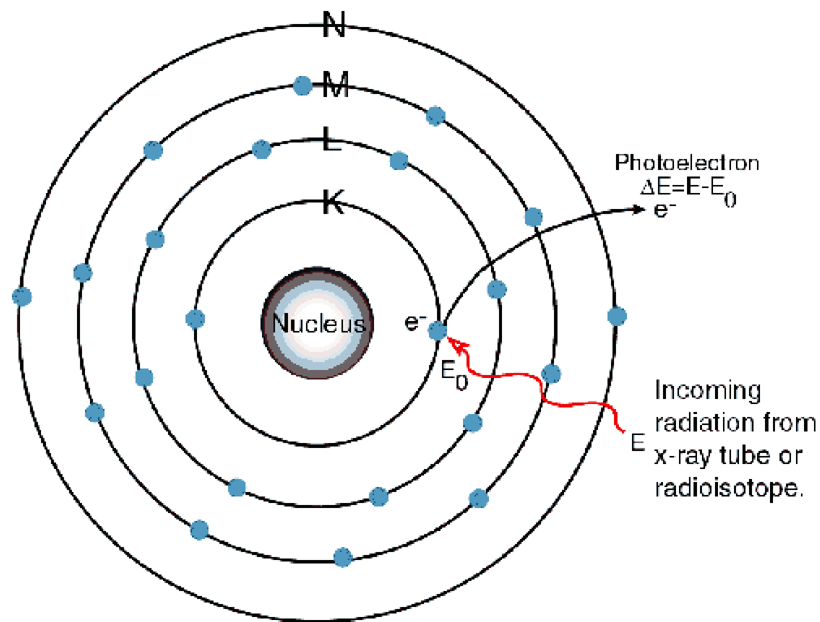
$$KE_e = E_{x-ray-in} - E_0$$

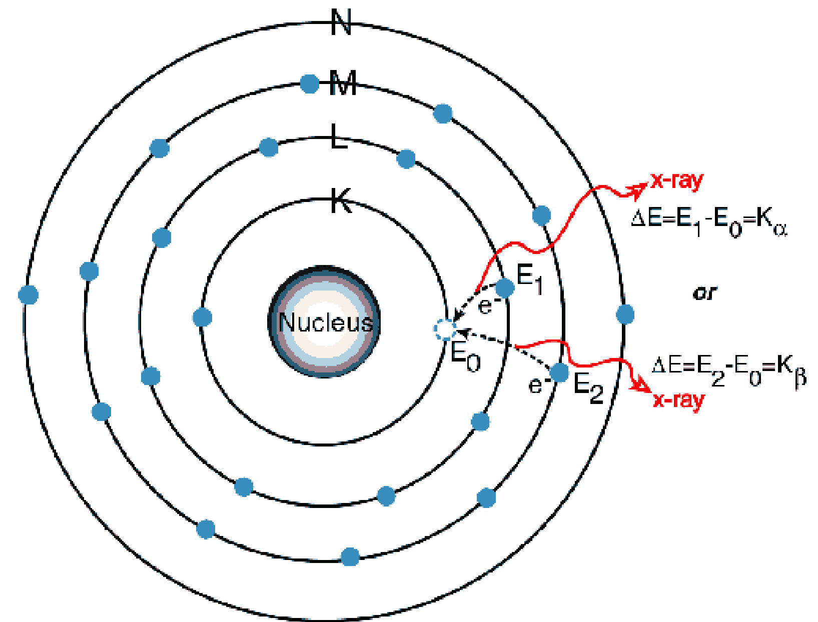
E_0 : Energy of core level e.

X-ray Fluorescence

Higher energy core electron fills empty electron level, and ejects an x-ray of fixed energy.

$$E_{x-ray-fl.} = E_1 - E_0$$





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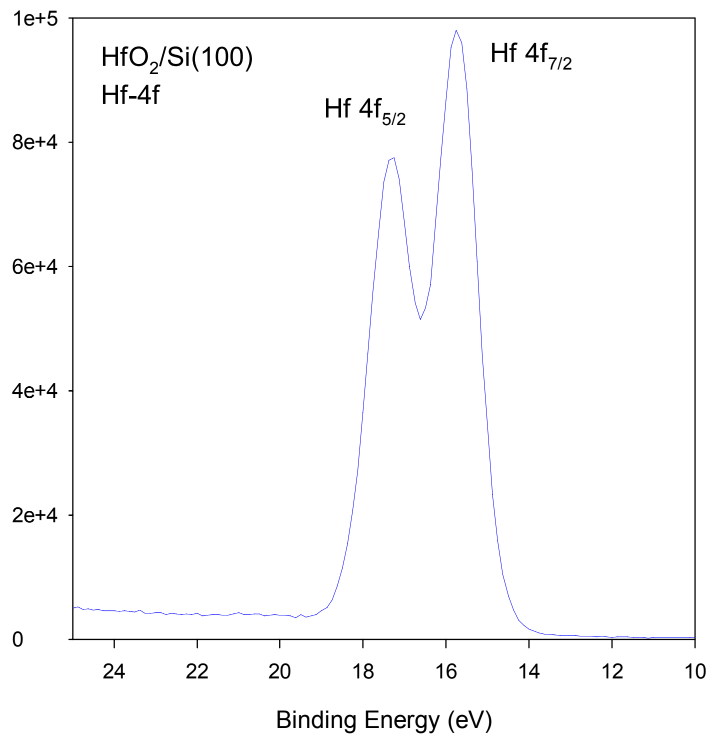
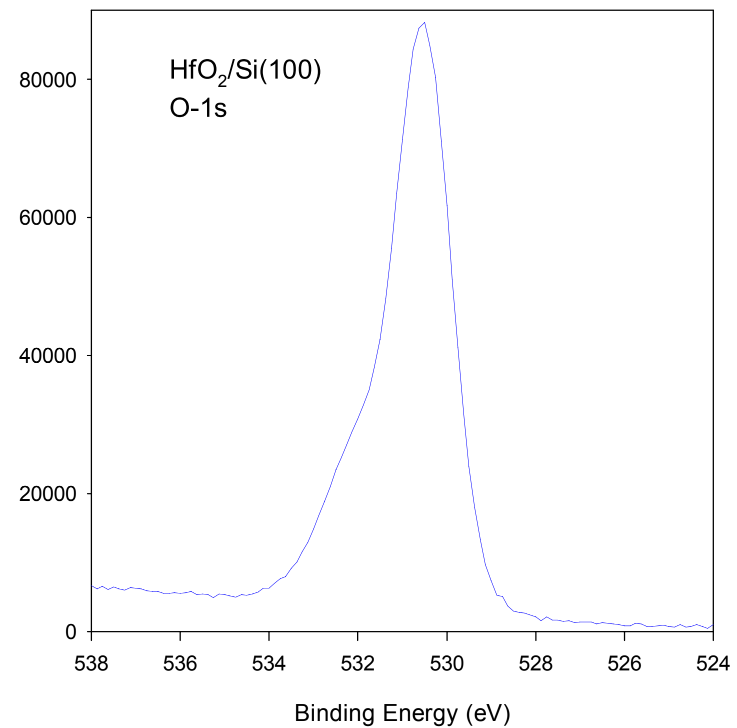
X-ray Photoelectron Spectroscopy for HfO_2/Si(100)

HfO_2: Fully oxidized



Shoulder: $HfSi_xO_y$ presence



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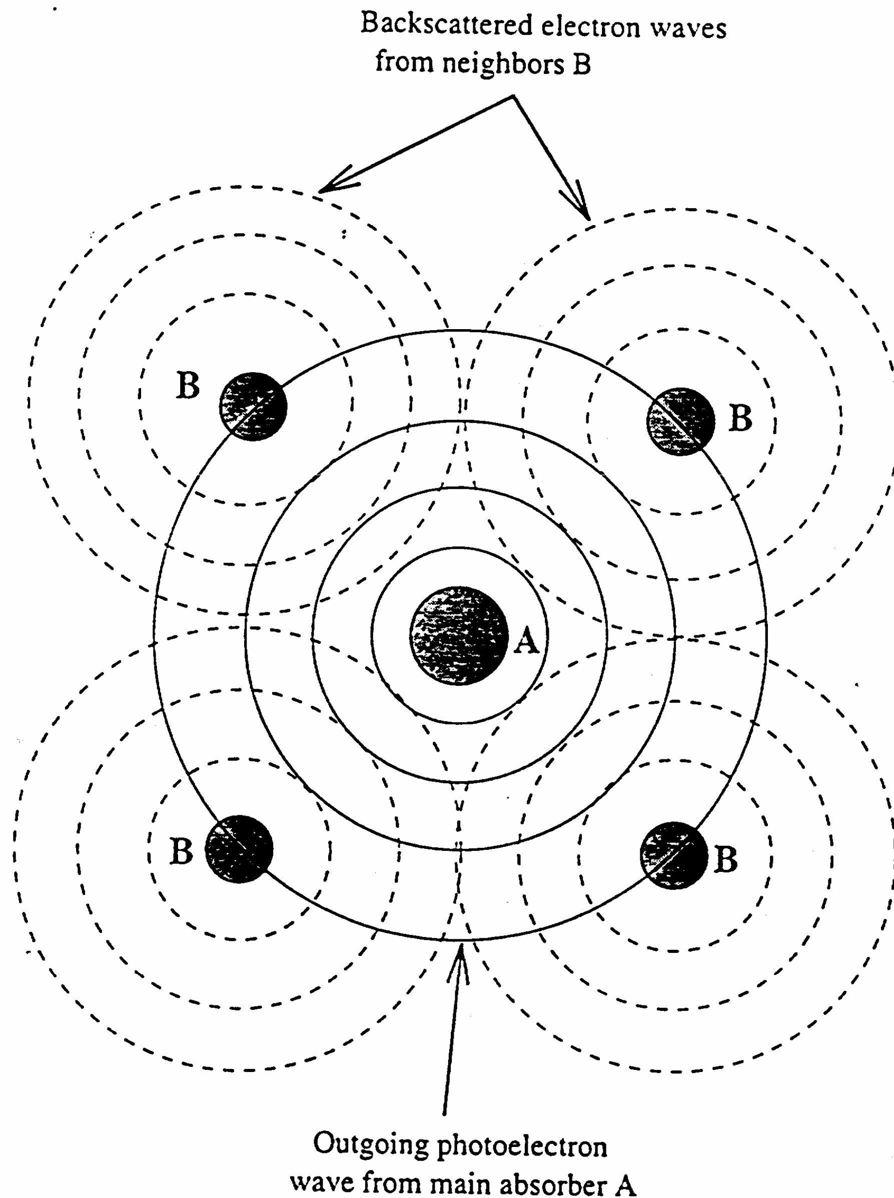
Backscattering and the Absorption Coefficient: Wave picture

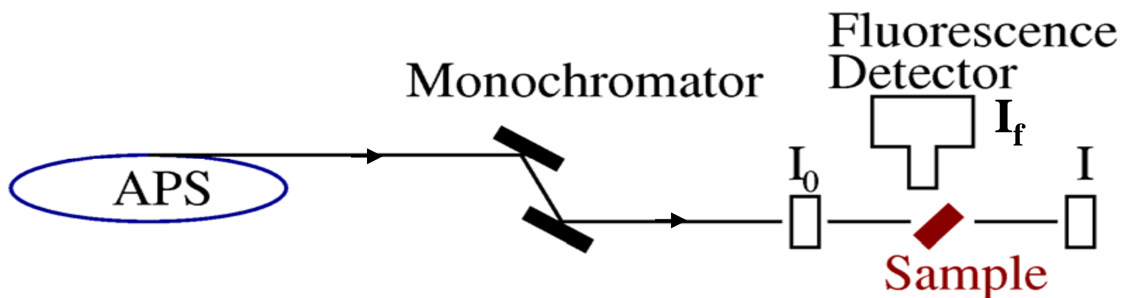


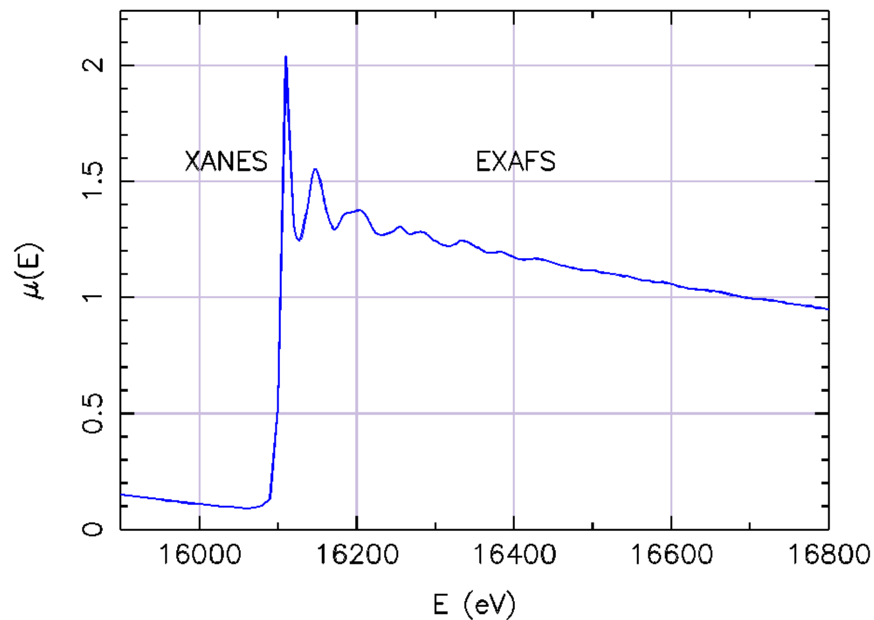
- Outgoing photoelectrons backscatter from near-neighbor atoms B.
- Interference between the outgoing and the backscattered photoelectron waves causes modulations (oscillations) in the x-ray intensity and thus the absorption coefficient.
- Therefore, the oscillations in the absorption coefficient have all the information about the local structure:

  - The distance between A and B;
  - How many and what kind of atoms A is surrounded with

X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopy: Measures energy-dependence of the x-ray absorption coefficient μ(E).





$$I = I_0 \exp[-\mu(E)d]$$

$$\mu(E) = \frac{1}{d}\ln(I_0/I)$$

$$\mu(E) \propto I_f/I_0$$

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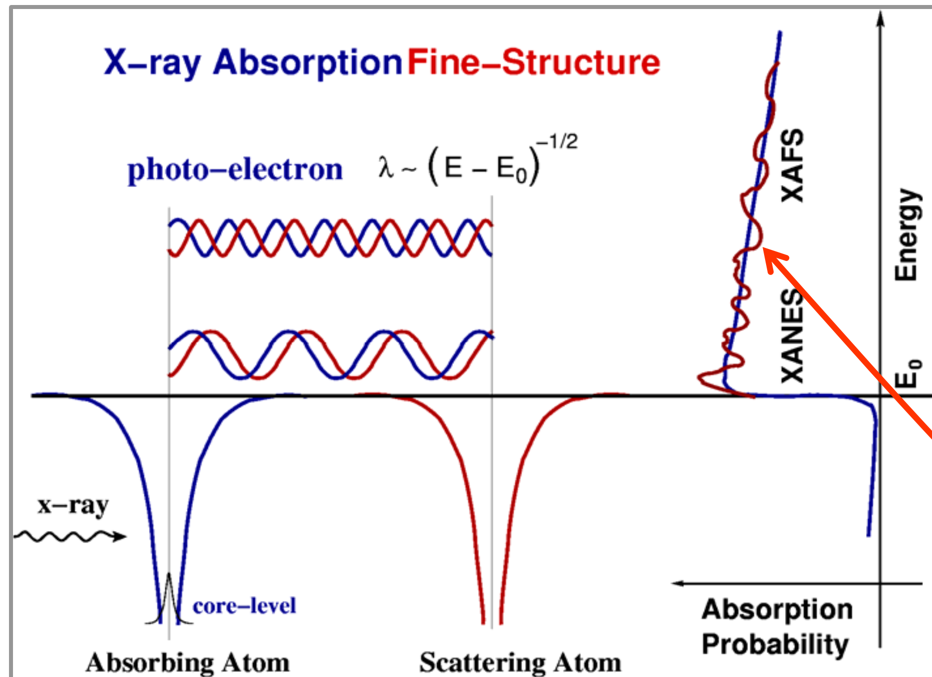
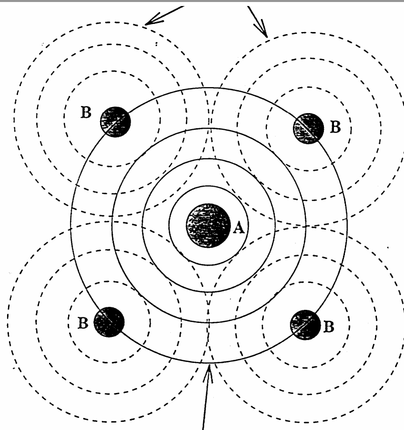
X-ray Absorption Fine-Structure Spectroscopy





- With another atom nearby, the photo-electron can ***backscatter*** from a neighbour atom.
- Interference between the outgoing and the backscattered photoelectron waves alters the photo-electron wave-function at the absorbing atom, modulating the absorption coefficient $\mu(E)$.
- Therefore, the oscillations in the absorption coefficient have all the information about the local structure:

- The distance between A and B.
- How many and what kind of atoms A is surrounded with.
- Local structural disorder

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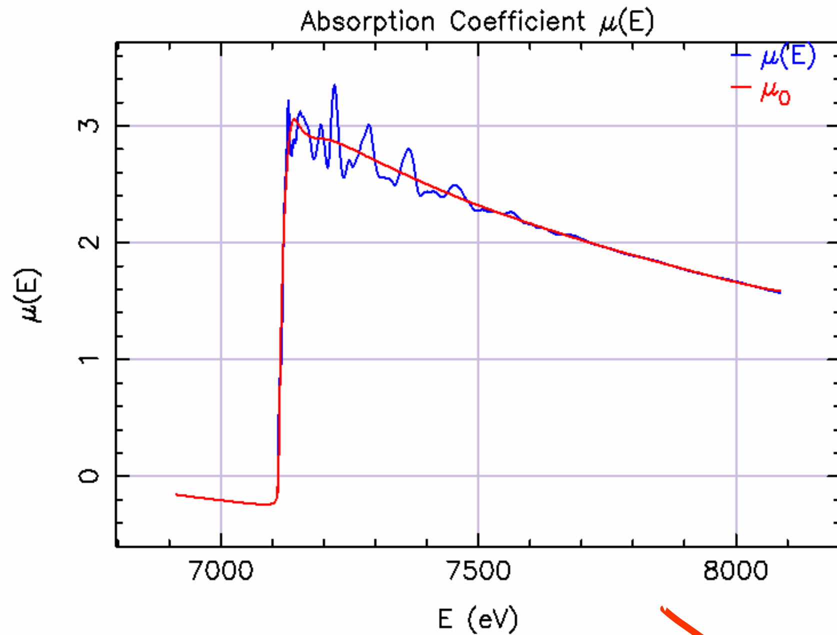
Extracting the oscillatory part: XAFS Function



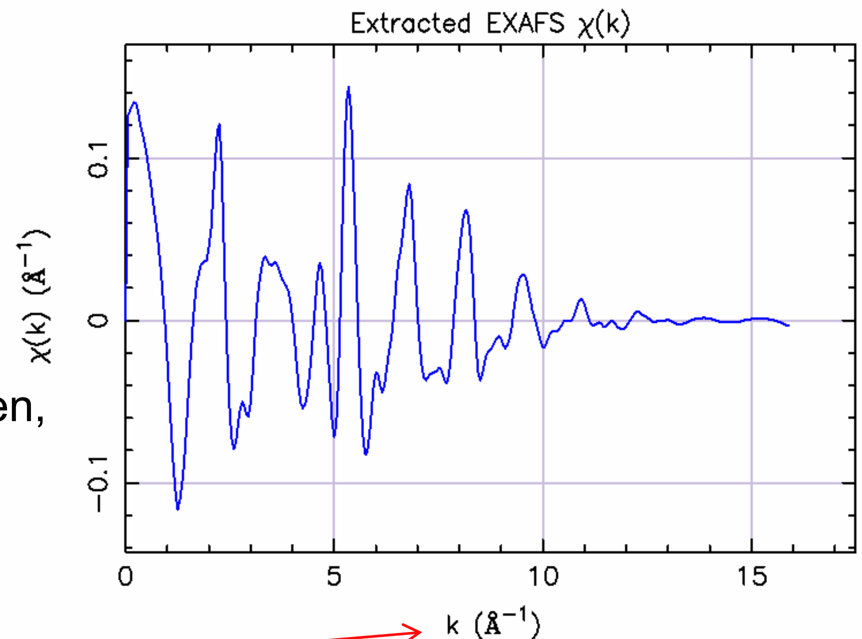
- After subtracting the atomic absorption, the oscillatory XAFS part of the modulating the absorption coefficient $\chi(k)$ is extracted

$$E - E_0 = KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$p = h/\lambda$; De Broglie wavelength or,

$p = hk/2\pi$; where $k = 2\pi/\lambda$ is the wave number then,

$$E - E_0 = \frac{(hk/2\pi)^2}{2m} \Rightarrow k = \sqrt{\frac{2m(E - E_0)}{(h/2\pi)^2}}$$



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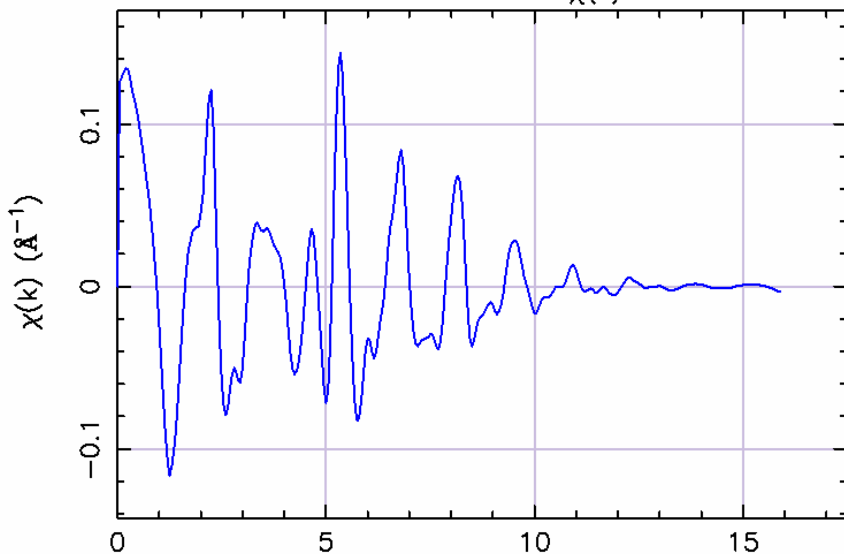
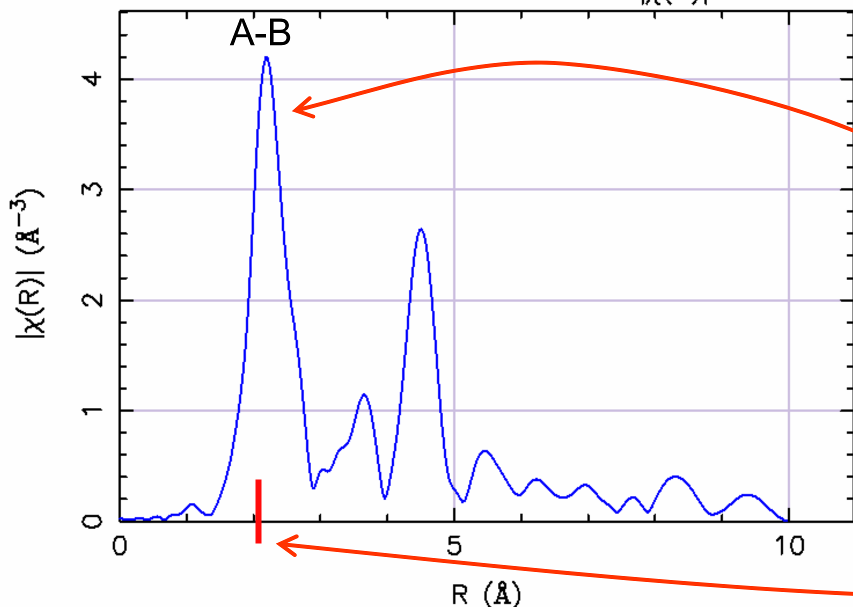
Structural Information From XAFS



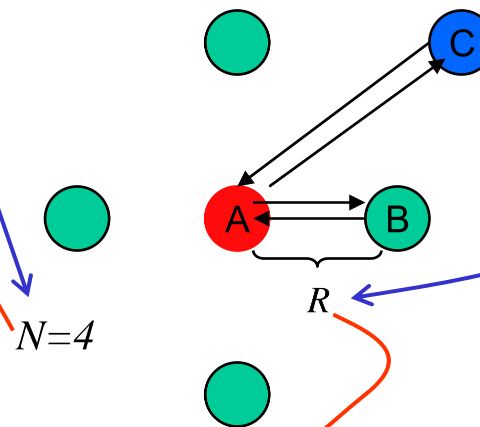


- $\chi(k)$ is a sum of sine waves with scattering amplitudes and phases.

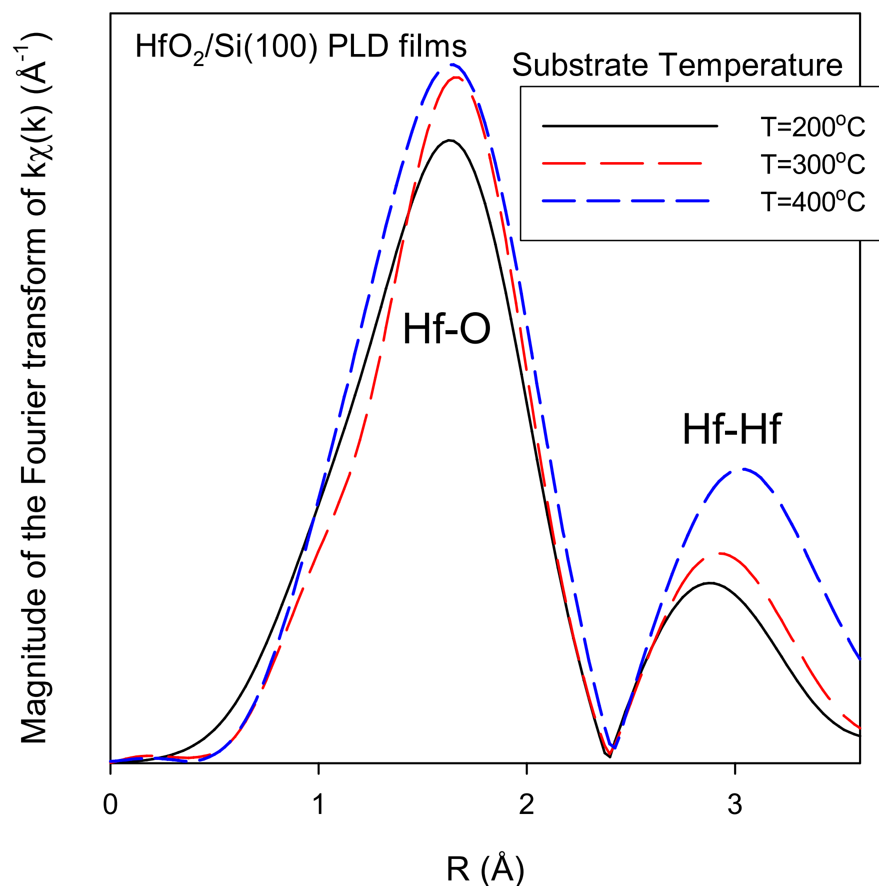
$$\chi(k) = \sum_j \chi_j(k) = \frac{Nf(k)}{kR^2}\sin[2kR + \delta(k)]$$

$f(k)$ is the scattering amplitude

$\delta(k)$ is the scattering phase



The Effect of the Substrate Temperature During Deposition



- HfO_2/Si(100) PLD with different substrate temperatures
- Fourier Transformed (FT) XAFS data shows an increase with substrate temperature for the first and second shell peaks
  - *Due to increase in the coordination numbers, (higher crystallinity)*

XAFS experiments at Beamline X23A2 of NSLS of Brookhaven National Laboratory

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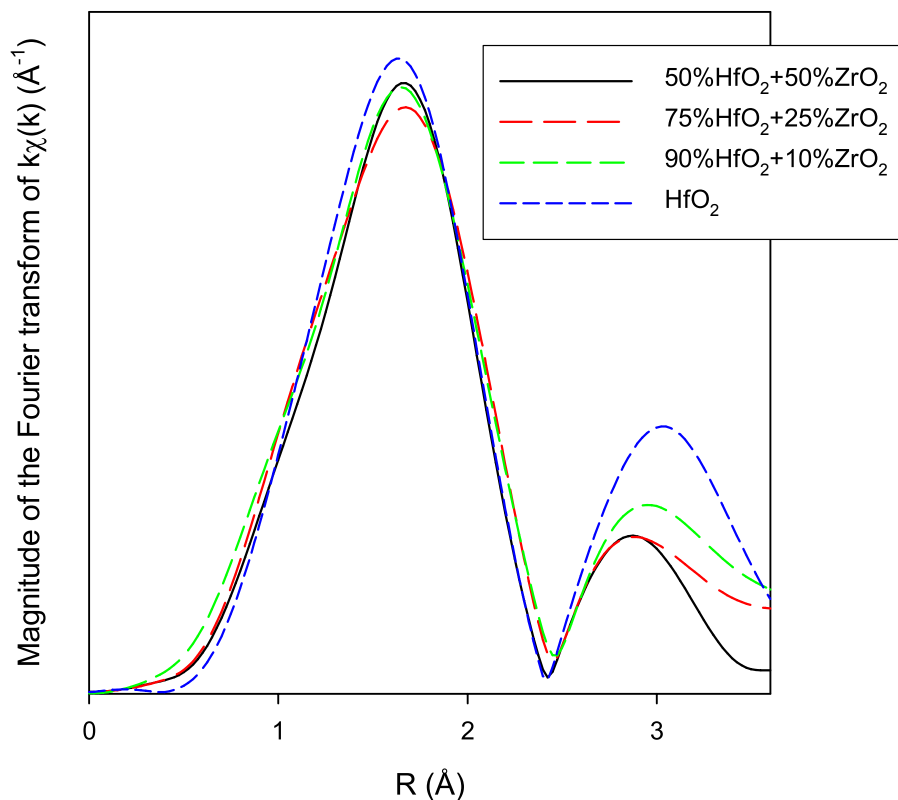
The Effect of Compositional Variance on the Local Coordination



- $(HfO_2)_x(ZrO_2)_{1-x}$/Si(100) films with x= 0.50, 0.75, 0.90, 1.00
- The second shell peak is affected more in the Fourier Transformed (FT) XAFS data.
  - *Hf-Hf coordination decreases with more Zr introduced to the system.*

M. A. Sahiner et al., Gordon Research Conference on Ceramics, Andover, NH (August 13-18, 2006)

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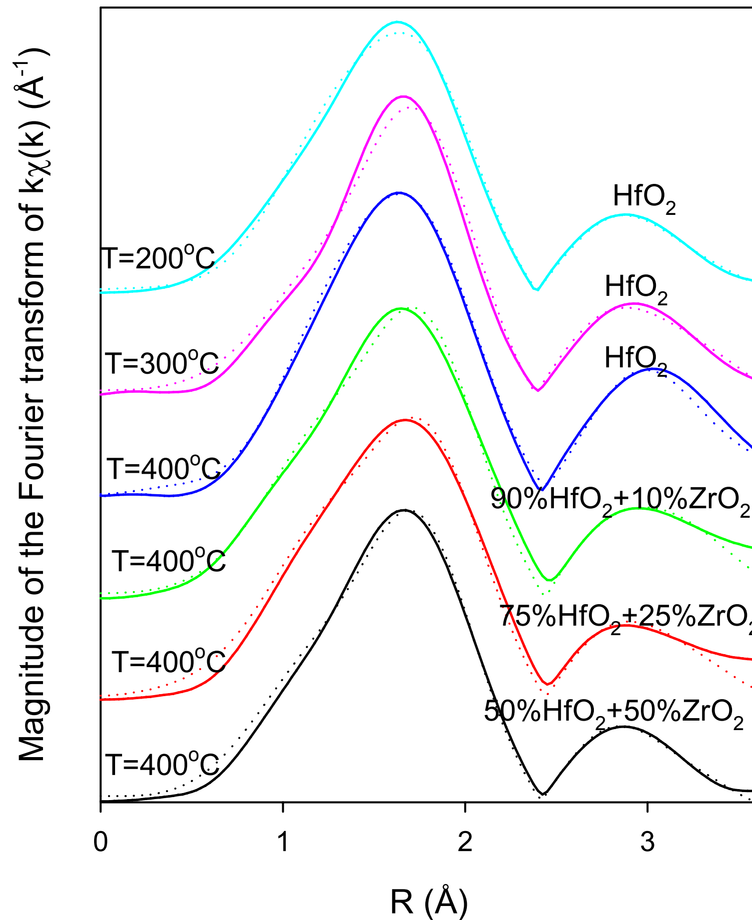
XAFS Data and the Non-linear Least-squares Fits to the Data for All the PLD Films[1]



- Top three: *temperature variation*
- Bottom four: *compositional variance*

XAFS fits were performed using FEFF8.2[2] calculations for scattering amplitudes and phases.

[1] M. A. Sahiner et al. Thin Solid Films- Elsevier (2006).

[2]Univ. Of Washington's multiple scattering simulation code

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XAFS Fit Results

	1st shell		2nd shell	
PLD Film	N_{Hf-O}	**R(Å)**	N_{Hf-Hf}	**R(Å)**
HfO_2/Si(100) T=200°C	5.52	2.01	4.59	3.47
HfO_2/Si(100) T=300°C	5.64	2.02	5.55	3.47
HfO_2/Si(100) T=400°C	6.39	2.02	8.28	3.48
$(HfO_2)_x(ZrO_2)_{1-x}$/Si(100) (x=0.90) T=400°C	6.09	2.01	6.23	3.47
$(HfO_2)_x(ZrO_2)_{1-x}$/Si (100) (x=0.75) T=400°C	6.00	2.01	5.02	3.47
$(HfO_2)_x(ZrO_2)_{1-x}$/Si(100) (x=0.50) T=400°C	5.91	1.99	4.19	3.47

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$(HfO_2)_x(ZrO_2)_{1-x}$/Si(100) **(x=0.50)** T=400°C	**5.91**	1.99	**4.19**	3.47

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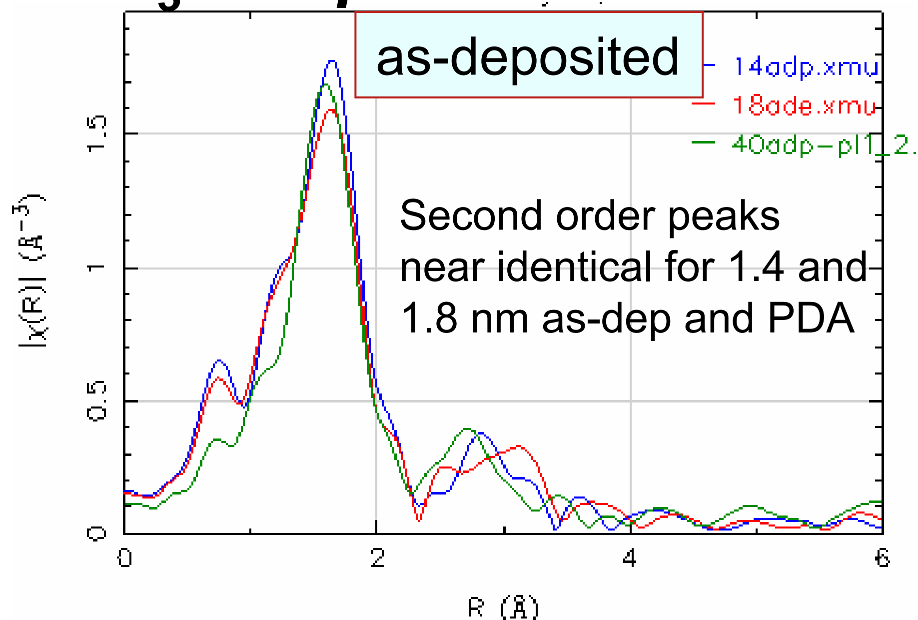
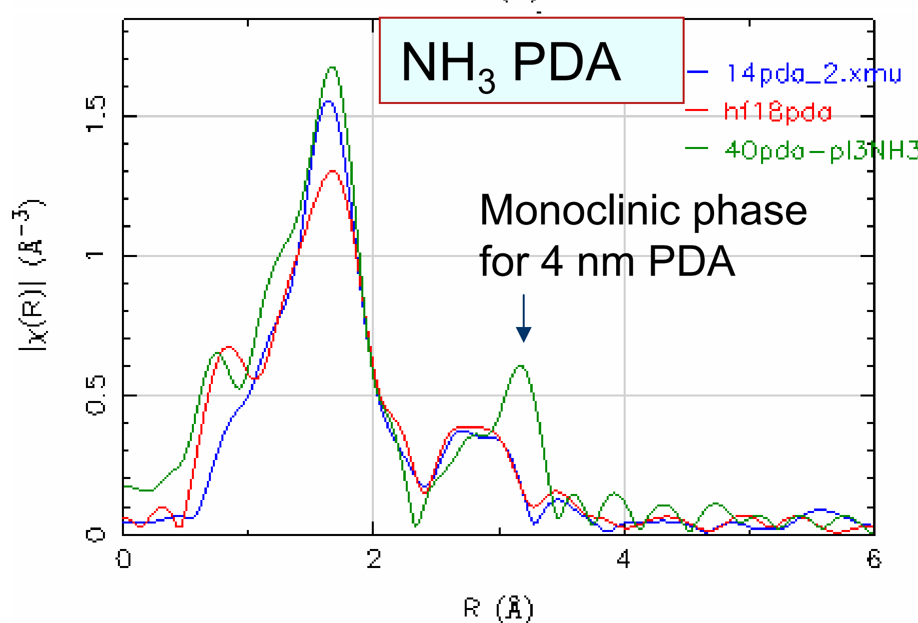
XAFS @ NIST Beamline X23A2 (NSLS/BNL)-w/SEMATECH

Hf L_3 FT Spectra of Scaled HfO_2





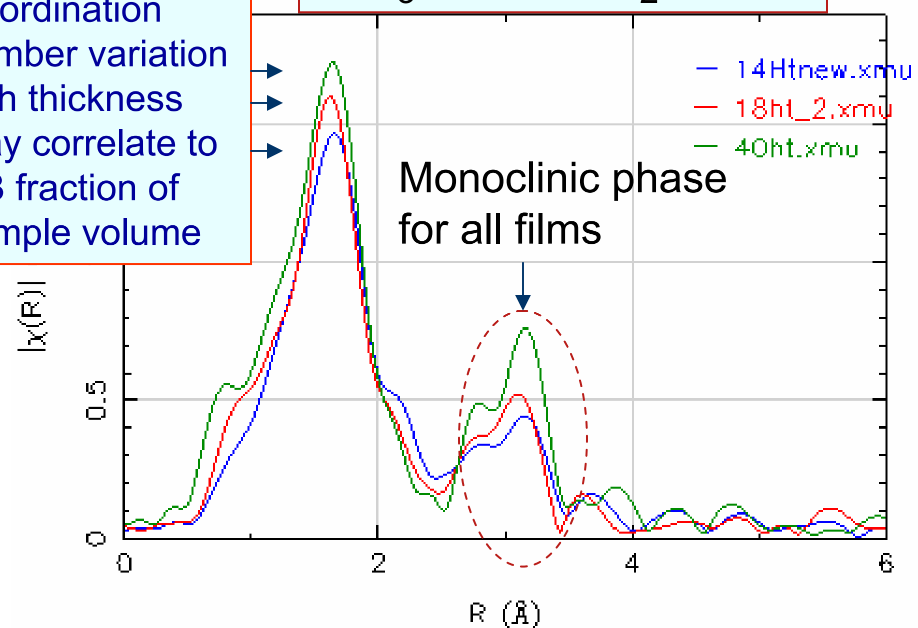
Thickness Effects

1.4, 1.8, and 4.0 nm HfO_2

Monoclinic phase emerges for all films post RTA, although suppressed for 1.4 and 1.8 nm

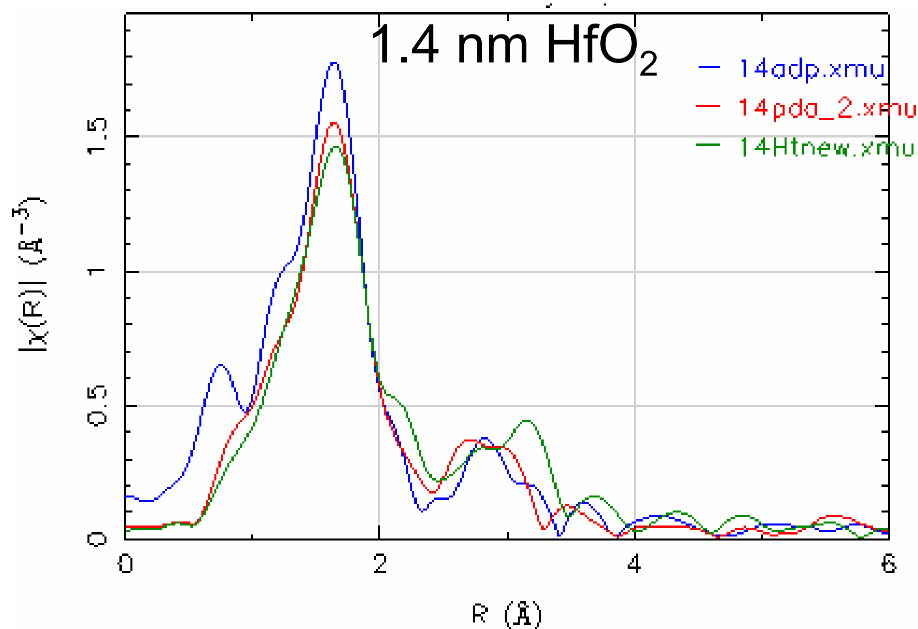
1.4 and 1.8 nm PDA and Ht sample second order peaks due to competition between phases

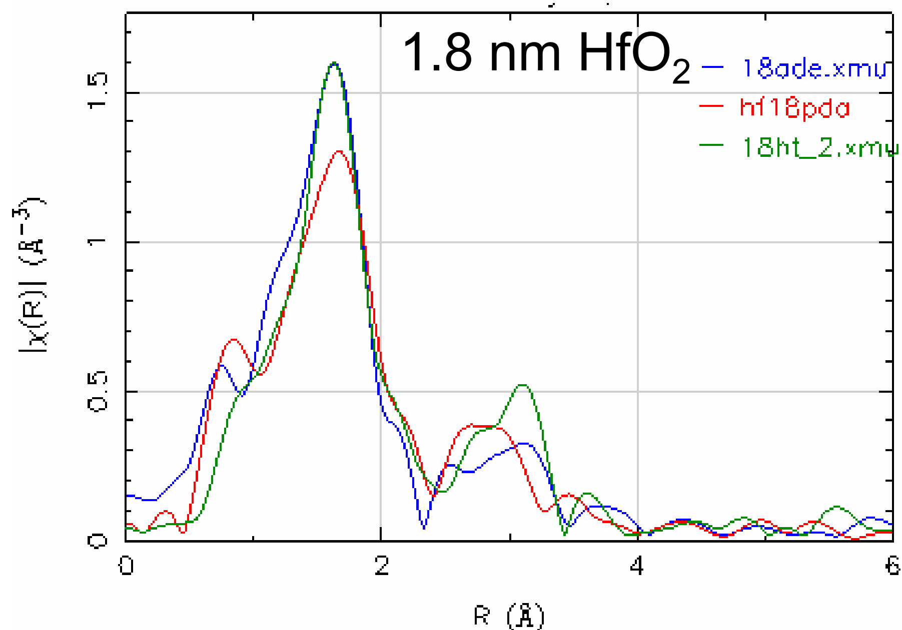
Coordination number variation with thickness may correlate to GB fraction of sample volume



XAFS @ NIST Beamline X23A2 (NSLS/BNL) w/SEMATECH

Hf L_3 - 1.4, 1.8, 4nm HfO_2 as f(temp)



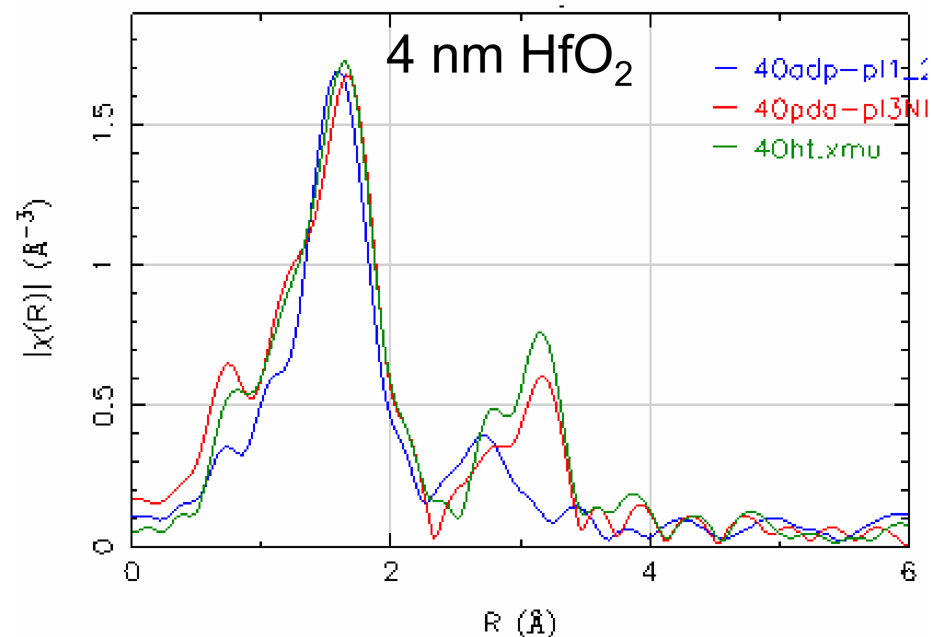


Temperature Effects

1.4, 1.8, and 4.0 nm HfO_2

All films appear structurally amorphous as-deposited with evidence for incipient nanocrystallinity

Monoclinic phase emerges for all films post RTA, although suppressed for 1.4 and 1.8 nm



Conclusions (high-k)

- XAFS local structural analysis:
  - Substrate temperature during deposition is closely correlated with the Hf near-neighbor correlations (Hf-O and Hf-Hf), could be used as a sensitive probe for crystalline quality *as higher the temperature closer to the monoclinic coordination numbers*
  - ZrO_2 incorporation does not affect the Hf-O coordination but Hf-Hf coordination in the second shell (Hf replacement by Zr).
  - A stable monoclinic phase is strongly dependent on thickness (1.8nm-4.0nm) and post deposition annealing process.
  - **Future work:** Very thin PLD films of Hf-based high-k dielectric materials will be (local) structurally analyzed by XAFS in order to probe the effects of the PLD parameters such as: temperature, laser energy, frequency, and partial oxygen pressure on the *interface.*

    Films will be annealed and local structures of single-crystal films will be probed.

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Region 2, Problem 2

Paul A. Packan from Intel, describing the current main challenges facing the semiconductor industry[1]:

"Although the transistors can shrink in size, the smaller devices still need to maintain the same charge. To do that, the silicon has to have a higher concentration of dopant atoms. Unfortunately, above a certain limit the dopant atoms begin to clump together, forming clusters that are not electrically active. You can't increase the concentration of the dopant, because all the extras just go into the clusters."

[1] Science, Volume 285, Number 5436, Issue of 24 September 1999

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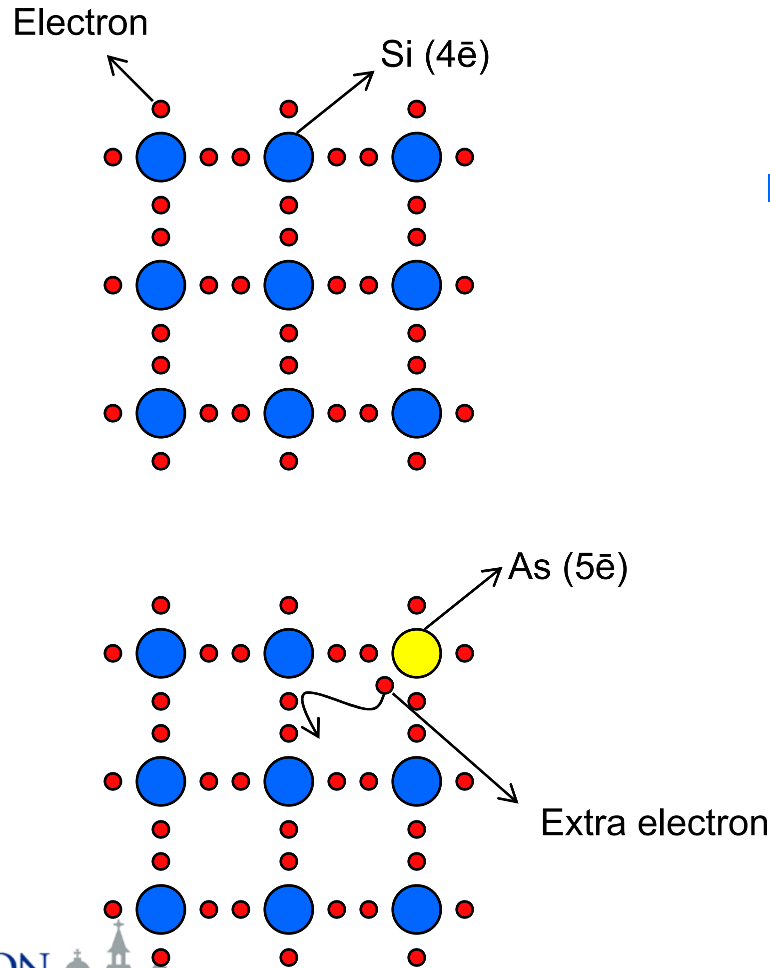
Doping of Semiconductors

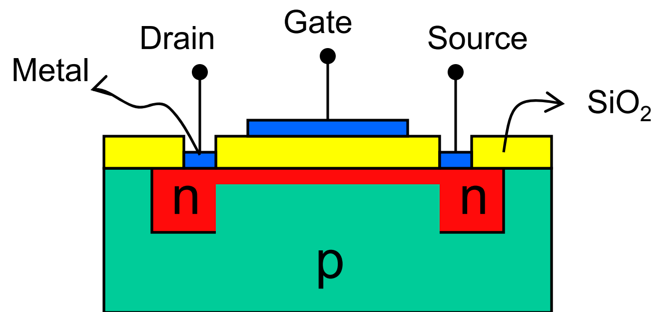


- Si : Intrinsic (undoped) semiconductor:
  - 4 outer shell electrons
  - Two electrons are shared between near-neighbors

- Arsenic (As) doped Si: *n-type* semiconductor
  - As has 5 outer shell electrons
  - One is free to move around
  - More dopant atoms ⇒more free charge carriers

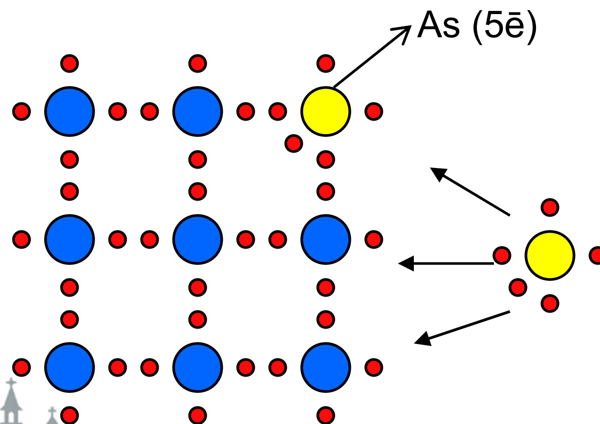
HIGHER CONDUCTIVITY

Region 2: Importance of High Level Doping in Transistors



n-channel MOSFET

- Although the transistors can shrink in size, the smaller devices still need to maintain the same charge.
- To do that, the silicon has to have a higher concentration of dopant atoms.



Solution: Put more dopant (arsenic) atoms into the Si crystal to increase the carrier concentration.

?

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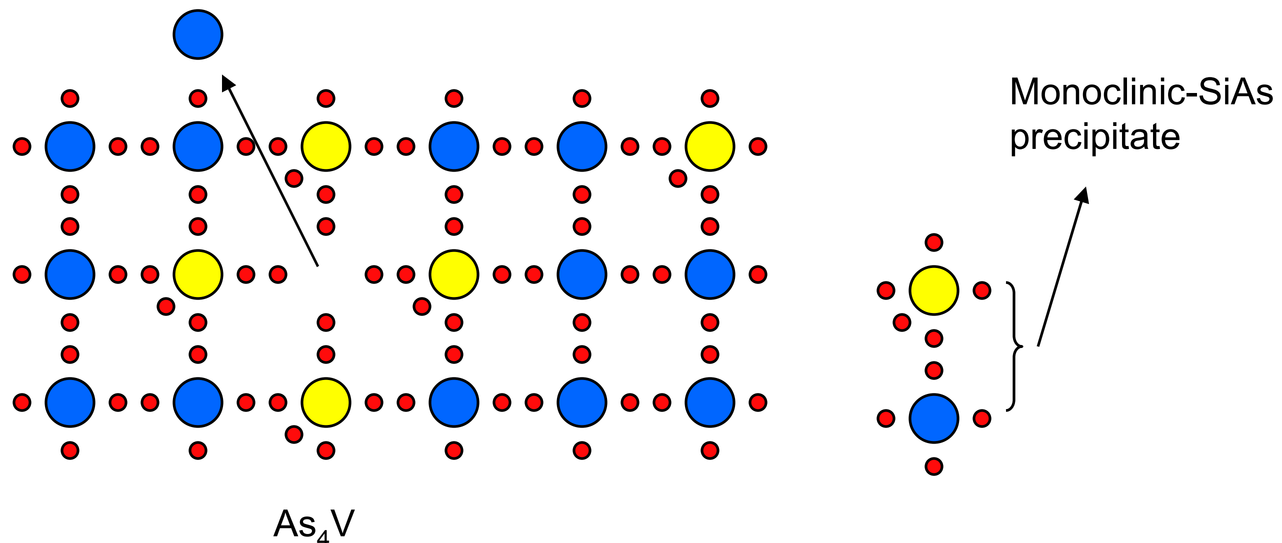
Region 2: Problems in High Level Doping in Transistors

- Unfortunately, above a certain limit the dopant atoms begin to clump together, forming clusters or precipitates that are *not electrically active.*
- One cannot increase the concentration of the dopant, because all the extras just go into the clusters



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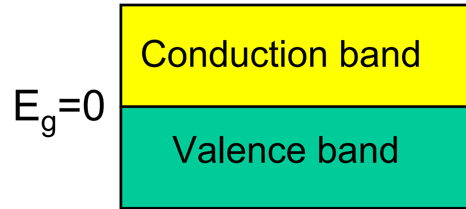
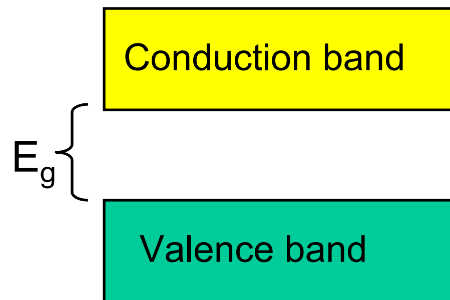
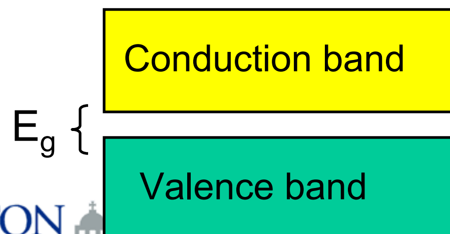
Energy Bands in Conductors, Insulators, and Semiconductors



- Conductors:
  - Energy gap (E_g) = 0
  - Resistivity ~10^{-6} ohm-cm



- Insulators:
  - E_g ~ 5-10eV
  - Resistivity ~10^{11}-10^{17} ohm-cm



- Semiconductors:
  - E_g ~ 1 eV
  - Resistivity ~10^{3}-10^{6} ohm-cm

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Problem 2 and proposed solution: annealing

- Some of the important challenges in the semiconductor technology are:
  - Doping intrinsic semiconductors with impurities above solid solubility limits to increase carrier concentration in shallow junctions.
  - Sustaining high level carrier concentration and eliminating any inactive structures (cluster or precipitates) formed by the dopants by annealing mechanisms.

Therefore, information on the local structure around the impurity atom is of crucial importance to face with these requirements.

Using x-rays:

- What can X-ray Absorption Fine Structure Spectroscopy (XAFS) do for me in clustering problem?

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Application to Problems in Semiconductor Industry

- XAFS being capable of probing
  - The short range order in crystalline and amorphous materials
  - One element at a time

- Can provide information on the number, distance and chemical identity of the neighbors of the main absorbing atom (e.g. As, Sb, B).

This information can be used to identify the nature and amount of any dopant-related inactive structures in the material[1,2,3,4].

[1]M. A. Sahiner et al., Microelectronics Journal (Elsevier), **36,** 522-526 (2005).

[2] M. A. Sahiner et al. IEEE Transactions on Electron Devices **52**, 2416-2421 (2005)

[3]M. A. Sahiner et al., MRS Publications **Vol. 717**, C3.6.1, (2004)

[4]M. A. Sahiner et al., IIT2000 IEEE **Vol. EX432**, 600 (2003)

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Arsenic in Si :

Effects of High Dose As Implantation on the Local Structure

- As ion implantation may lead to:
  - Substitutional As:
    - Nearest neighbor : Si
    - Coordination number: 4 (4 Si atoms around)
    - Nearest neighbor distance (R): ~2.40 Å
  - Precipitates in the form of monoclinic SiAs
    - Nearest neighbor: Si
    - Coordination number: 3 (3 Si atoms around)
    - Nearest neighbor distance (R): ~2.37 Å
  - As_2V, As_4V clusters (V: vacancies):
- XAFS analysis provides the coordination numbers and the nearest neighbor distances around As.
- In this way, we are going to determine the structure of the As at different As doping levels after annealing

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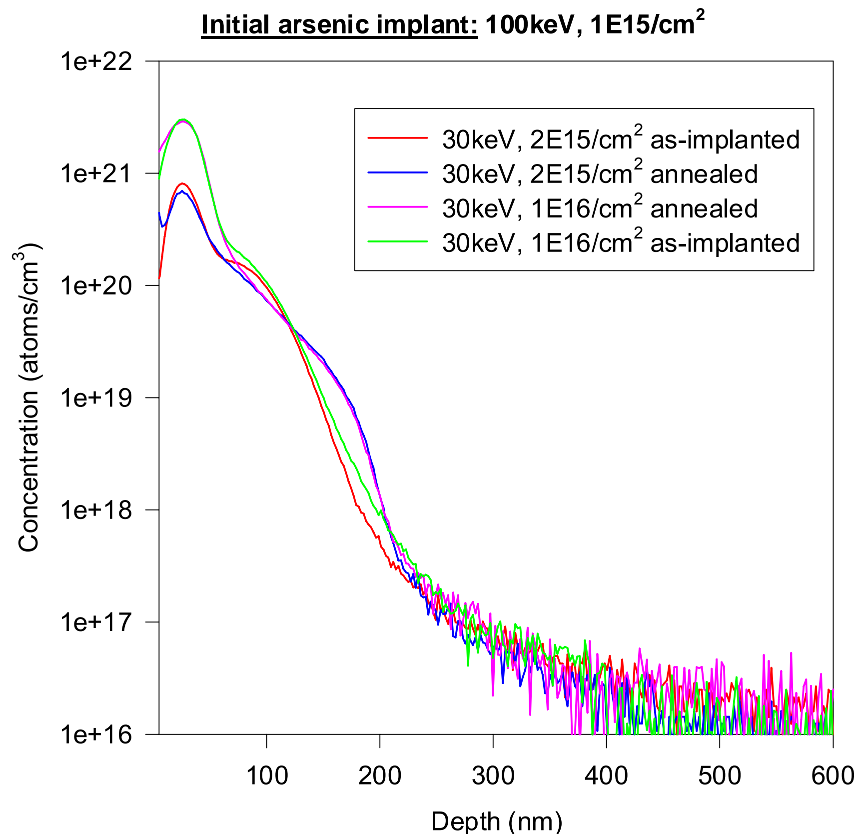
Comparison of Low and High Dose As Implants- Secondary Ion Mass Spectroscopy



- Are the concentrations for the 1E16/cm^2 second implants higher than critical clustering/precipitation concentration?
- XAFS information is needed to investigate if there is any clustering/precipitation or not.

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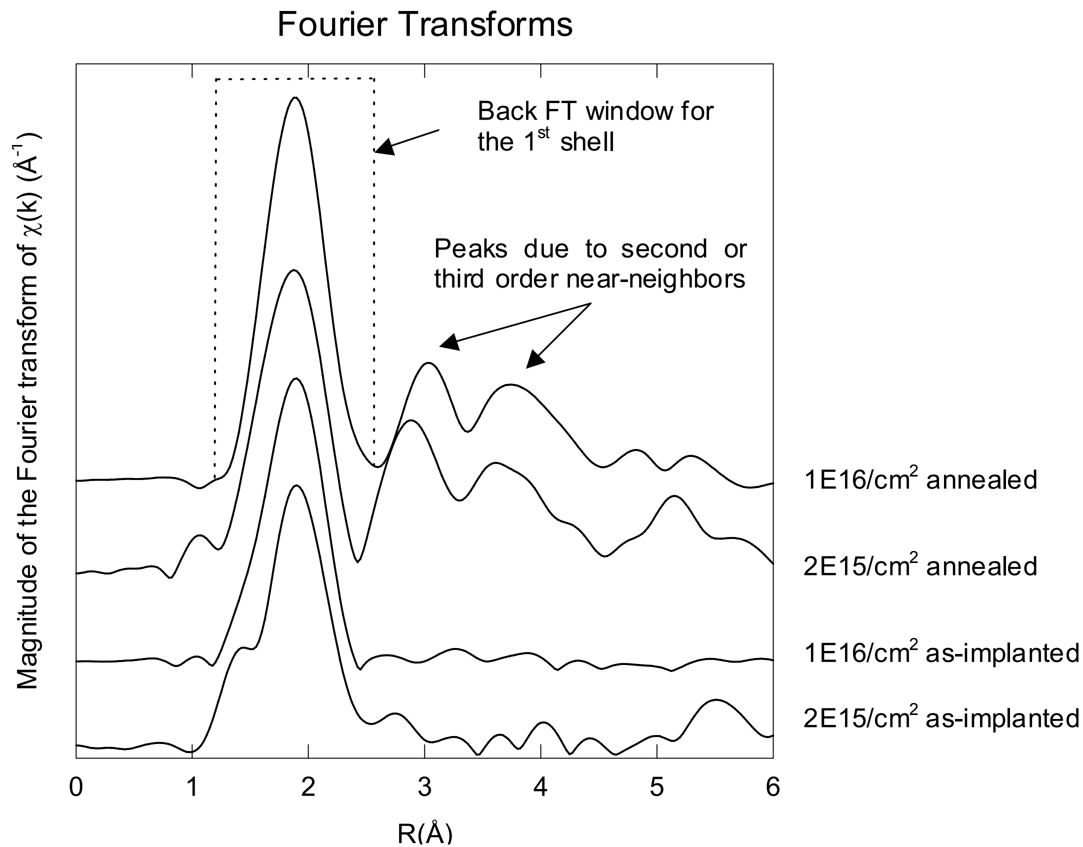
Structural Information from Arsenic XAFS Data



- The first peak shows the As-Si scattering
- First shell peaks are well-resolved so the coordination numbers and near neighbor distances can be extracted easily by working on this peak only.

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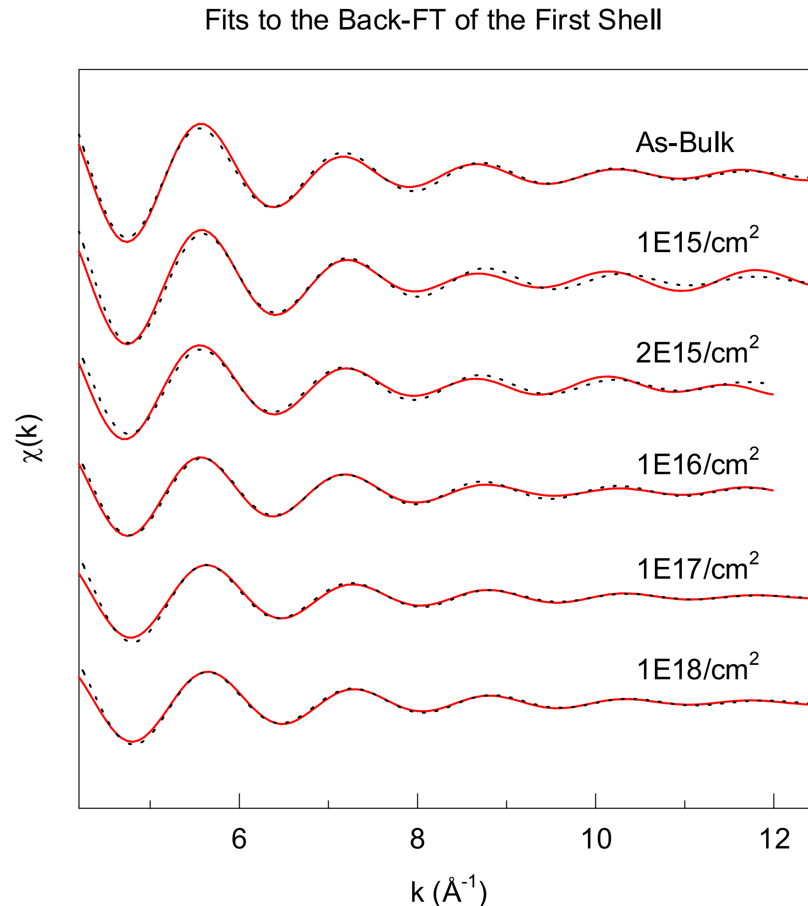
Least Square Fits to the Back-Fourier Transforms



As Conc./Dose	R(Å)	N	Structure of As
As-Bulk	2.40	3.98	Substitutional
1E15/cm^2	2.39	3.61	Substitutional
2E15/cm^2	2.39	3.50	Cluster/precipitate
1E16/cm^2	2.38	3.27	Cluster/precipitate
1E17/cm^2	2.37	3.13	Cluster/precipitate
1E18/cm^2	2.36	3.01	Cluster/precipitate

- These results indicate high dose arsenic implants (>1E16/cm^2) forms As clusters and precipitates in the form of SiAs causing electrical deactivation.

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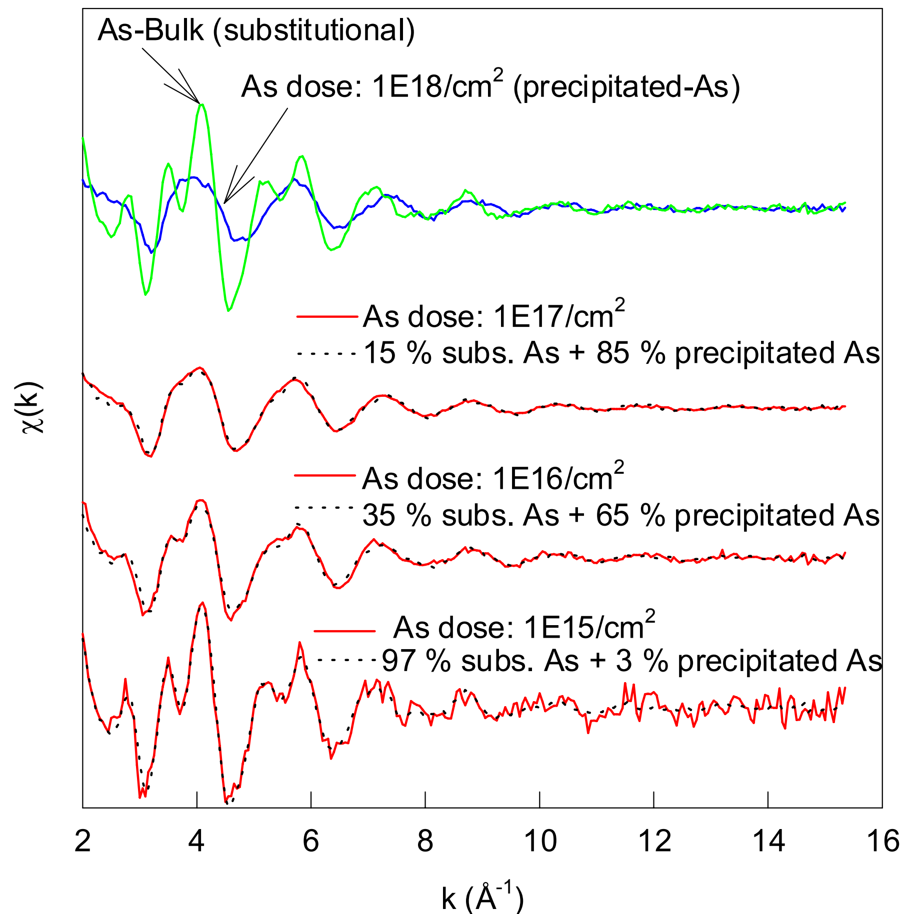
Substitutional vs Precipitated Arsenic Ratio



- As bulk with low As concentration is a standard for pure substitutional As.
- As implanted Si at a very high dose of 1E18/cm^2 serves as a pure precipitate standard.
- Using the linear combinations of XAFS functions of these two standards, the percentages of the substitutional As can be determined at different implant doses.

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Conclusion (As in Si)

- XAFS can directly probe the clustering/precipitation/substitution problem in ion-implanted Si crystals. The weight of these three mechanisms can be manipulated by modifying the annealing conditions and impurity concentrations in the light of the local structure information.
- The critical concentration values for the cluster/precipitate formation under different annealing conditions can be determined.
- Using the substitutional and precipitated forms of arsenic as standards, the ratios of the substitutional vs precipitated arsenic in a specific sample can be determined.