The relation between crystalline phase, electronic structure and dielectric properties in high-K gate stacks

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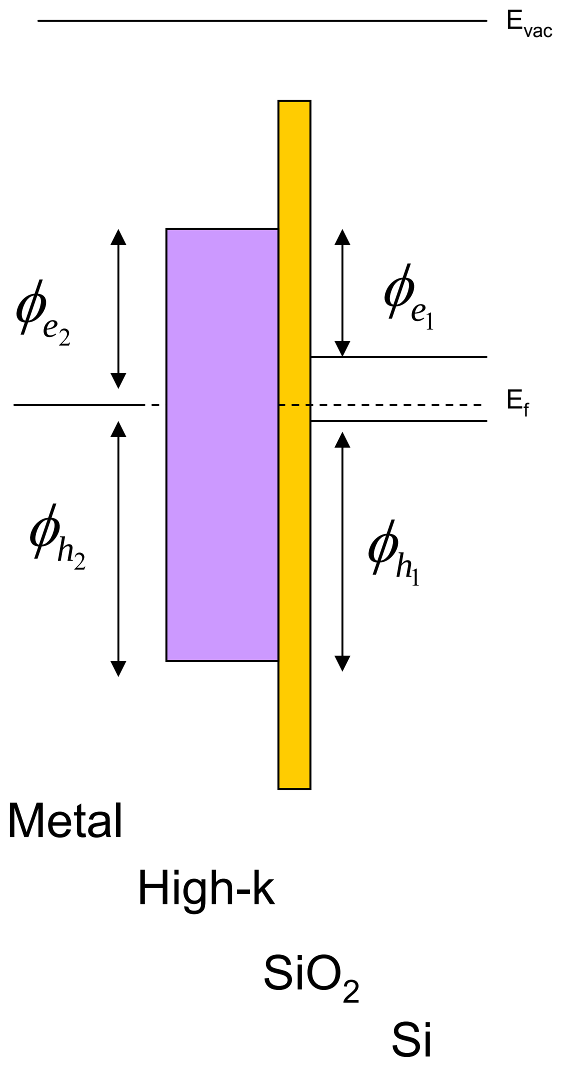
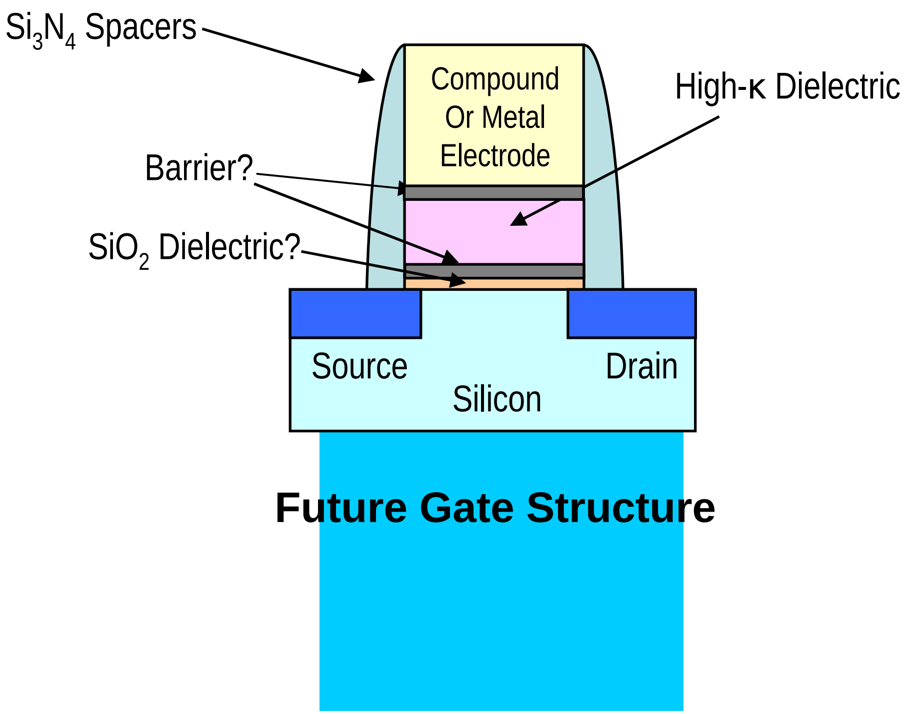
Scaling the MOSFET Gate Stack Structure

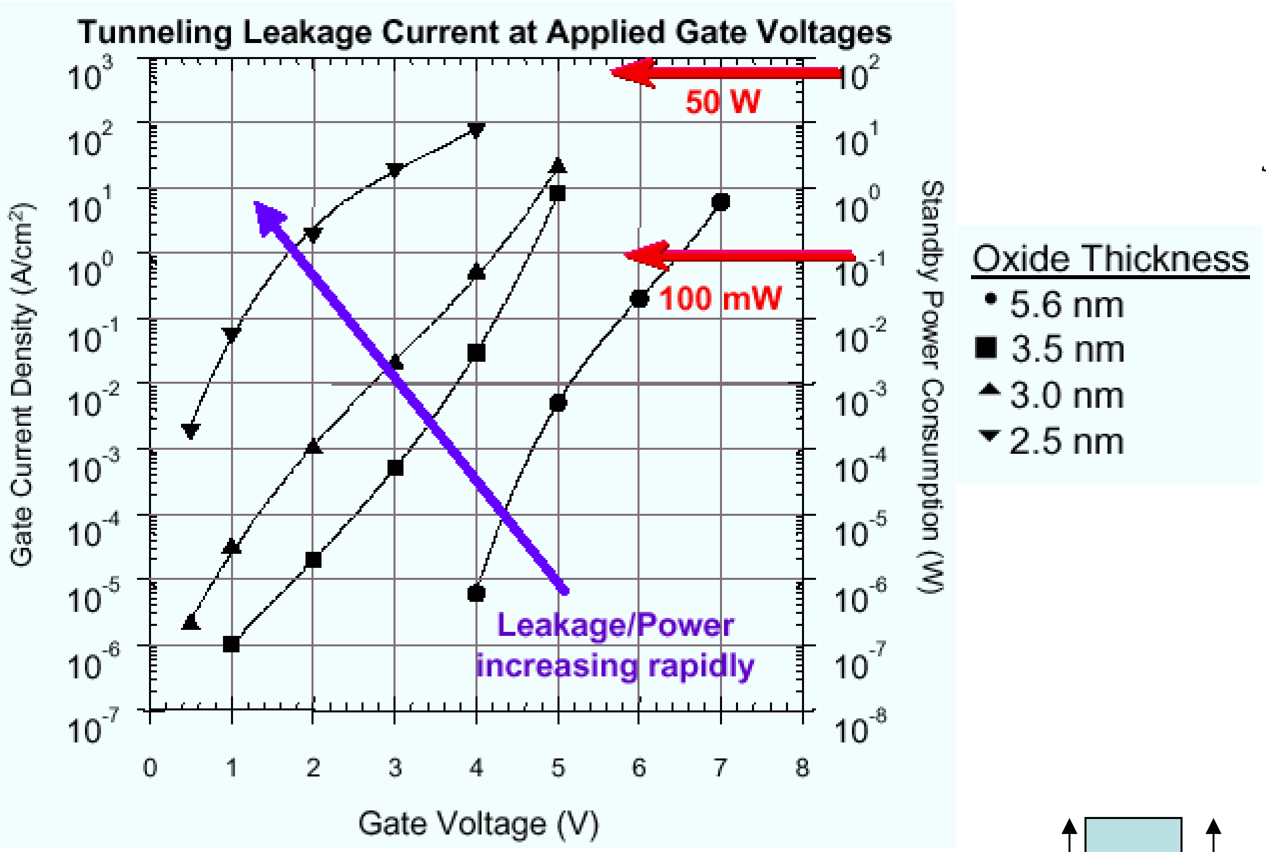




Future Gate Structure

- Si-compatible high-k dielectric
- Barrier layers and stacked structures
- New electrode: Ge doped Si, metal, metallic oxide or nitride
- EOT 10⇒5Å?

Benefit of integrating high-k material in CMOS devices



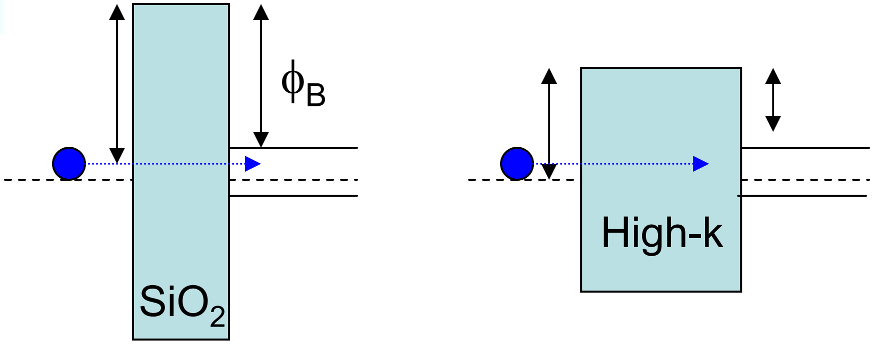
$$J \alpha T^2 \exp\left[\frac{q\left(-\phi_B + \sqrt{\frac{qE}{4\pi\varepsilon_i}}\right)}{kT}\right]$$

$$J \alpha E \exp\left[\frac{q\left(-\phi_B + \sqrt{\frac{qE}{\pi\varepsilon_i}}\right)}{kT}\right]$$

$$J \alpha \frac{q^3E^2}{\phi_B} \exp\left(\frac{-c\left(q\phi_B\right)^{\frac{3}{2}}}{qE}\right)$$

reduction in tunneling current

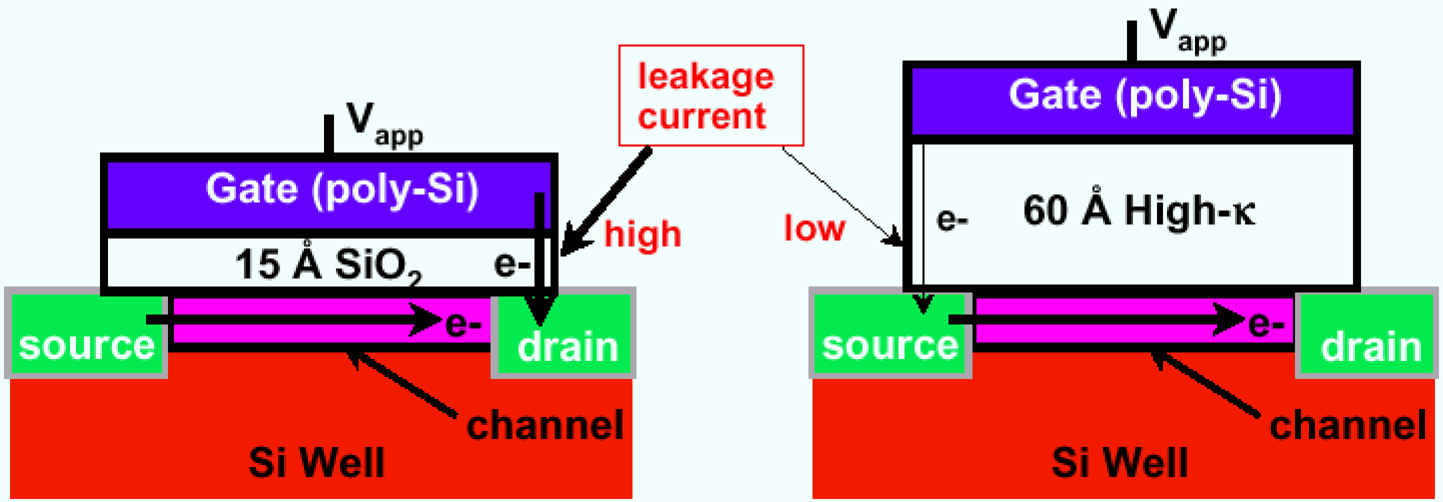
Less power dissipation



Trade-off: ϕ_B ↓ thickness ↑

G. D. Wilk, et.al, JAP 89, 5243 (2001)

Benefits of using a high-k material

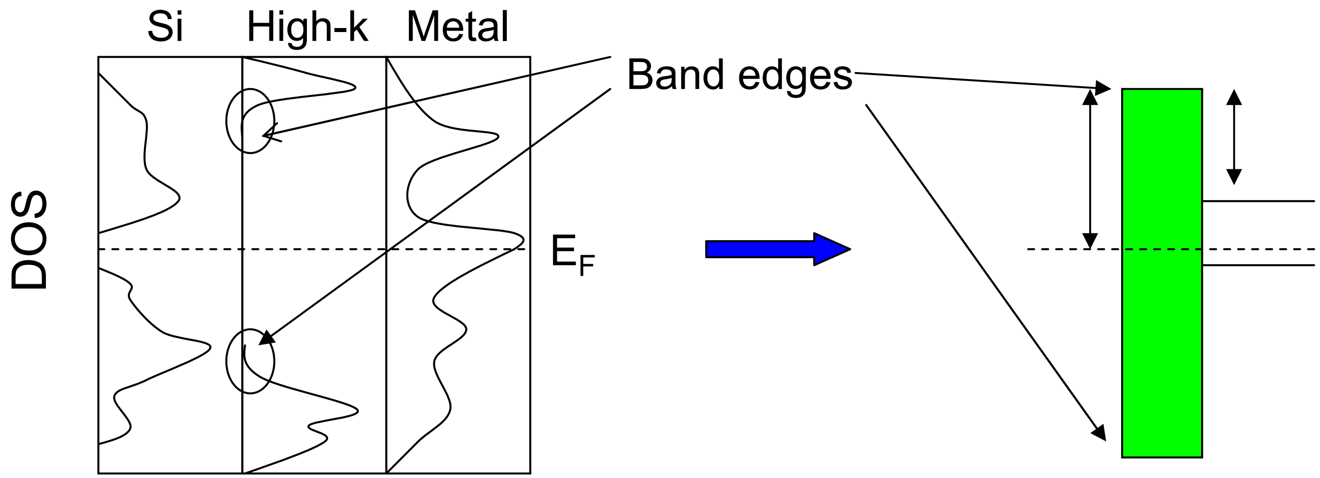


High-κ film ⇒ thicker gate dielectric ⇒ lower leakage w/ same performance

$$C_{ox} = \frac{\kappa \varepsilon_0 A}{t_{ox}} \Rightarrow t_{high-\kappa} = \left(\frac{\kappa_{high-\kappa}}{\kappa_{SiO_2}} \right) \cdot t_{SiO_2}$$

G.D. Wilk

How to locate the valence and conduction band positions?

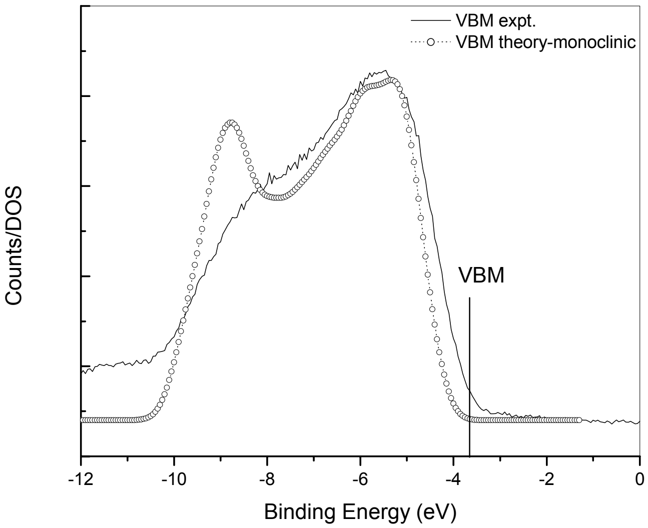


- Theoretical density of states (probably the best method)

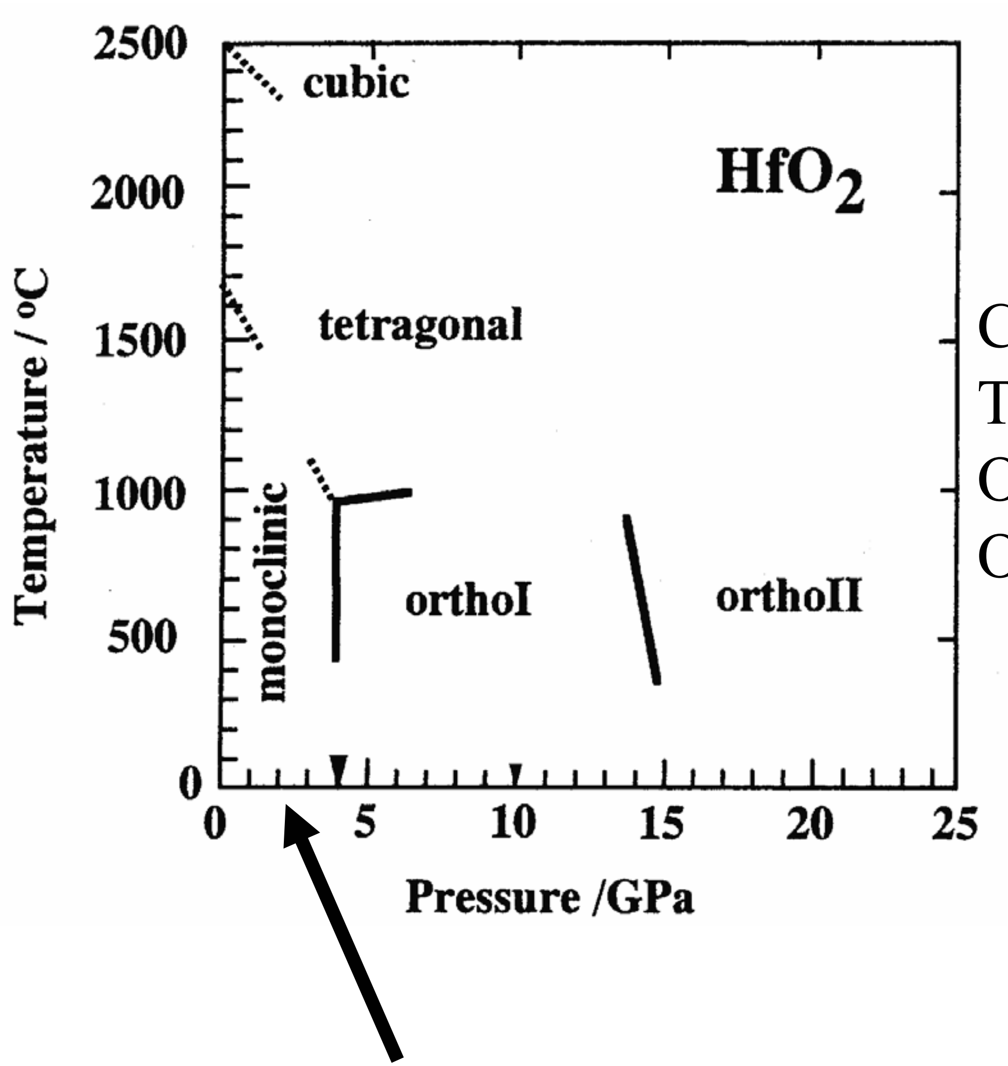
$$N_v(E)=\int_0^{\infty} n_v(E')g(E-E')dE'$$

Theoretical DOS

Response function



Phase Diagram for HfO_2



- 5 identified phases of HfO_2

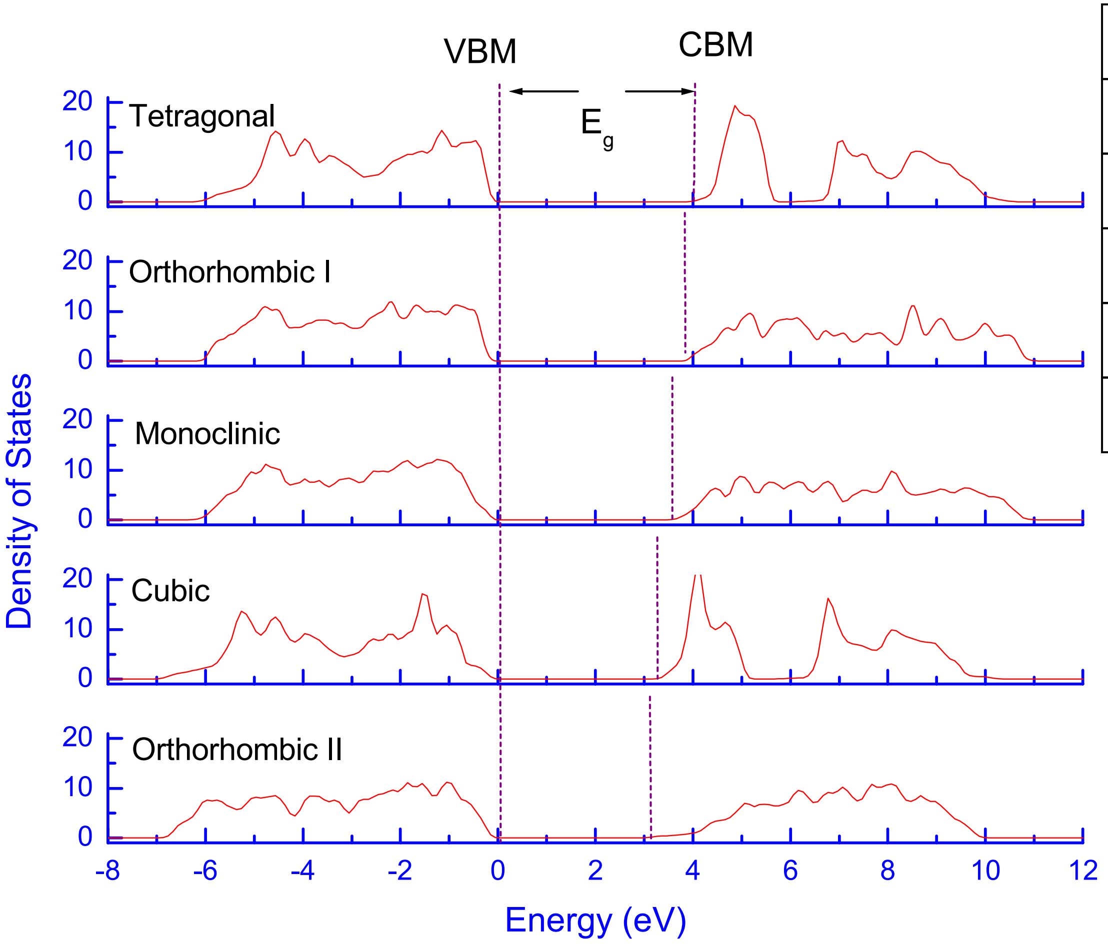
Cubic
Tetragonal
Orthorhombic I
Orthorhombic II

Meta-stable

May be <u>stabilized</u> by
- film stress
- grain-size effects
- impurities

<u>Monoclinic</u> - <u>stable phase</u>
at ambient temperature and pressure

Density of States for all phases of HfO_2



Crystal Phase	Band gap (eV)
Orthorhombic II	2.94
Cubic	3.15
Monoclinic	3.45
Orthorhombic I	3.75
Tetragonal	3.84

- Band gap values are different for phases!

- Effects on band alignment?

- Crystal structure can have considerable effect on measured band gap and hence barrier heights

Approach:

XRD, XAS, HRTEM, FTIR – for phase identification

DFT calculations – to determine DOS for the identified phase

Photoemission (PES) using soft x-rays – for mapping occupied densities of states

Inverse Photoemission (IPES)– for unoccupied densities of states

Sample preparation:

CVD HfO_2 using Hf-tetra-tert.-butoxide 400C in the thickness regime of 10 Å - 1μ

ALD ZrO2 using $ZrCl_4/H_2O$ chemistry at 300C in the thickness regime of 30-100 Å

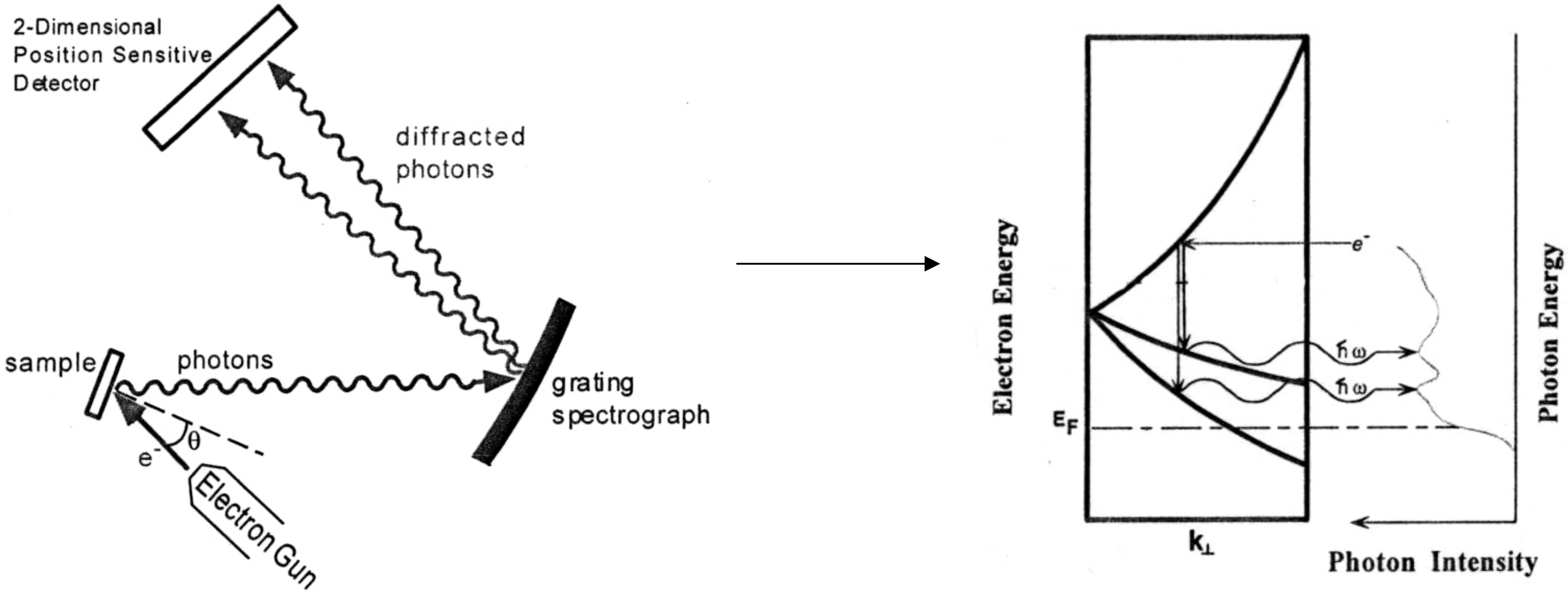
Photoemission Spectroscopy (PES):

Brookhaven National Laboratories – beamline U8b (100-350 eV)

Inverse Photoemission Spectroscopy IPES:

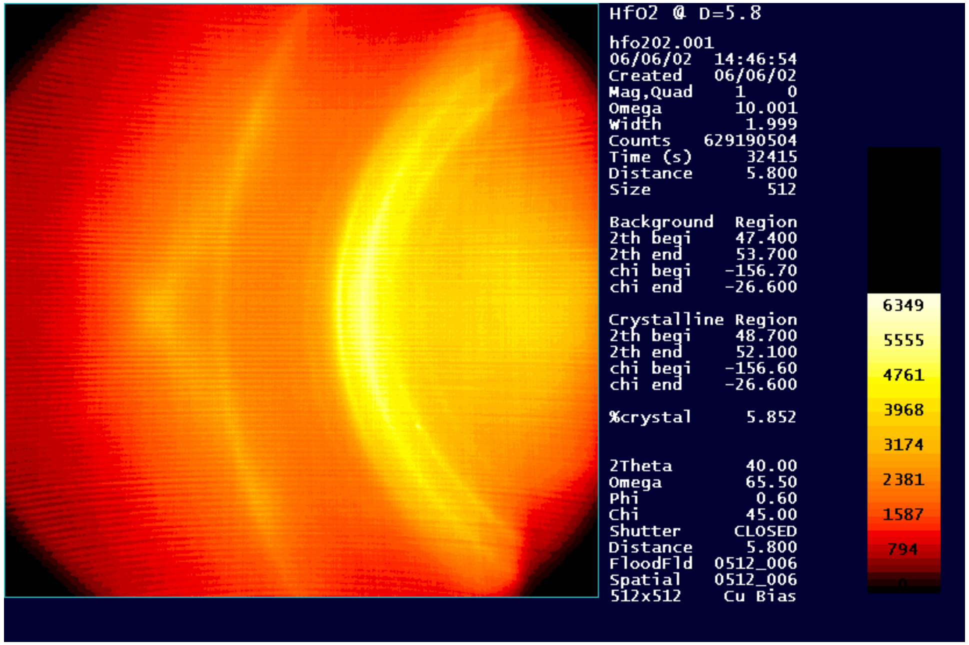
Rutgers University (15-40 eV)

Inverse Photoemission Spectroscopy (IPES)

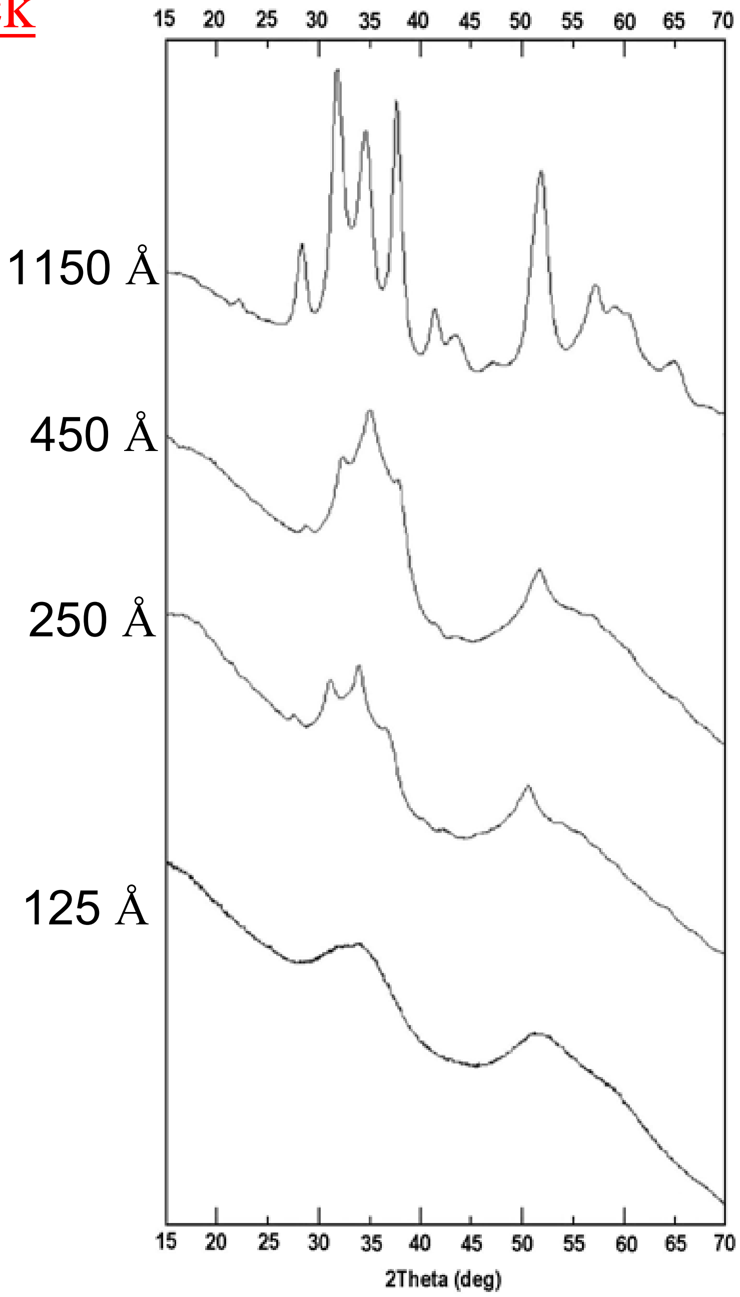


- IPES provides information on states above Fermi level
- Mapping of unoccupied states is possible
- Complementary technique to photoemission (PES)

XRD Studies on $HfO_2/SiO_xN_y/Si$ gate stack
Crystal structure – film thickness

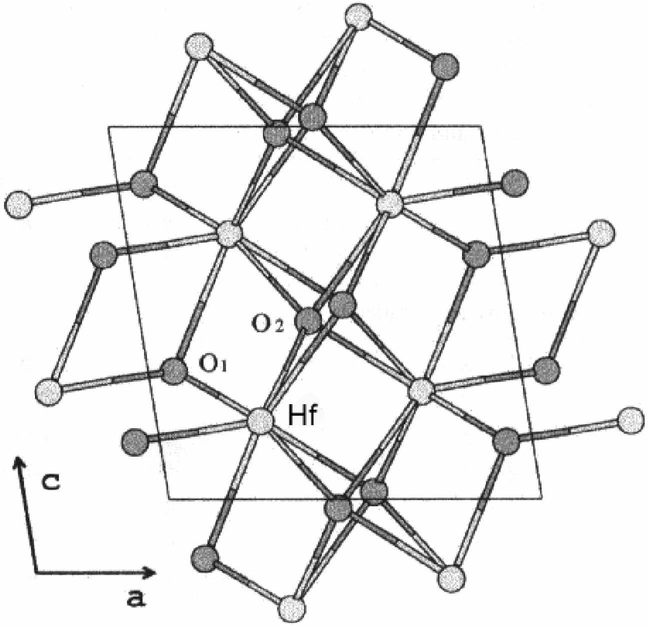


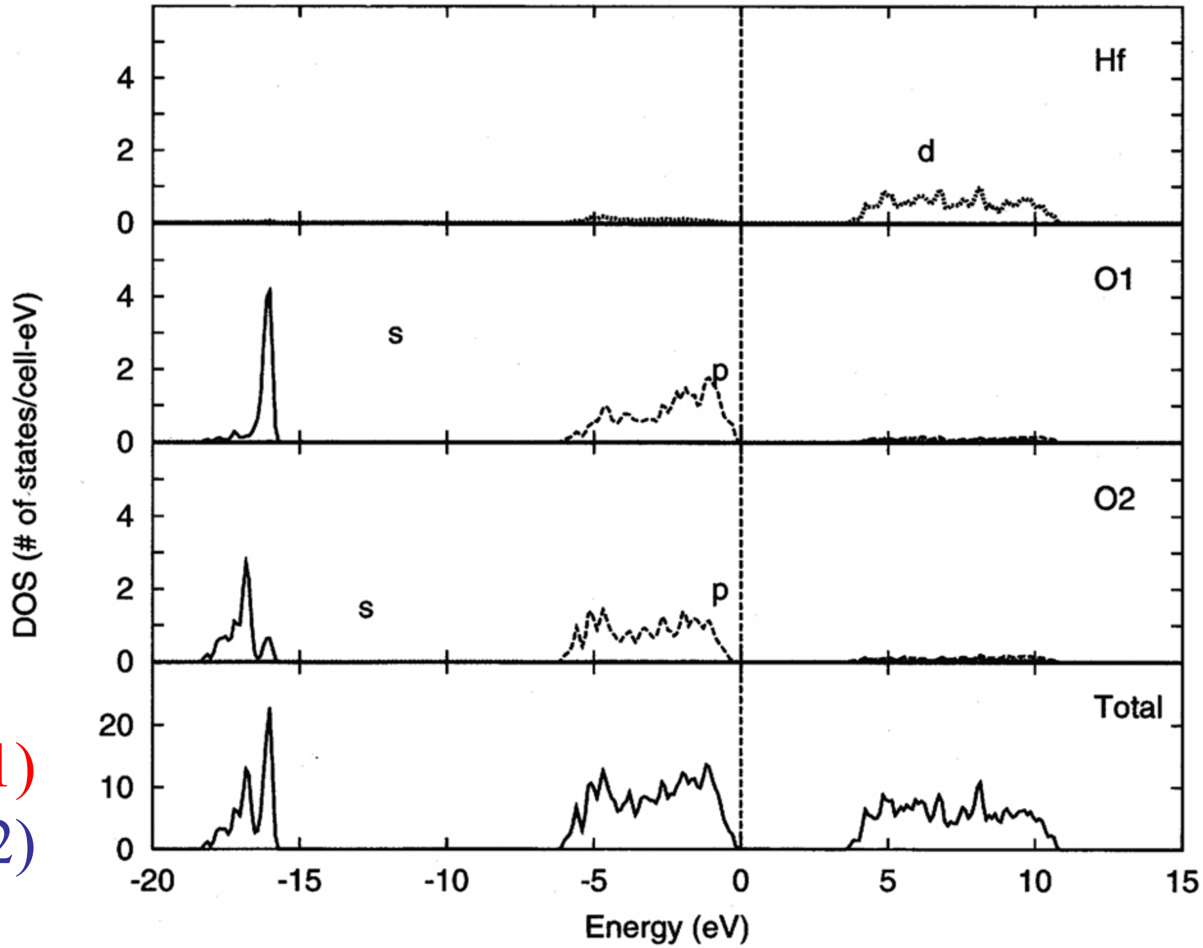
```
HfO2 @ D=5.8

hfo202.001
06/06/02   14:46:54
Created    06/06/02
Mag,Quad      1     0
Omega        10.001
Width         1.999
Counts    629190504
Time (s)      32415
Distance      5.800
Size            512

Background  Region
2th begi    47.400
2th end     53.700
chi begi   -156.70
chi end    -26.600

Crystalline Region
2th begi    48.700
2th end     52.100
chi begi   -156.60
chi end    -26.600

%crystal     5.852


2Theta       40.00
Omega        65.50
Phi           0.60
Chi          45.00
Shutter     CLOSED
Distance     5.800
FloodFld  0512_006
Spatial   0512_006
512x512    Cu Bias
```



- Thicknesses are determined by Rutherford Backscattering Spectroscopy (RBS)
- The diffraction peak positions are consistent with <u>monoclinic</u> structure
- As the films get thinner, average crystal size decreases, indicating more disorder

Partial DOS for monoclinic HfO_2



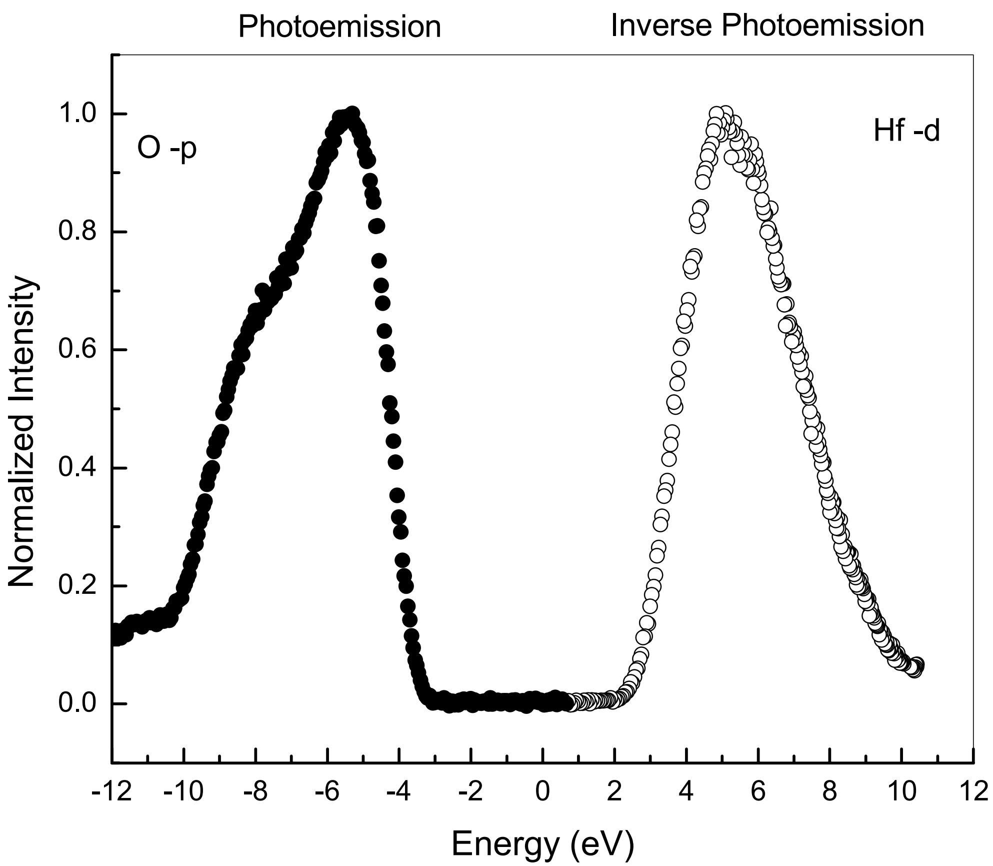


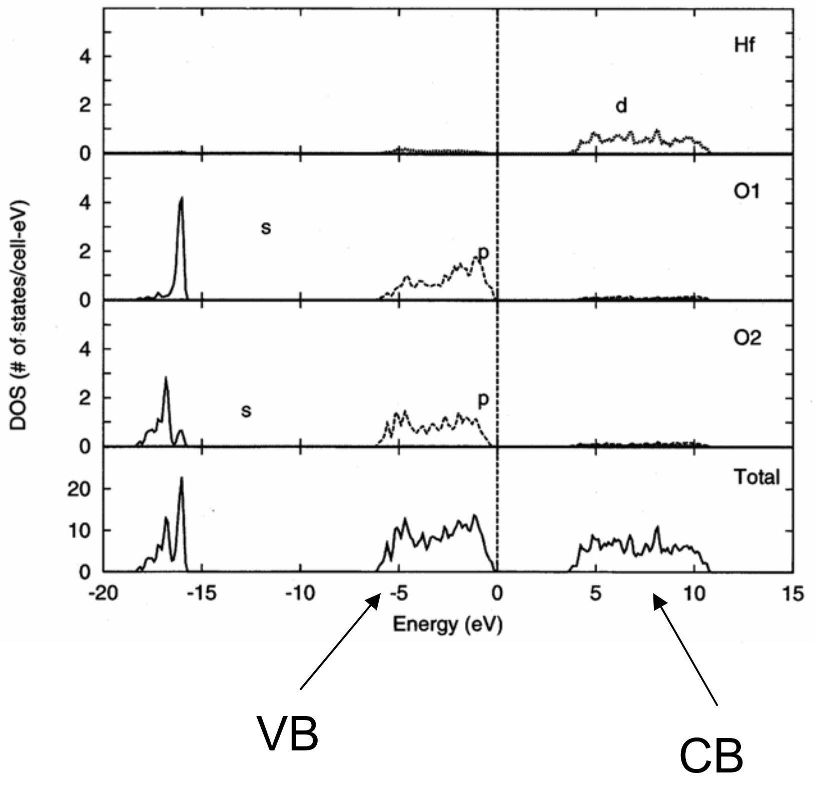
3-fold coordinated O (1)

4-fold coordinated O (2)

- •Valence band is predominantly composed of O-like bands
- •Valence band edge is determined by three-fold coordinated O
- •Conduction band is predominantly – Hf d-like bands

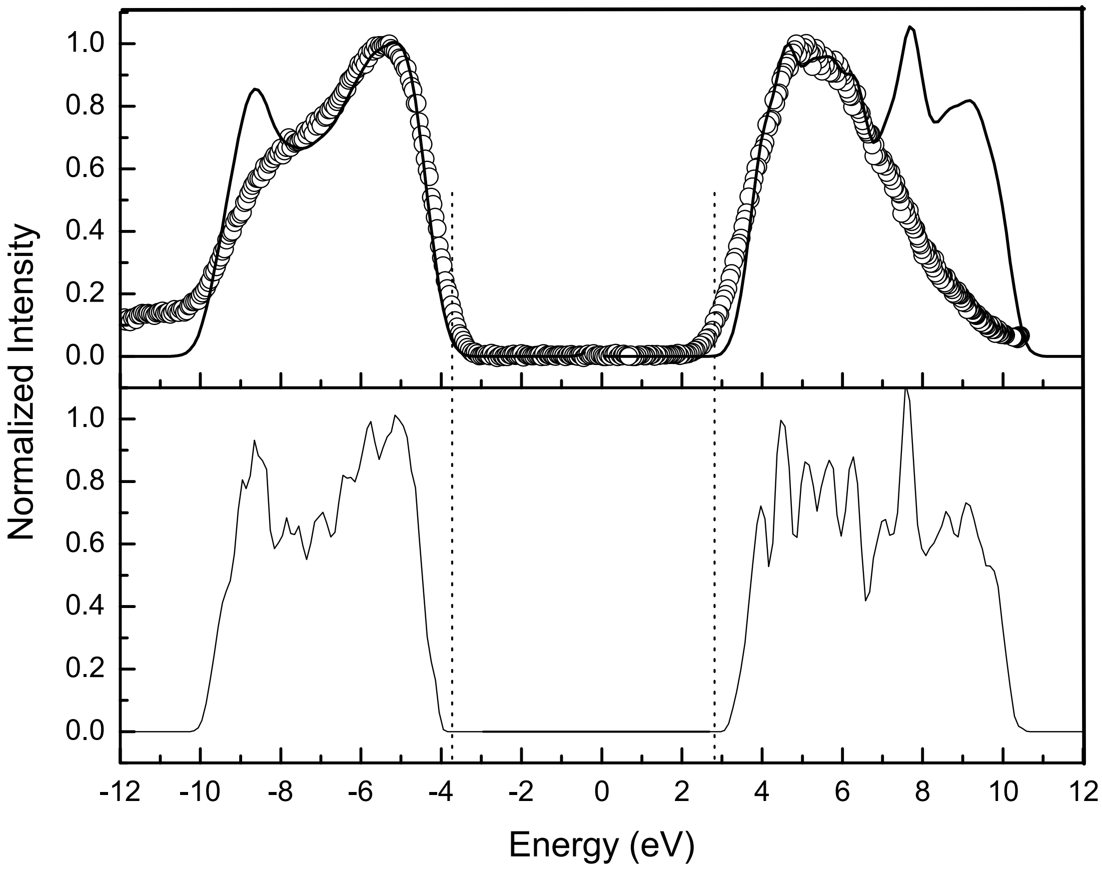
Results of combined photoemission and inverse photoemission studies





- Valence band is predominantly composed of O-like bands
- Conduction band is predominantly – Hf d-like bands

Locating Valence Band Maximum (VBM) and Conduction Band Minimum (CBM)



$$N_v(E)=\int_0^\infty n_v(E')g(E-E')dE'$$

Response function

Theoretical DOS for monoclinic HfO_2

- Extract VBM and CBM from band structure calculations

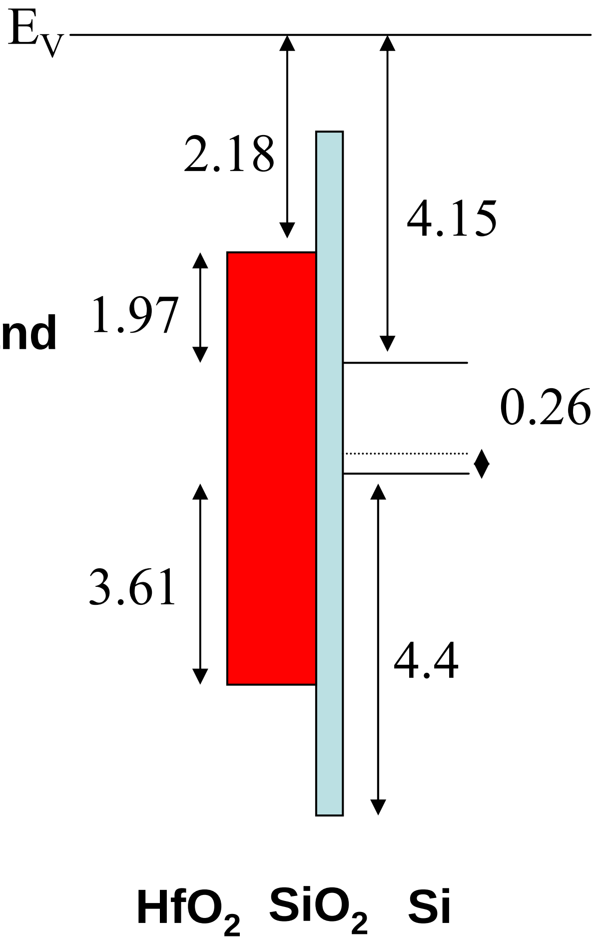
- Agreement between theory and experiment is remarkable (width of bands, and main features)

- Even though the DOS is not corrected for PES and IPES cross-sections

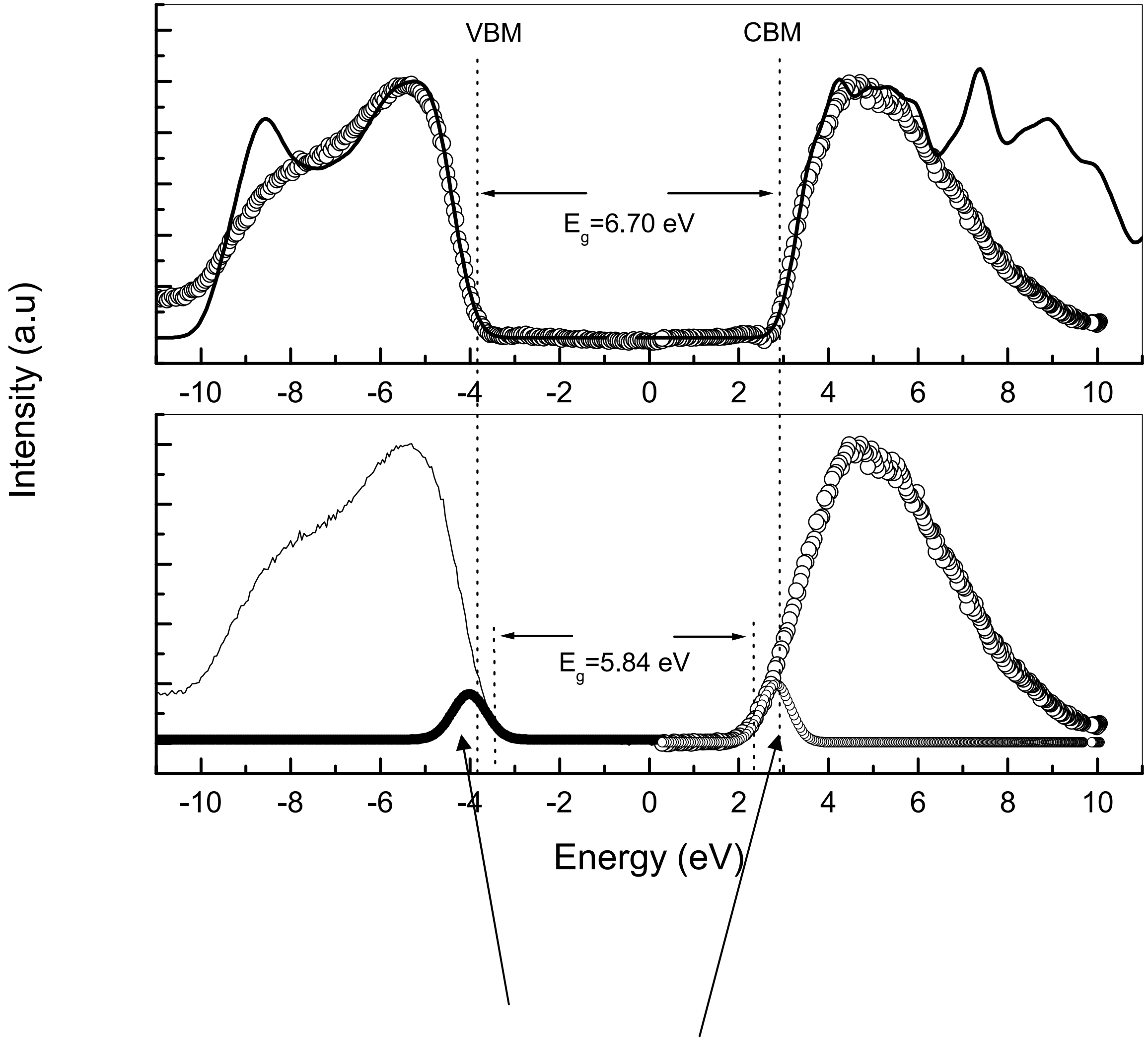
- However note the disagreement between theory and experiment close the band edges

Results from combined theory and experiment

- Theoretical DOS is convoluted with the appropriate response function
- VBM and CBM energy positions are extracted from band structure calculations
- Electron affinity for HfO_2 is ~2.2 eV
- Using the position of Fermi level within silicon gap
- Φ_n~2.0 eV and Φ_h ~3.6 eV – sufficiently large from leakage point of view



Band-tail-States – “Effective” band gap



Band-tail-states

Band-tail-states

↓

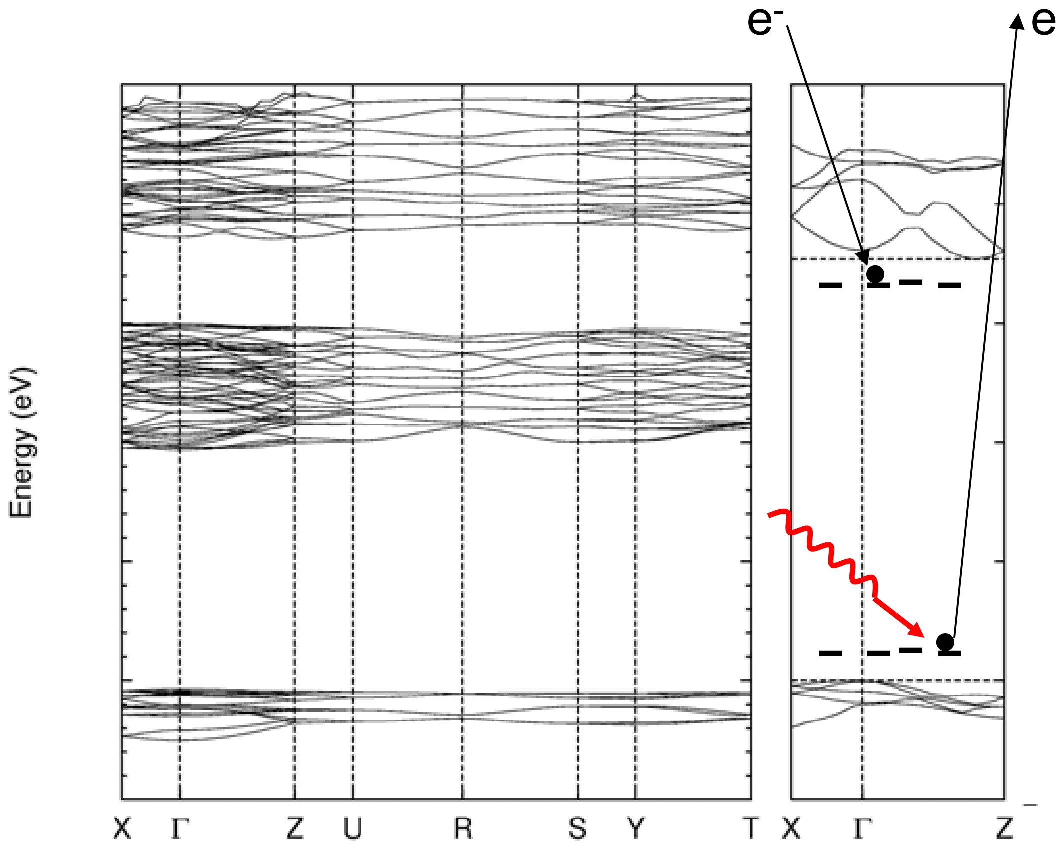
Order to disorder transition

Can result from:

- Crystal imperfections
- Defects
- Impurities
- Stoichiometry

- Theory and experiment comparison yielded a gaussian distribution of these states centered close to band edges

Defect – edge transitions - the effective gap and barriers

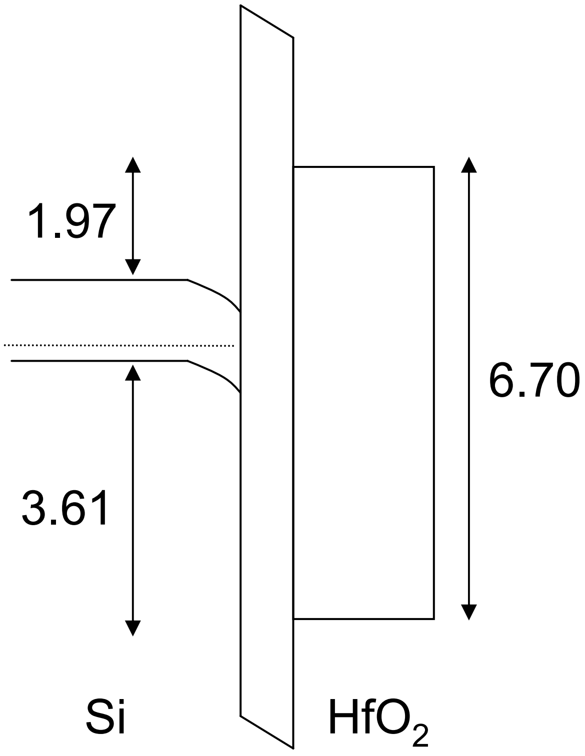


- XRD reveals that the films are predominantly monoclinic
- Therefore finite crystallinity
- On the other hand, theoretical calculations considers perfect crystal
- Disorder in the film will result in appearance of band-tail states

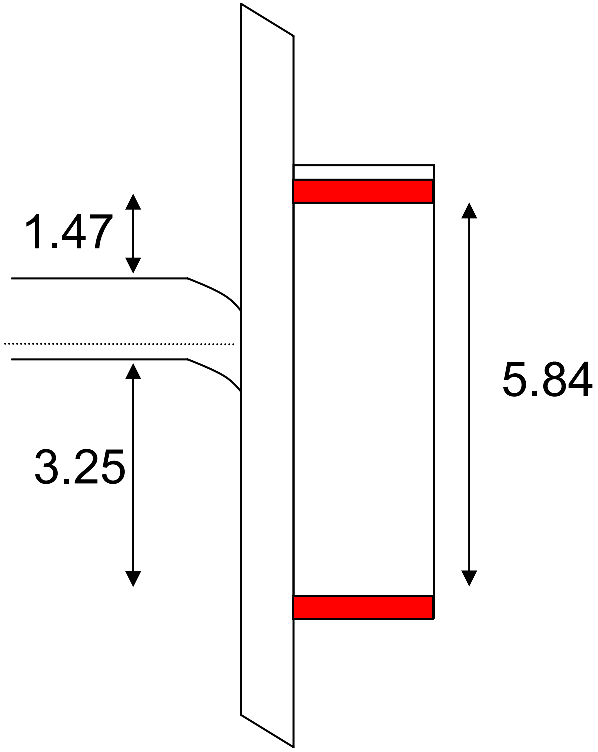
- Therefore intrinsically the perfect crystals have larger band gap
- However due to the presence of band-tail-states, gap is reduced
- Concept of “effective” gap as well as barrier heights can be more meaningful

Energy band diagrams

Intrinsic



Including band-tail states



- **A perfect HfO_2 crystal intrinsically has a larger band gap (than reported to date)**
- **The presence of defect states close to band edges results in a smaller "effective" band gap and barrier heights**

Summary of band alignment for HfO_2/SiO_2/p-Si gate stack

- Occupied and unoccupied densities of states of HfO_2 is studied by PES and IPES
- VBM and CBM are located by combining theoretical calculations with expt data
- Comparison of theory and experiments suggested presence of band tail states in proximity of band edges
- Due to the presence of band tail states, concept of “effective” band gap may be more meaningful
- The extracted “effective” band gap, electron affinity and barrier heights are 5.84, 2.68, 1.47 and 3.25 eV

Develop understanding of the electronic structure of different crystal phases of HfO_2 and ZrO_2 and the effect of annealing on physical and electronic properties

Background: Compare HfO_2 and ZrO_2, and show results of relevance to phase and electronic structure issues in gate stack engineering

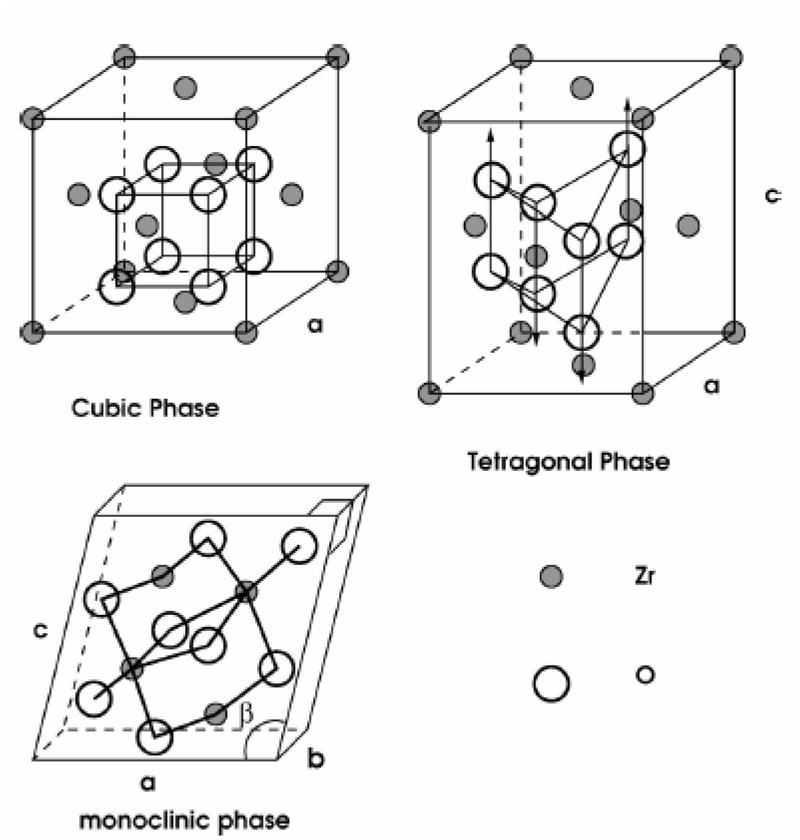
One Problem: A broad range of dielectric constants, band gaps and barrier heights are reported in the literature.

Question: Can the phase of ZrO_2 (present in different films prepared by different deposition techniques and anneals) be responsible for the difference in measured values?

Solution: Use array of experimental methods and DFT calculations to determine phase and electronic properties.

DFT calculations: excellent for structure and energetics but underestimates the true band gaps however, consistent and comparable.

Dielectric Constant for Different Phases of ZrO_2



ε_o

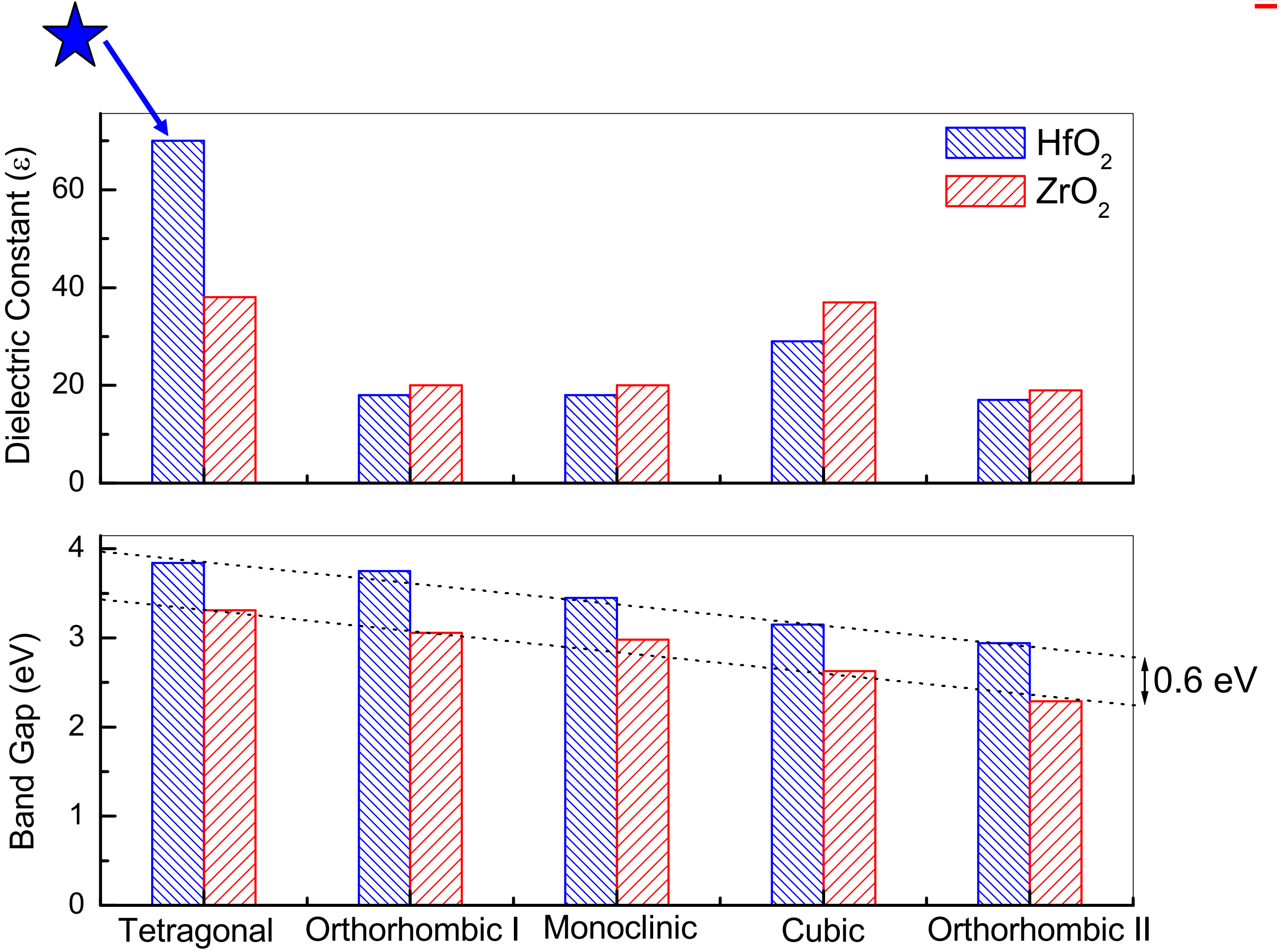
$$\epsilon^{\mathrm{latt}}_{\mathrm{cubic}} = \begin{pmatrix} 31.8 & 0 & 0 \\ 0 & 31.8 & 0 \\ 0 & 0 & 31.8 \end{pmatrix}, \Rightarrow \sim 37$$

$$\epsilon^{\mathrm{latt}}_{\mathrm{tetra}} = \begin{pmatrix} 41.6 & 0 & 0 \\ 0 & 41.6 & 0 \\ 0 & 0 & 14.9 \end{pmatrix}, \Rightarrow \sim 47$$

$$\epsilon^{\mathrm{latt}}_{\mathrm{mono}} = \begin{pmatrix} 16.7 & 0 & 0.98 \\ 0 & 15.6 & 0 \\ 0.98 & 0 & 11.7 \end{pmatrix}. \Rightarrow \sim 20$$

Static dielectric tensor =
purely electronic screening (10-25%) +
lattice contribution (IR-active phonons, 75-90%)

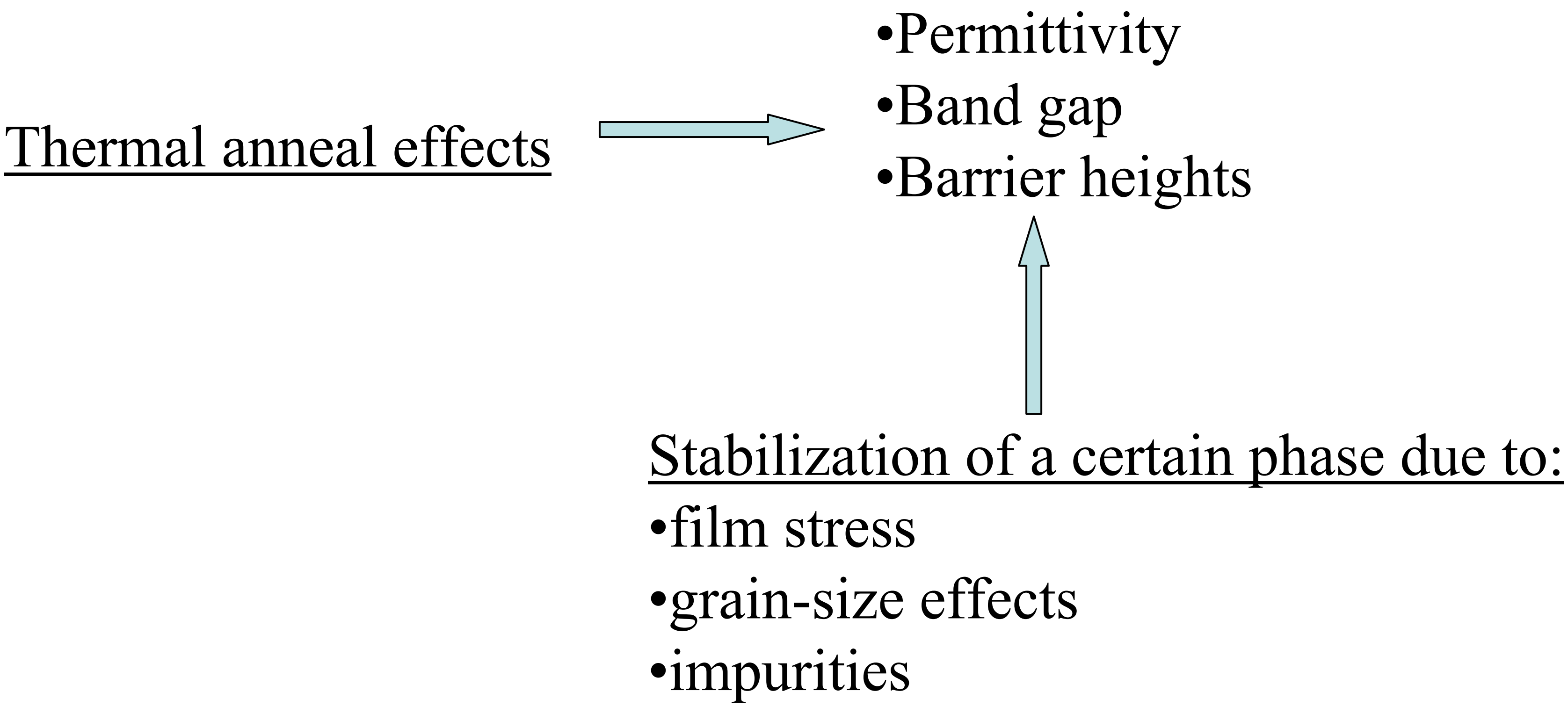
Dielectric constant and Band Gap of all phases of HfO_2 and ZrO_2



- **Tetragonal phase of both oxides have high dielectric constant and band gap**
- **If tetragonal thin ZrO_2 can be prepared, full advantage can be taken**
- **HfO_2 has a <u>higher band gap</u> than ZrO_2 (~0.6 eV) for the same phase**

Summary of theoretical calculations

- Crystal structure can have considerable effect on measured permittivity, band gap and barrier heights
- Crystal structure of thin films needs to be determined and stated in studies
- Tetragonal phase of both oxides have high dielectric constant and band gap



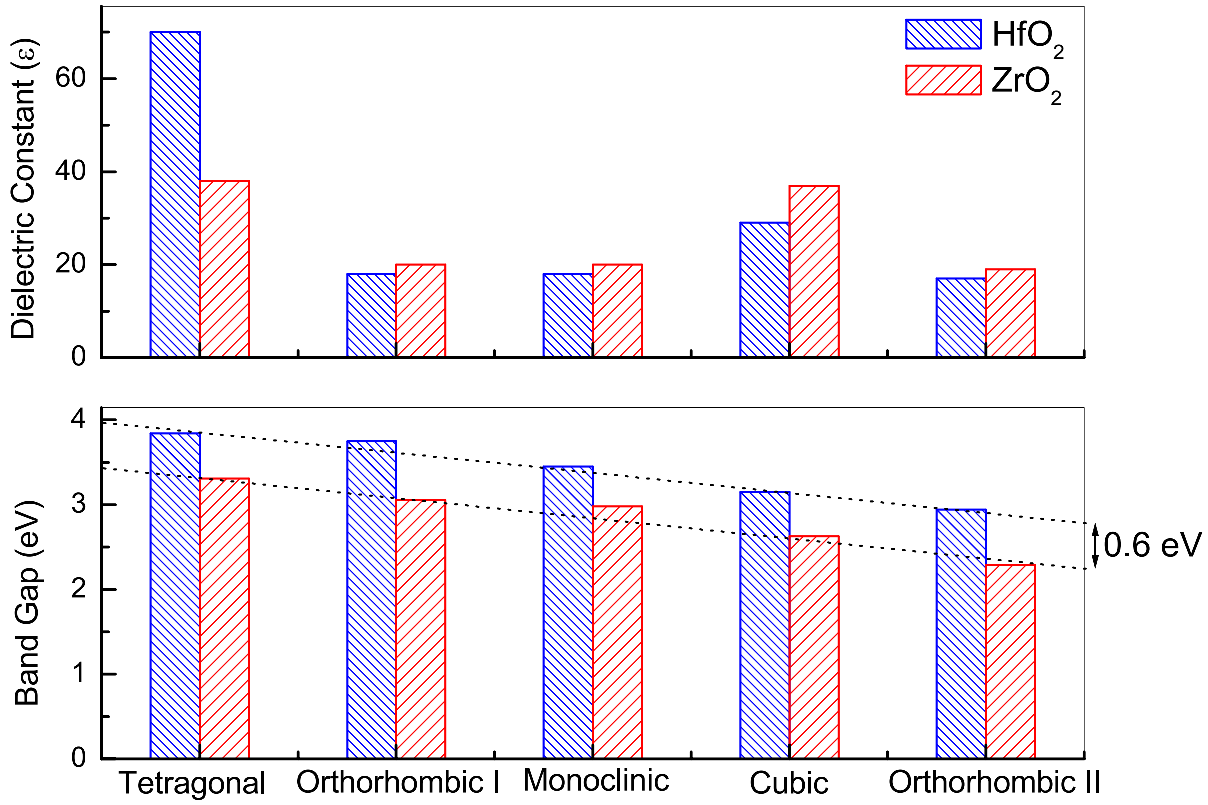
Thermal anneal effects

- Permittivity
- Band gap
- Barrier heights

Stabilization of a certain phase due to:

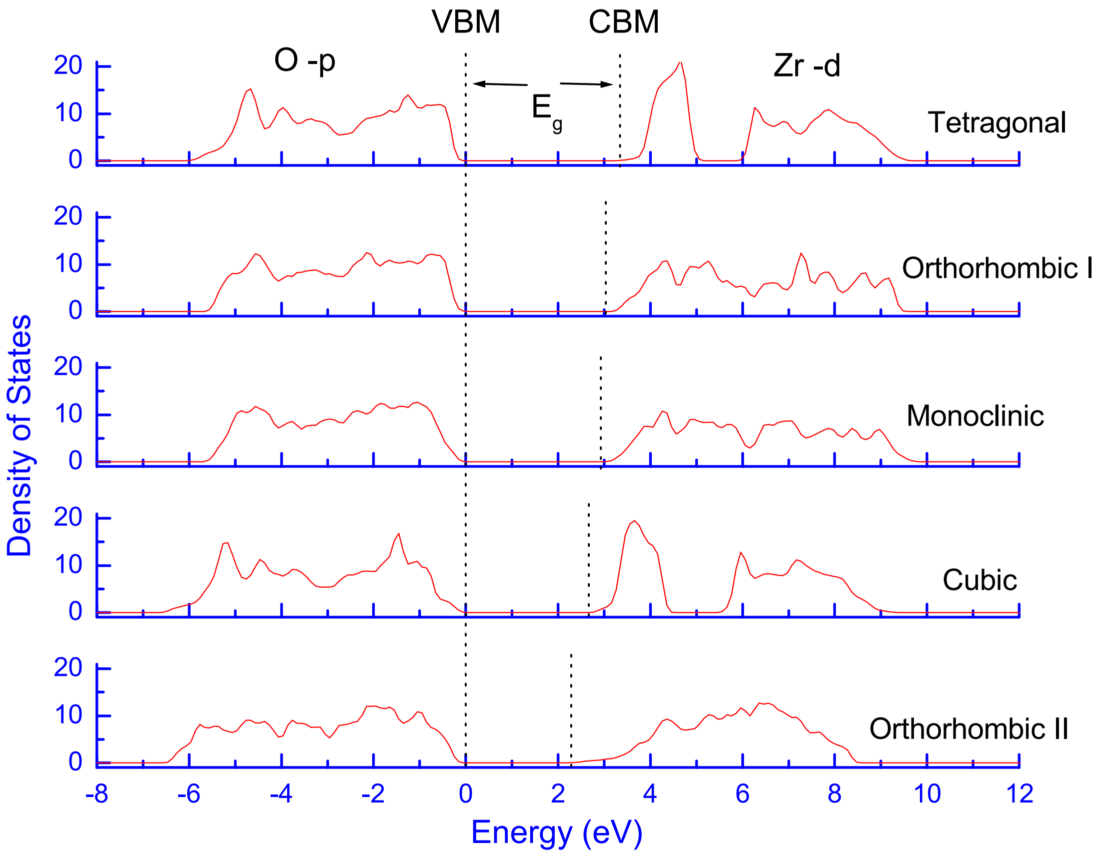
- film stress
- grain-size effects
- impurities

- Can tetragonal ZrO_2 be prepared (in gate stack)?



- **Tetragonal phase of both oxides have high dielectric constant and band gap**

Density of States for all phases of ZrO_2



Crystal Phase	**Band gap (eV)**
Orthorhombic II	2.29
Cubic	2.63
Monoclinic	2.98
Orthorhombic I	3.06
Tetragonal	**3.31**
Amorphous	**2.71**

- Band gap values are different for phases!

↓

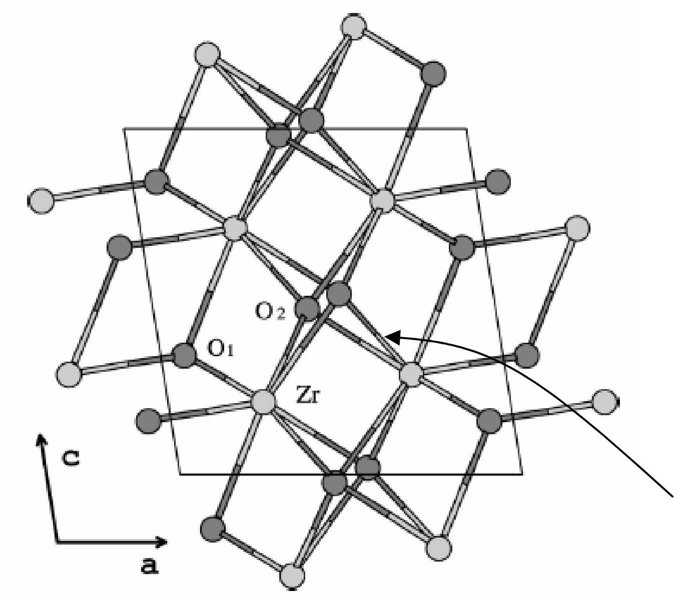
- Effects on band alignment ???

- Crystal structure can have considerable effect on measured band gap and hence barrier heights

If tetragonal phase can be prepared, a high dielectric constant and band gap should be expected.

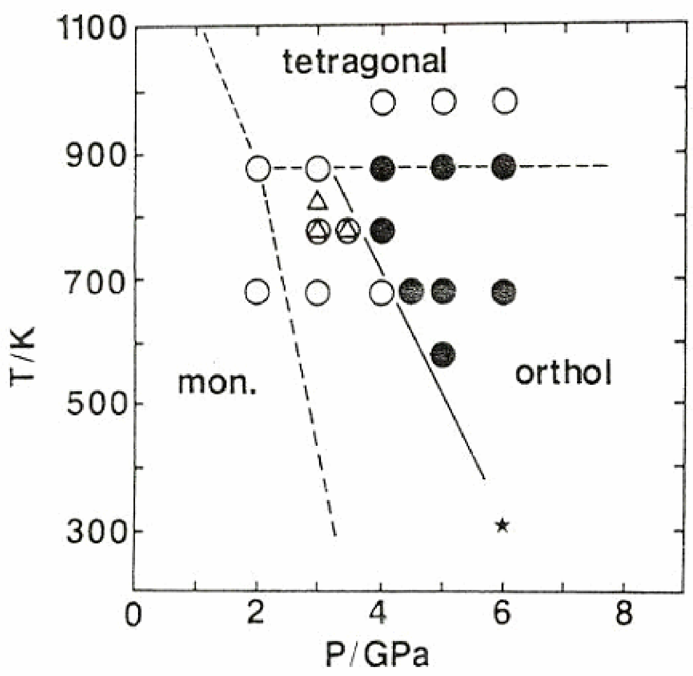
A couple of approaches:

1. Increasing the coordination of metal cation (Hf, Zr)
2. Move to conditions where tetragonal thermo. dominate
3. Lock in metastable phase kinetically.



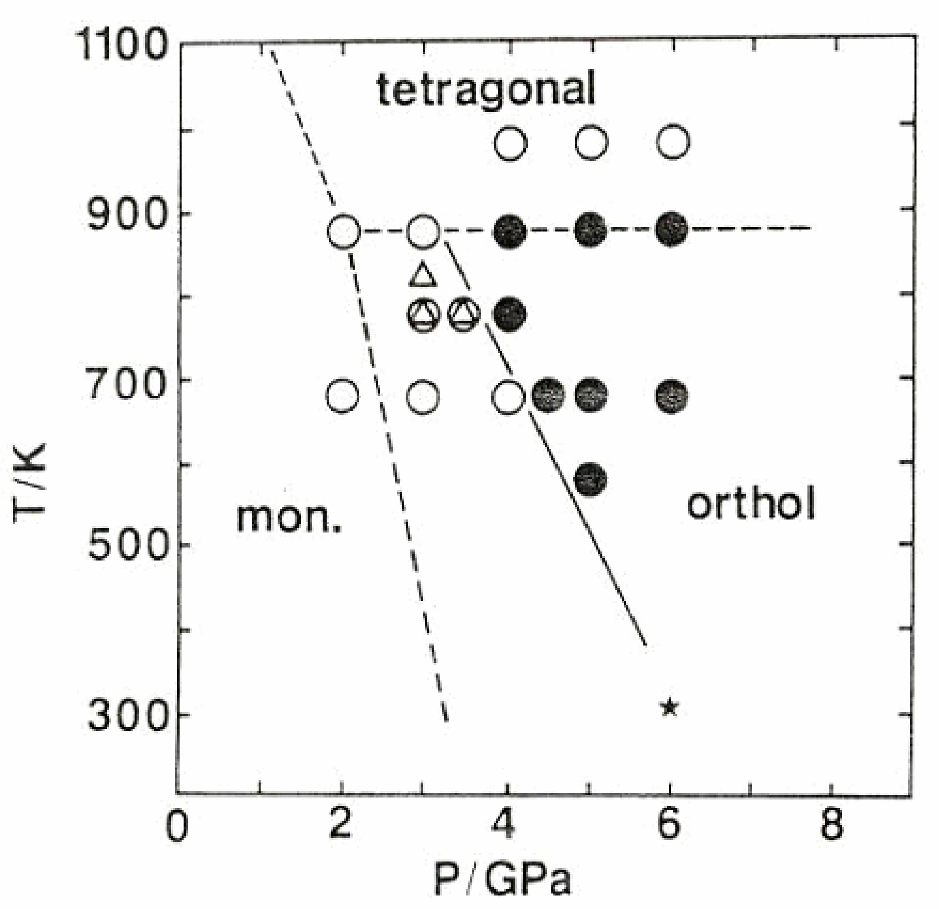
O, H

In monoclinic structure, Zr is 7-fold coordinated

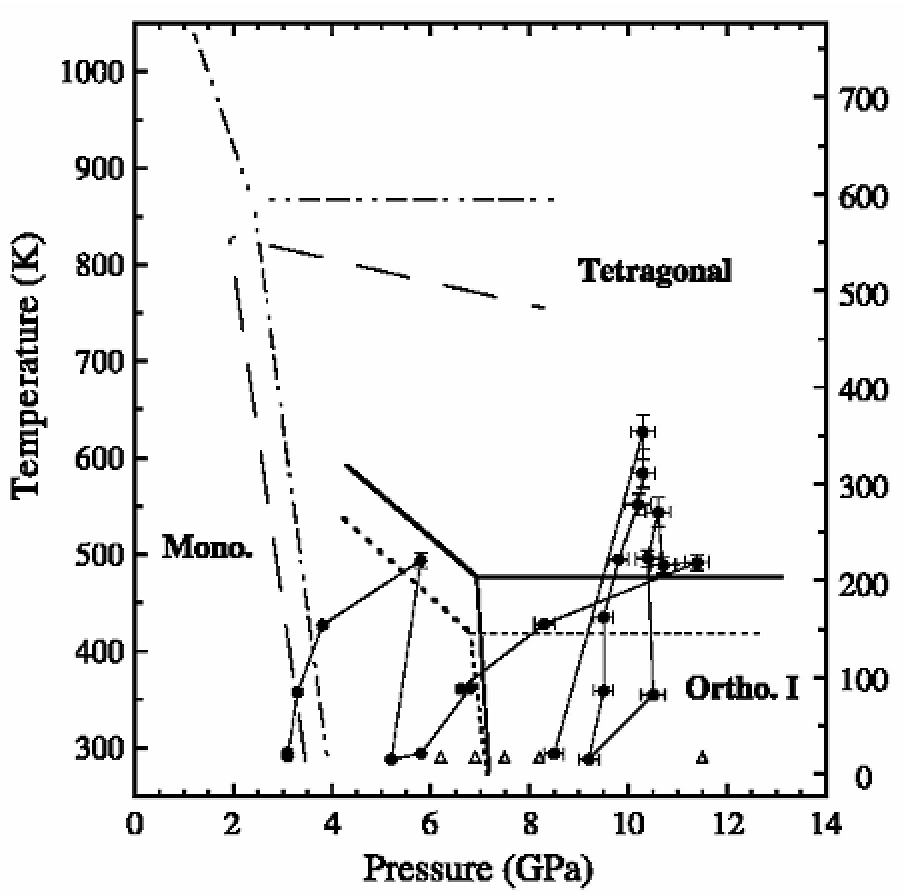


High temperatures are required for the desired phase stabilization

BULK PHASE DIAGRAM



NANO - PHASE DIAGRAM

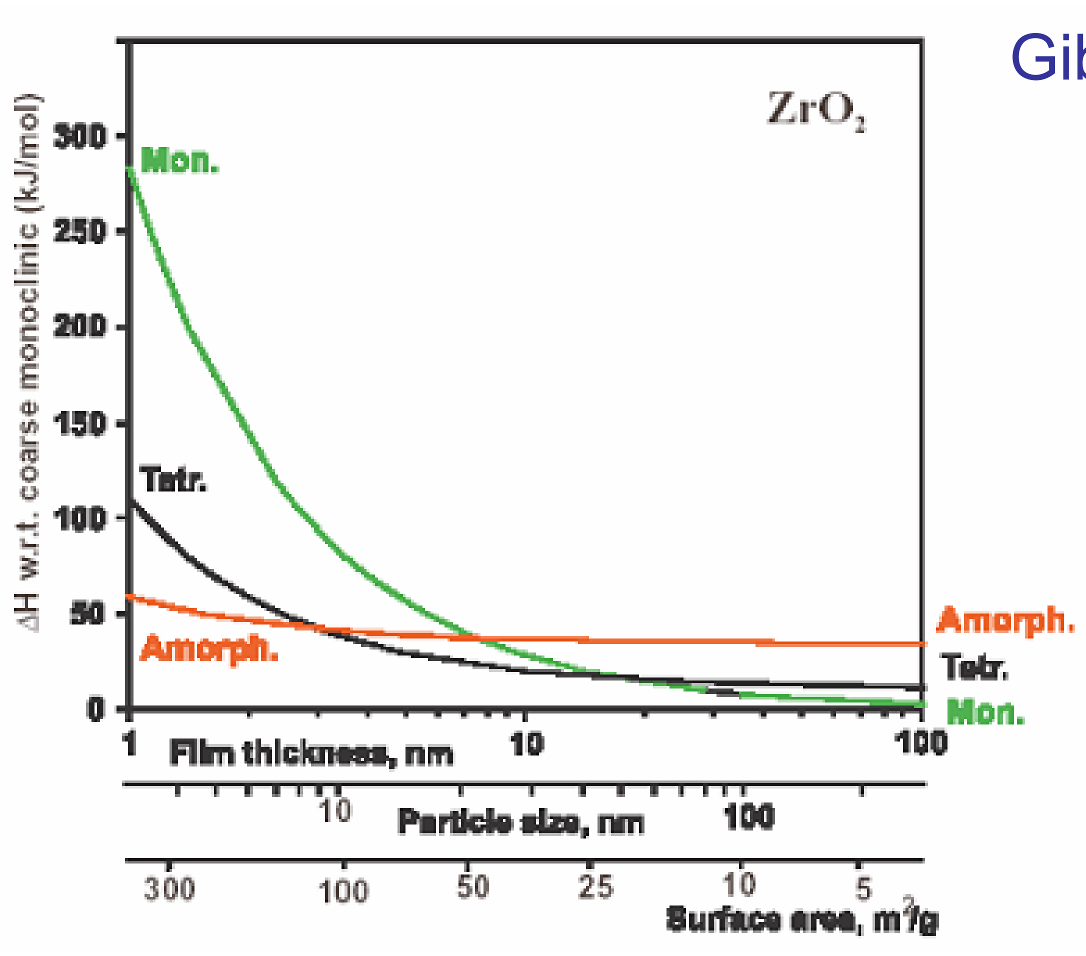


- **Melting and transformation temperature depends on the radius of crystallites**

- **Small crystallite size, decreases the transformation temperature**

O. Ohtaka, Journal of the American Ceramics Society, 74 (1991) 505-509
P. Bouvier, Journal of Nuclear Materials 300 (2002) 118–126

Nanocrystallite size effect on the P–T Phase Diagram



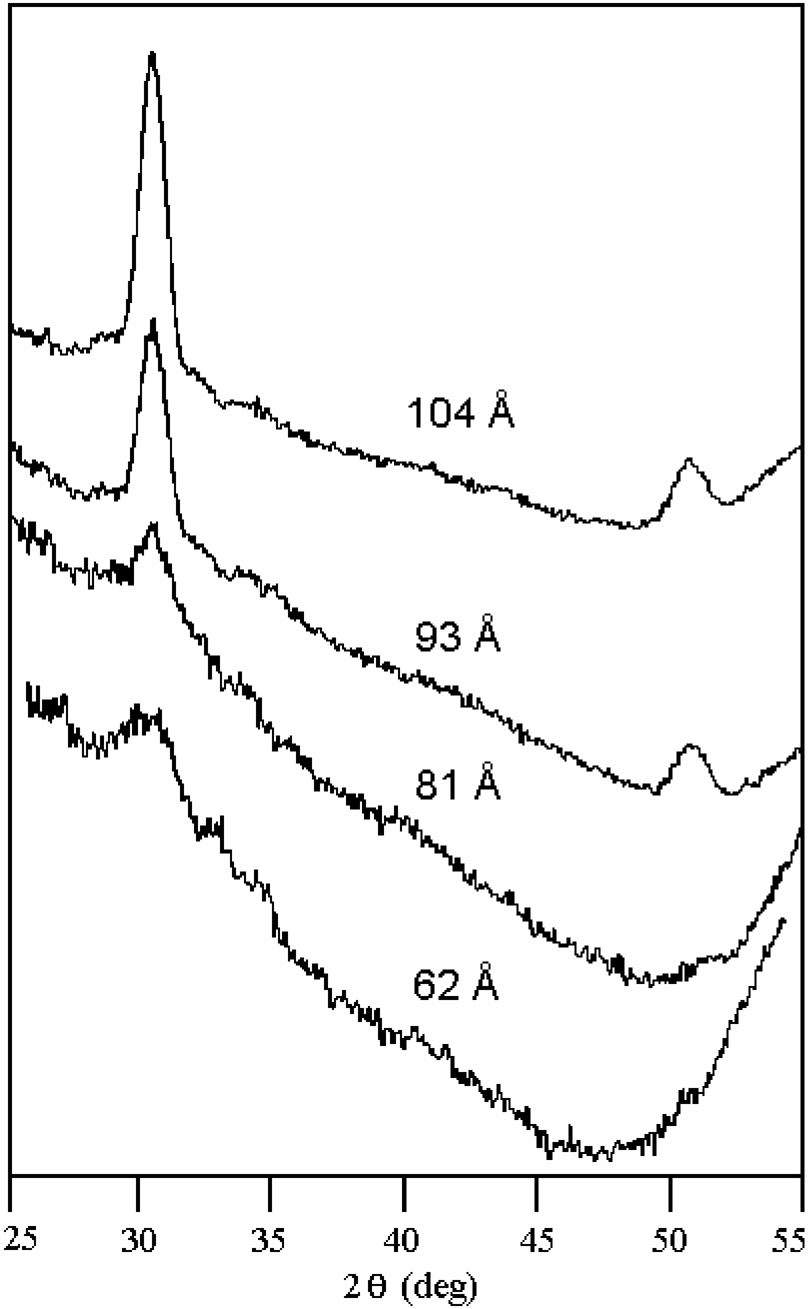
Gibbs – Thomson Relationship

$$\swarrow\ \frac{T - T_0}{T_0} = -\frac{2V_T}{\Delta H_{M\text{-}T}}\sigma\frac{1}{r}.\ \swarrow$$

- Melting and transformation temperature depends on the radius of crystallites
- T, P, and grain size plays an important role in the stabilization of the tetragonal form

Pitcher, Ushakov, Novratsy, to be published.

XRD Studies on ALD ZrO_2 thin films

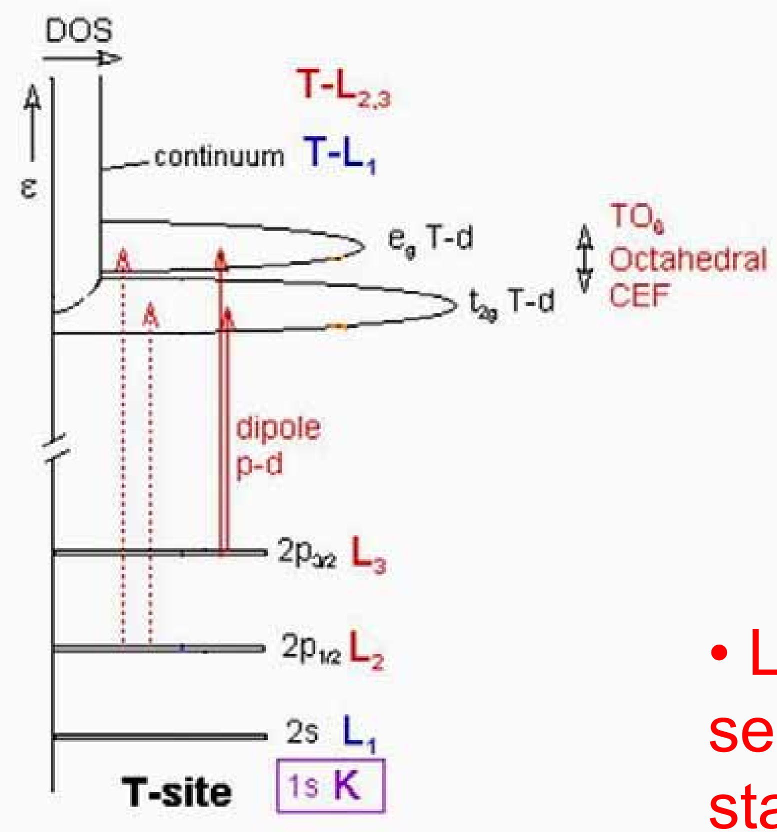


- Crystal structure – film thickness dependence is studied by wide angle x-ray scattering WAXS

- The 62 Å films is found to be predominantly amorphous.

- XRD spectra of thicker films are consistent with tetragonal phase of ZrO_2

How to Identify the Phase of Thin Films by X-ray Absorption Spectroscopy (XAS)



dipole/quadrupole operator

$$\mu(E) = \sum_{\text{final states}} \left| \langle \Psi_f | \hat{H} | \Psi_i \rangle \right|^2 \rho(E_f)$$

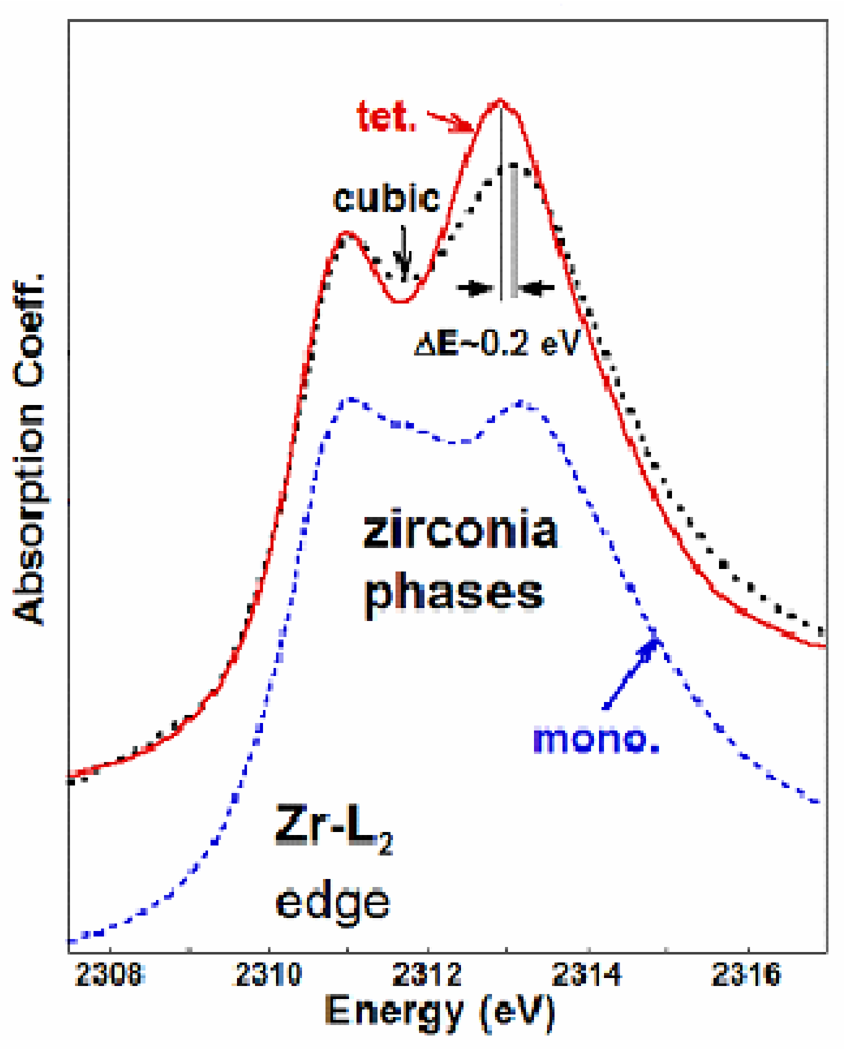
i = core level

f = empty d-states

- $L_{2,3}$ edges of transition metals (T) serve as a direct probe of empty T-d states, as well as the crystal structure

- **Approach : Comparison with reference materials of known crystal structure**

Phase Identification of ZrO_2 films by XAS

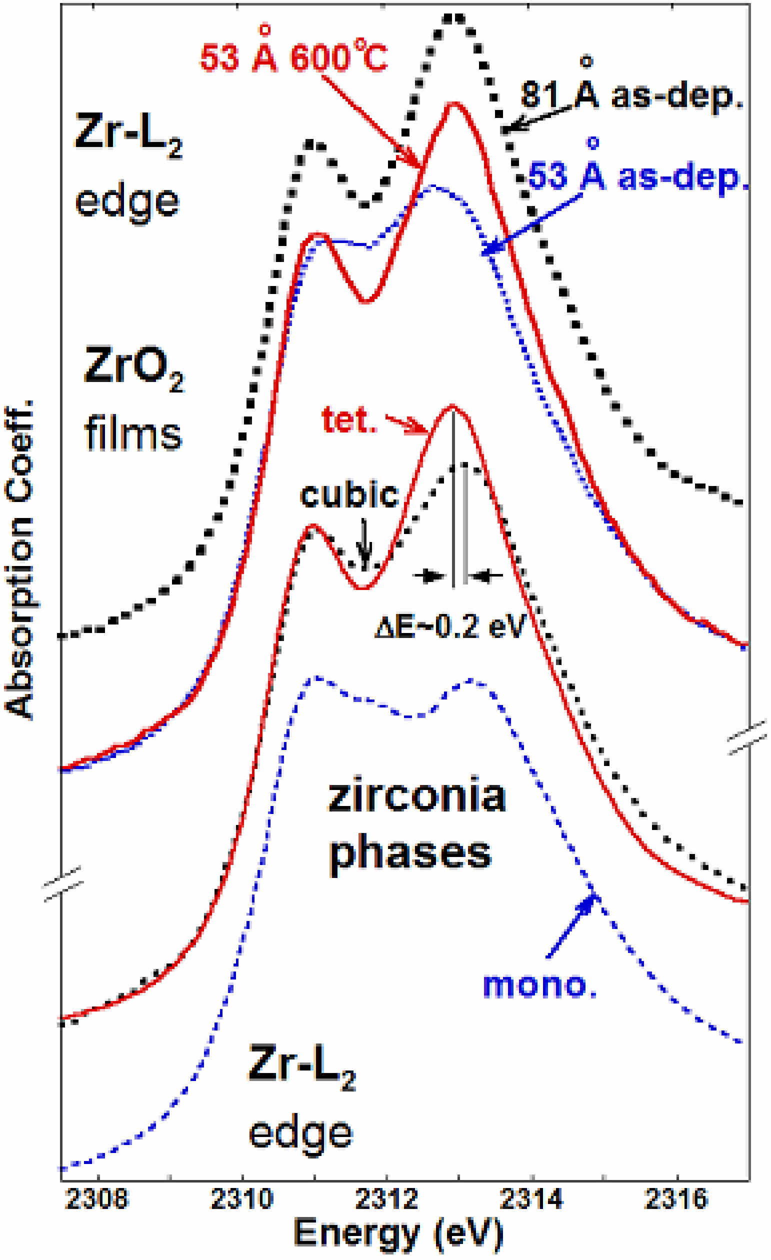


- XAS L_2 and L_3 edges of Zr are dominated by transitions into unoccupied Zr-4d states.

- XAS of $ZrO_2/SiO_2/Si$ compared with reference materials of known crystal structure

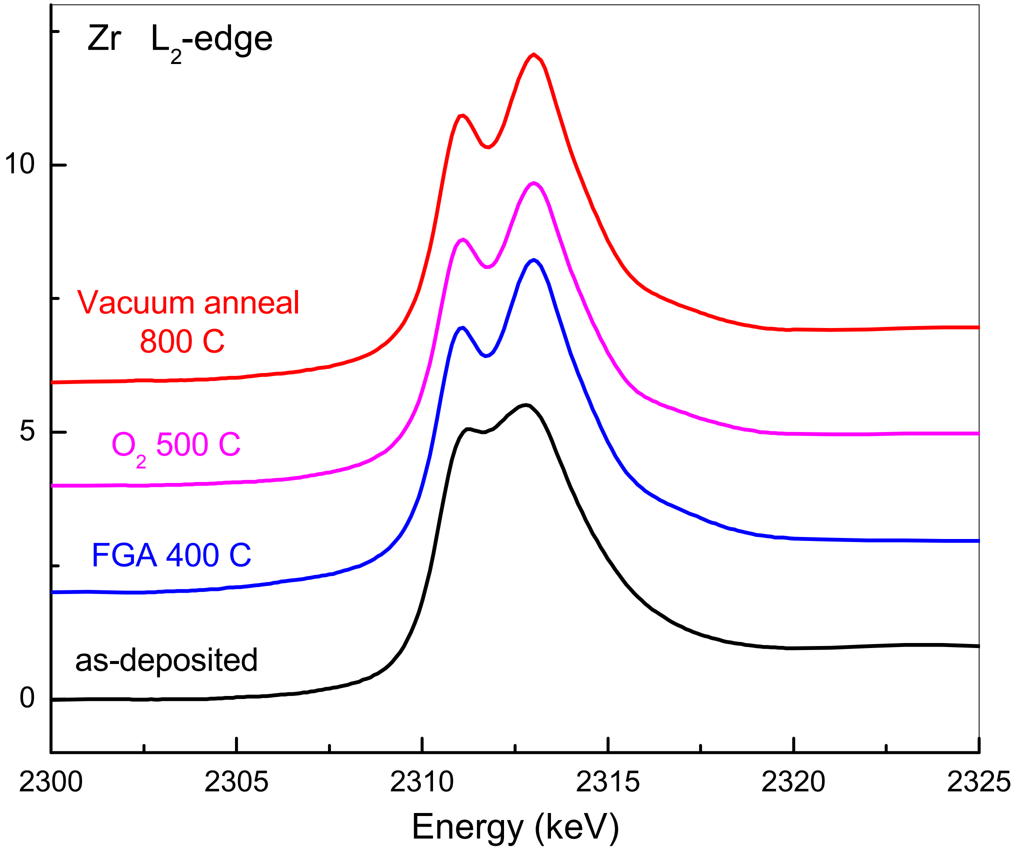
- Zr- L_2, L_3 edge measurements provide a convenient tool for identifying the structural changes in ZrO_2 films.

XAS Studies on $ZrO_2/SiO_2/Si$ gate stack



- XAS L_2 and L_3 edges of Zr are dominated by transitions into unoccupied Zr-4d states.
- Thin film (53 Å) spectrum is <u>not</u> consistent with any of the known phases of ZrO_2
- XRD on thin films indicate amorphous structure
- The spectrum for the thicker film (81 Å) is consistent with that of the tetragonal phase.
- Spectrum obtained for the 53 Å films following 600C thermal anneal is consistent with that of tetragonal phase.
- Zr-L_2 edge measurements provide a convenient tool for identifying the structural changes in ZrO_2 films.

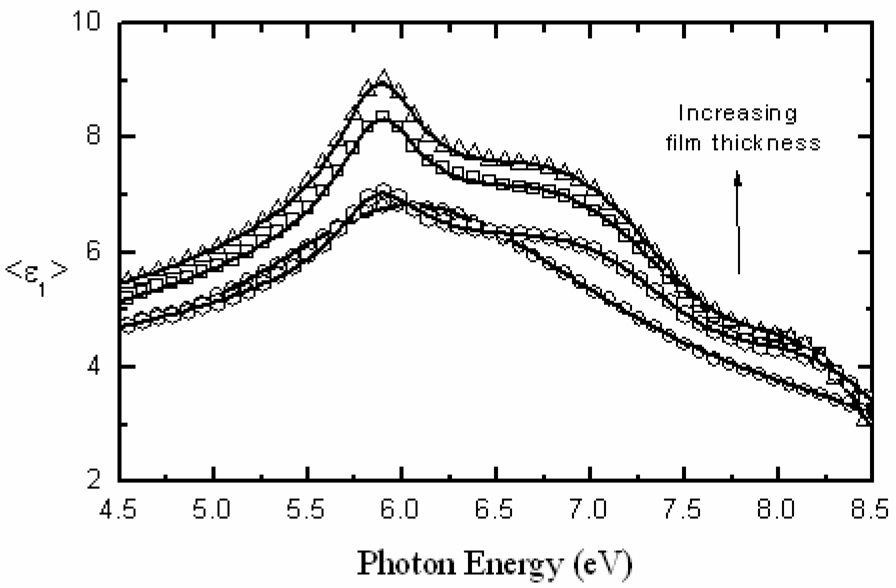
Thermal Anneal Effects on Crystal Structure of ZrO_2 Film Studied by XAS

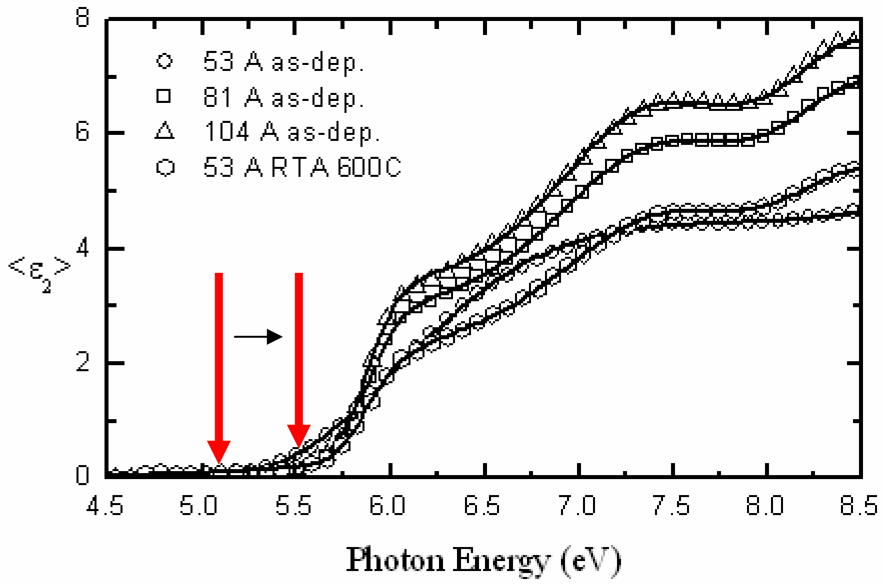


- **Thermal anneals resulted in phase change as apparent from the XAS measurements**

Amorphous → Tetragonal

Spectroscopic VUV Ellipsometry





$$\varepsilon = \varepsilon_1 + i\varepsilon_2$$

real

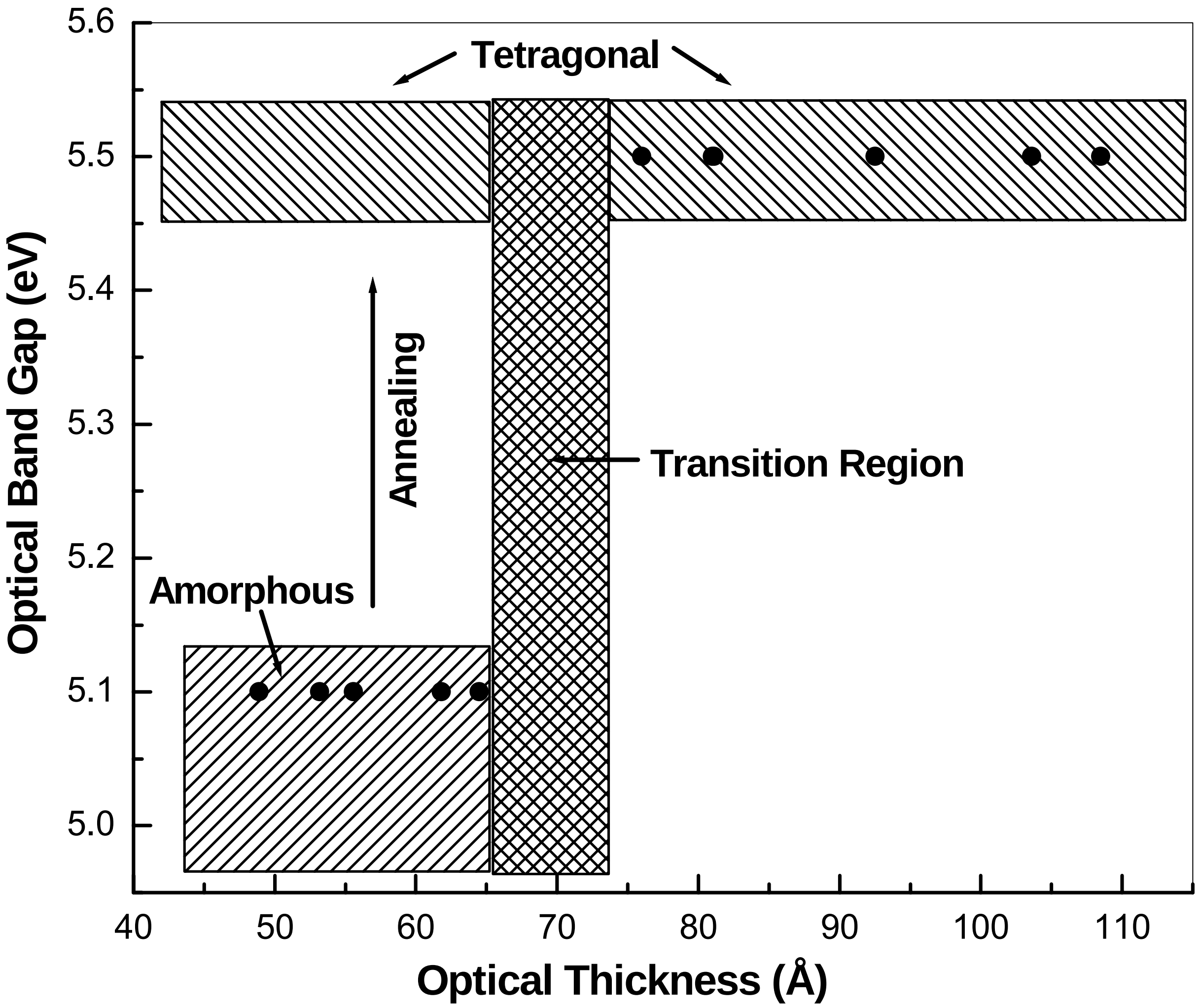
imaginary

- **Two important trends:**
  - **Thickness**
  - **Thermal anneals**

•As thickness of the as-deposited films increase above some transitional value, bandgap increases from 5.1 eV to 5.5 eV.

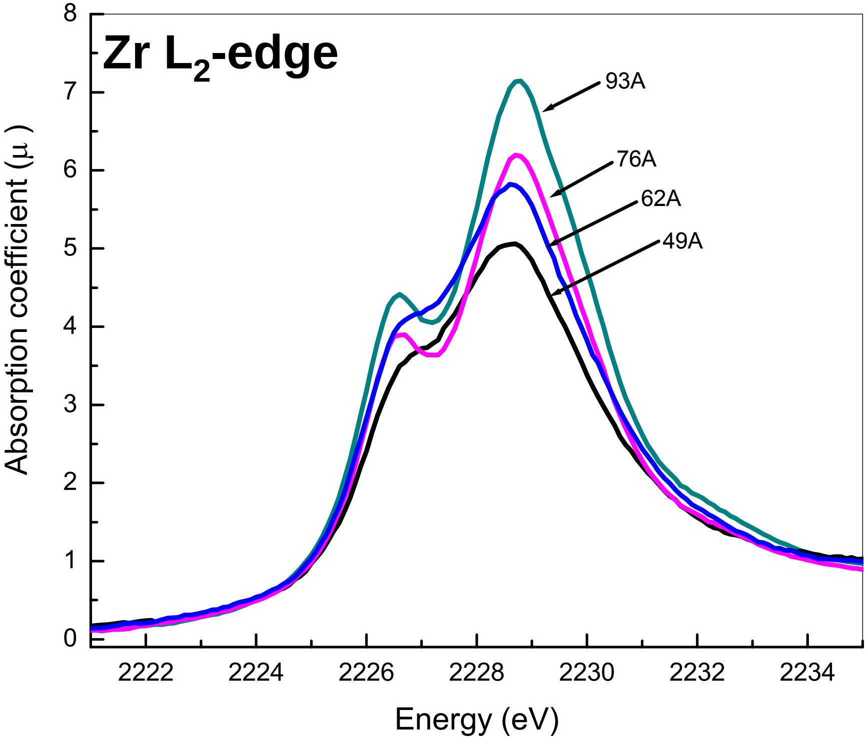
- **The bandgap of the thin sample increased after being annealed to 600C**

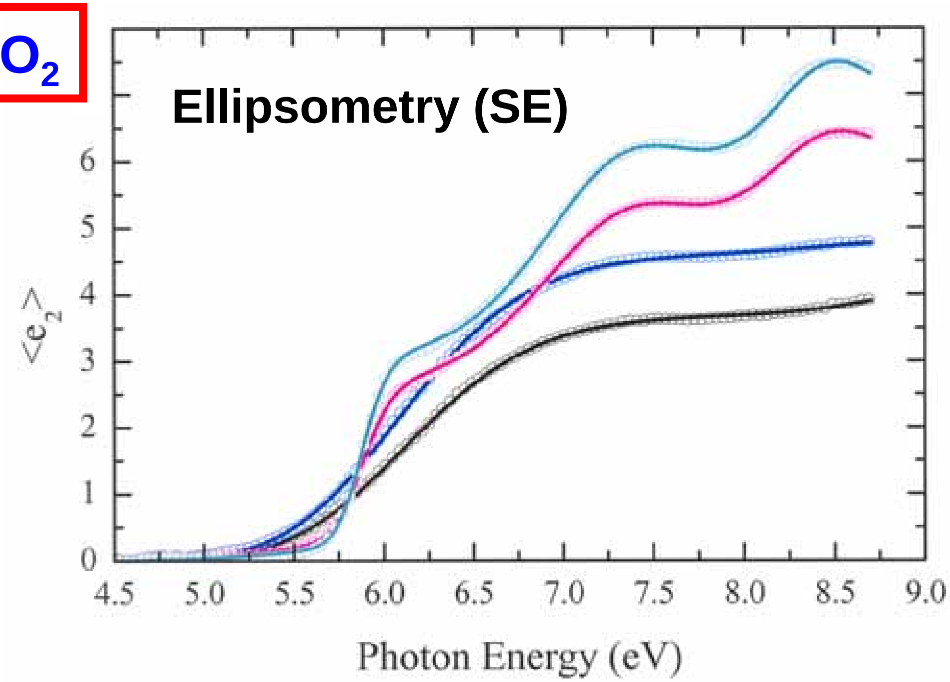
Simplified phase diagram of optical band gap versus optical thickness (small but important portion of phase space)

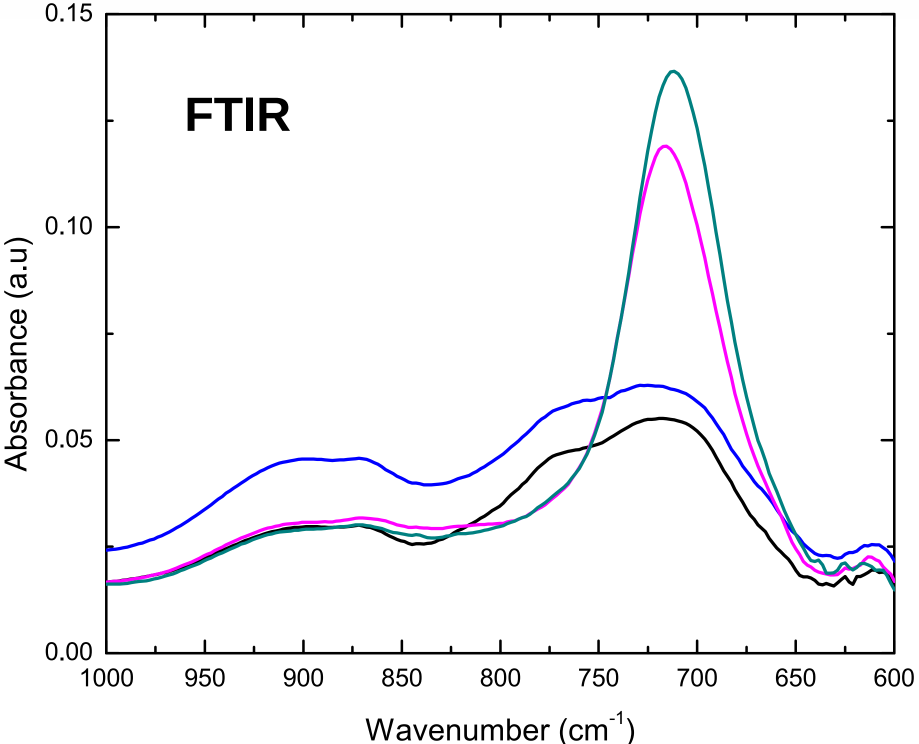


- In this thickness regime, there is a transition from an amorphous to a tetragonal phase
- There is some transitional value (65-75Å optical thickness) at which this occurs.

XAS, SE and FTIR studies on ALD ZrO_2







<u>As thickness increases;</u>

- **Crystal structure becomes tetragonal**
- **Bandgap increases**
- **Dielectric function increases**

<u>XAS, SE and FTIR for high-κ materials:</u>

- **Powerful**
- **Non-destructive**
- **Complimentary techniques**

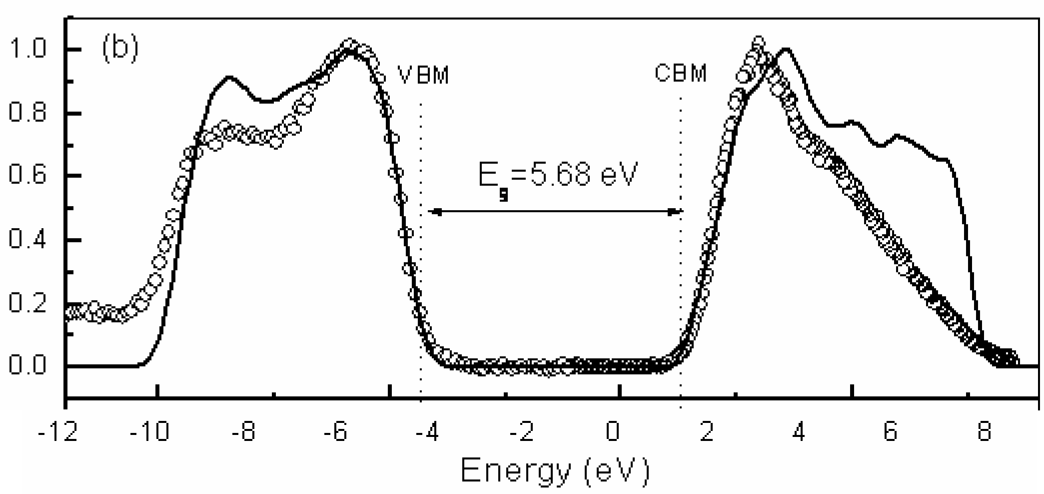
Summary

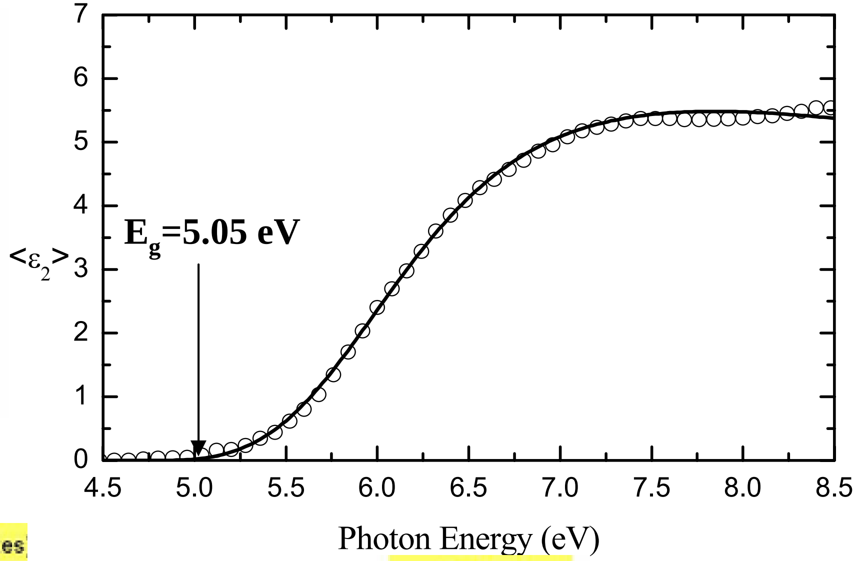
- **It is desirable to make tetragonal ZrO_2 (ε_0 ~35).**
  - (i) Tailoring films thickness
  - (ii) Annealing
  - (iii) Impurities (e.g. cubic ZrO_2)

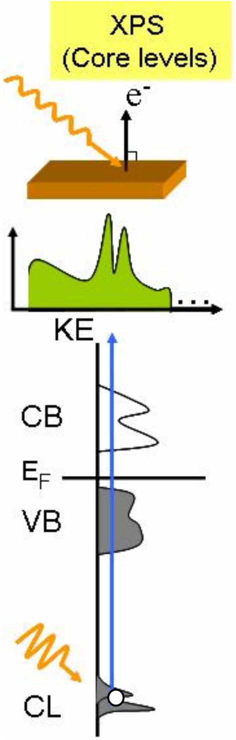
- **Important consequences:**
  - (i) Higher ε_0, lower EOT
  - (ii) Larger bandgap, different band offsets, affects charge transport
  - (iii) Metrology: determination of true dielectric constant, thickness

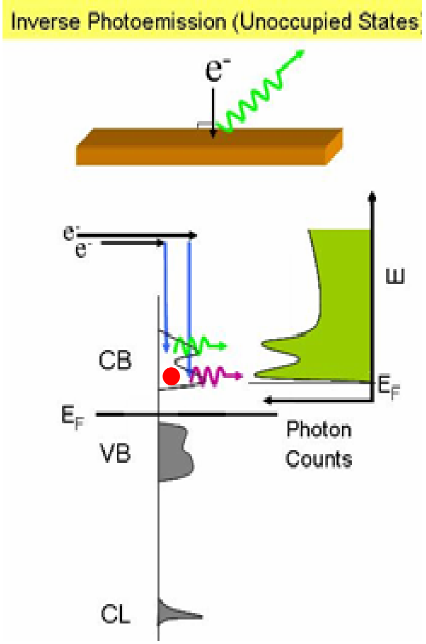
- **Issues:**
  - (i) Crystal sizes, leakage
  - (ii) Gate length vs crystal sizes
  - (iii) Phase variations in the dielectric and channel mobility
  - (iv) In addition to coulomb and phonon scattering, potential variations in the channel due to existence of multiple phases)

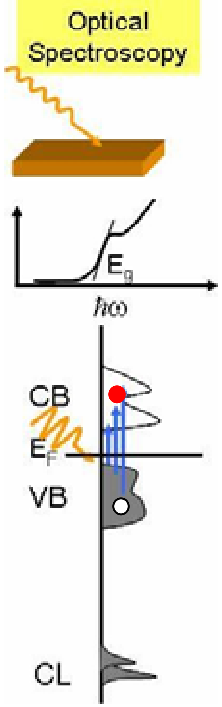
Band gap measurements of ZrO_2 – PES/IPES vs. Ellipsometry











- The crystal structure for ZrO_2 is determined to be amorphous
- ΔE_g~0.6 eV
- Difference originating from final state effects

FINAL REMARKS:

Issues regarding band gap and band offset determination:

Measurement of E_g and ϕ_e, ϕ_h will depend on:

- Crystal structure
- Method used (PES/IPES, SE, etc..) – Question: which is more relevant???
- Band tail states – how to include in the effective values

Issue regarding dielectric constant determination

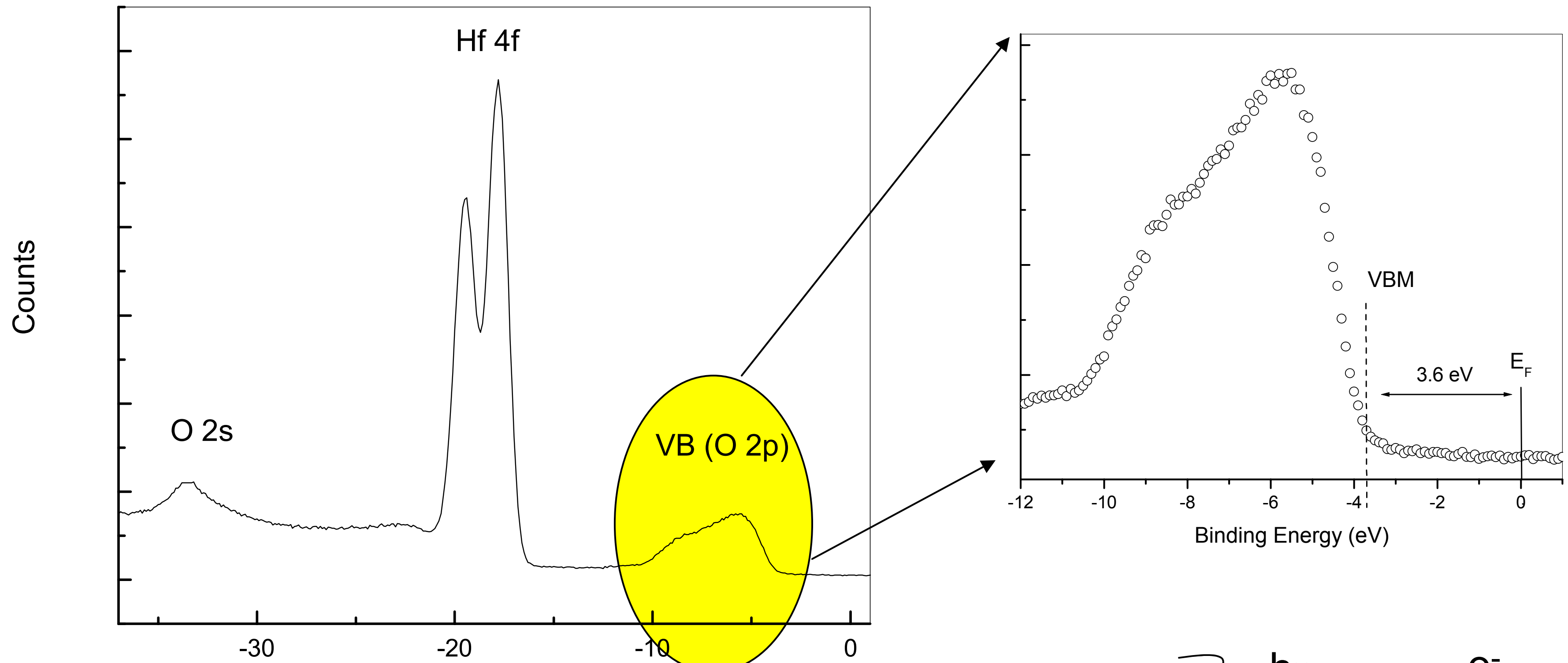
- Film thickness regime – key factor in regulating crystal structure
- Crystal structure
- Processing history
- Impurities, stress – effect on stabilizing crystal structure

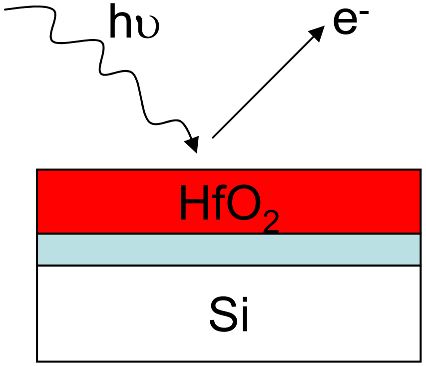
Non-destructive analytical techniques for crystal structure determination:

- Zr-L_2 edge XAS measurements provide a convenient and sensitive tool for identifying the structural changes in these ZrO_2 films.

- FTIR – Grazing angle total attenuated reflectance: powerful technique to study phonon modes

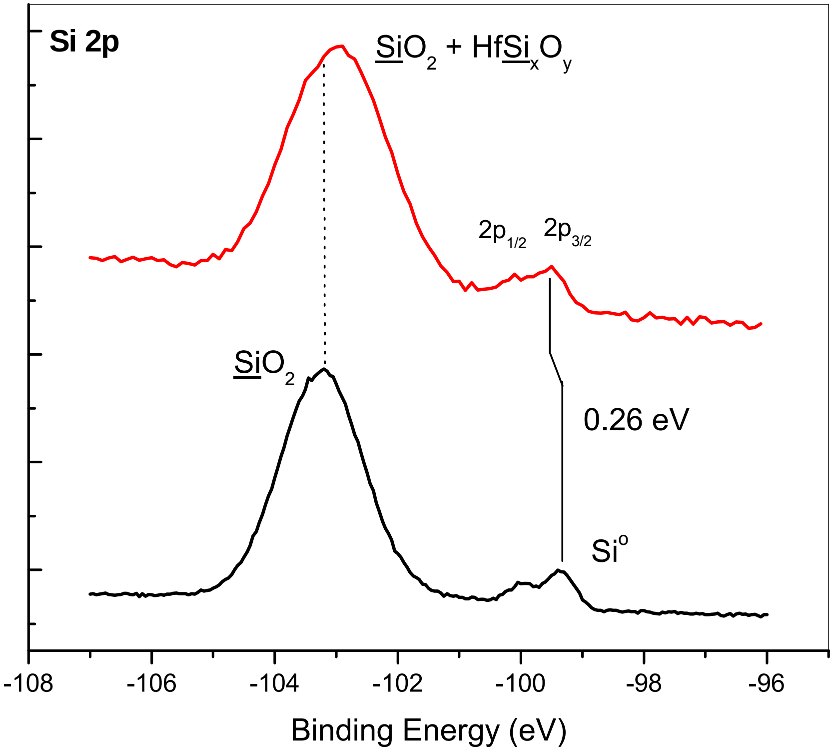
Soft x-ray photoemission spectrum of 28Å HfO_2/SiO_2/p-Si gate stack

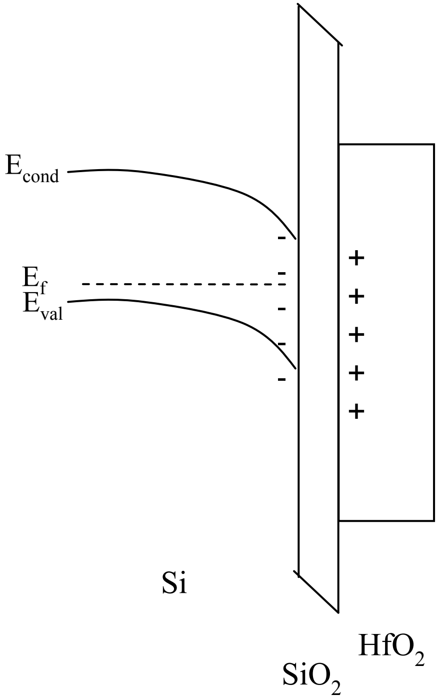


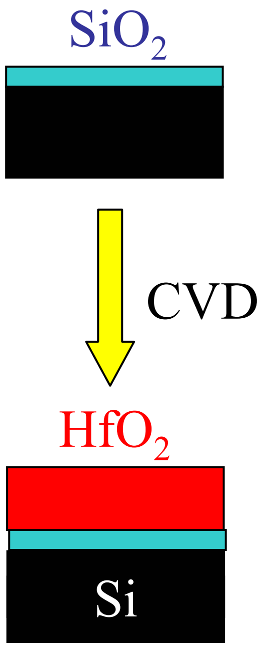


- •**Hf 4f spin-orbit doublet – Hf $4f_{7/2}$ binding energy 17.65 eV**
- •**Hf $4f_{7/2}$ – VBM energy separation = 14.14 eV**

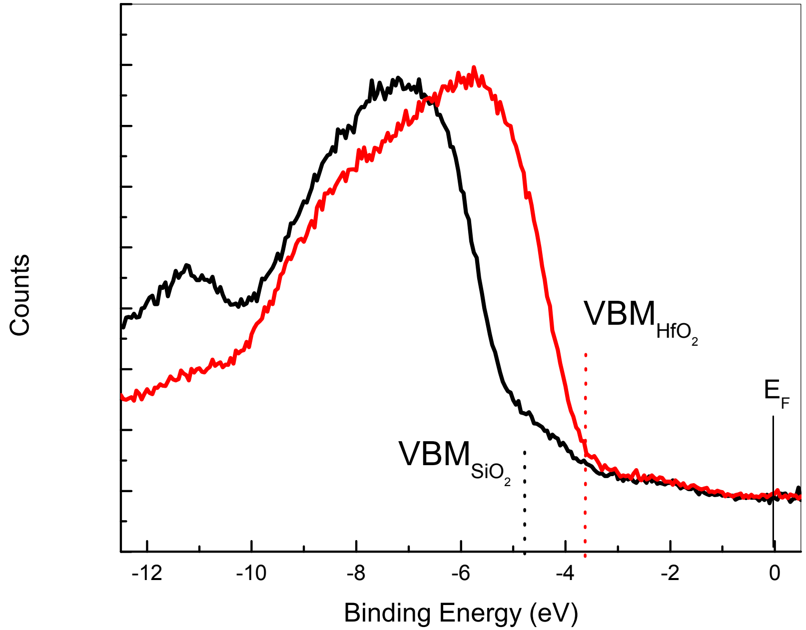
Electronic structural changes upon CVD HfO_2 deposition



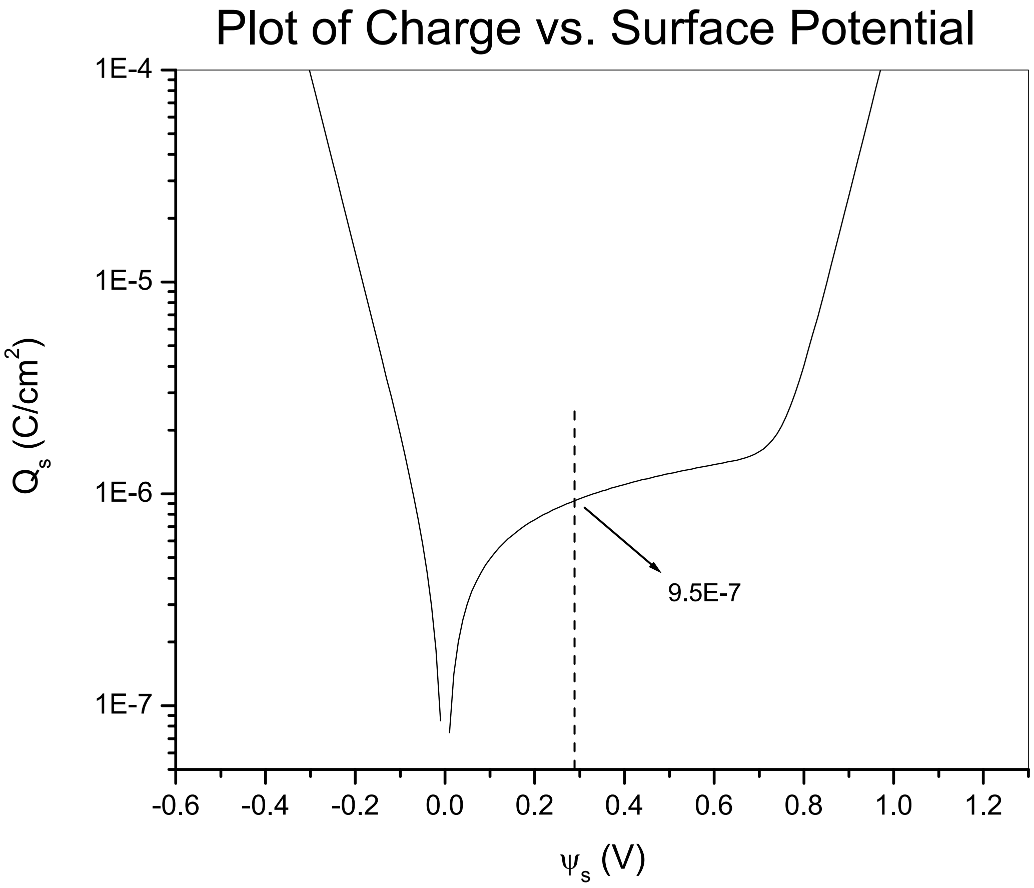




- Si 2p binding energy shifts ~0.26 eV towards higher BE
- Consistent with downward band bending in Si
- Downwards band bending for p-Si indicates presence of negative charge



Estimation of charge from band bending



- Using the measured band bending and $N_A=1\times10^{15}$ cm^{-3}
- The charge can be calculated $Q_s \sim 9.5\times10^{-7}$ C/cm^2

$Q \sim -6\times10^{12}$ cm^{-2}

This is in good agreement with the reported value*

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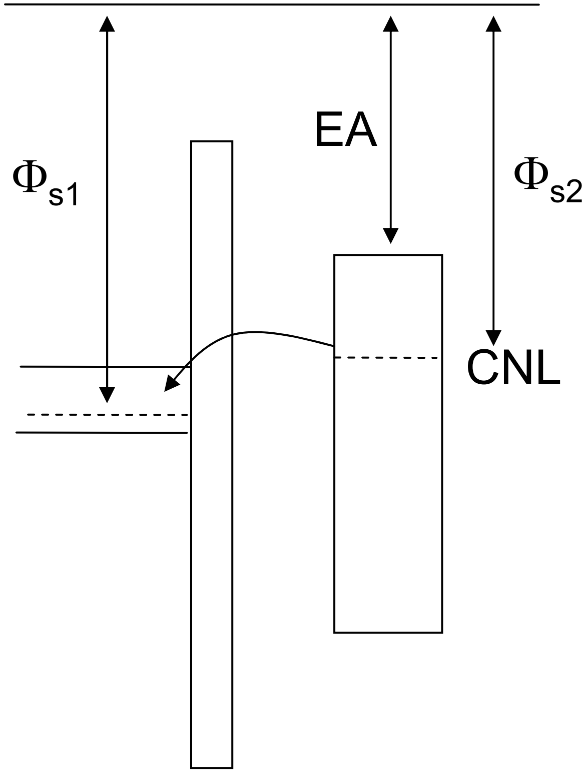
* E. Cartier et.al. "Characterization of the V_t-instability in SiO_2 / HfO_2 gate dielectrics"

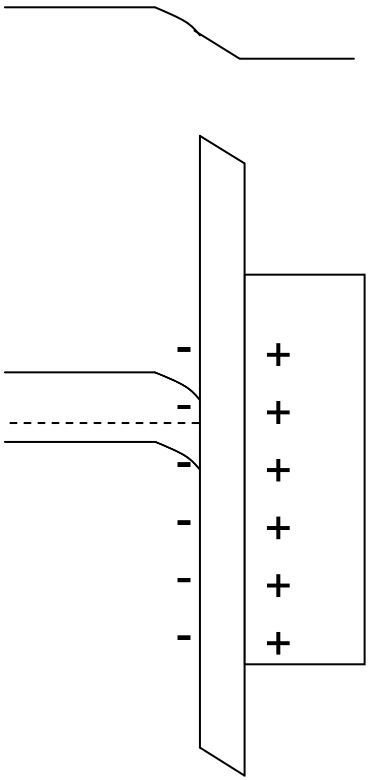
Origin of observed band bending - Electrostatics



(Before contact)

$$\Phi_{s1} > \Phi_{s2}$$

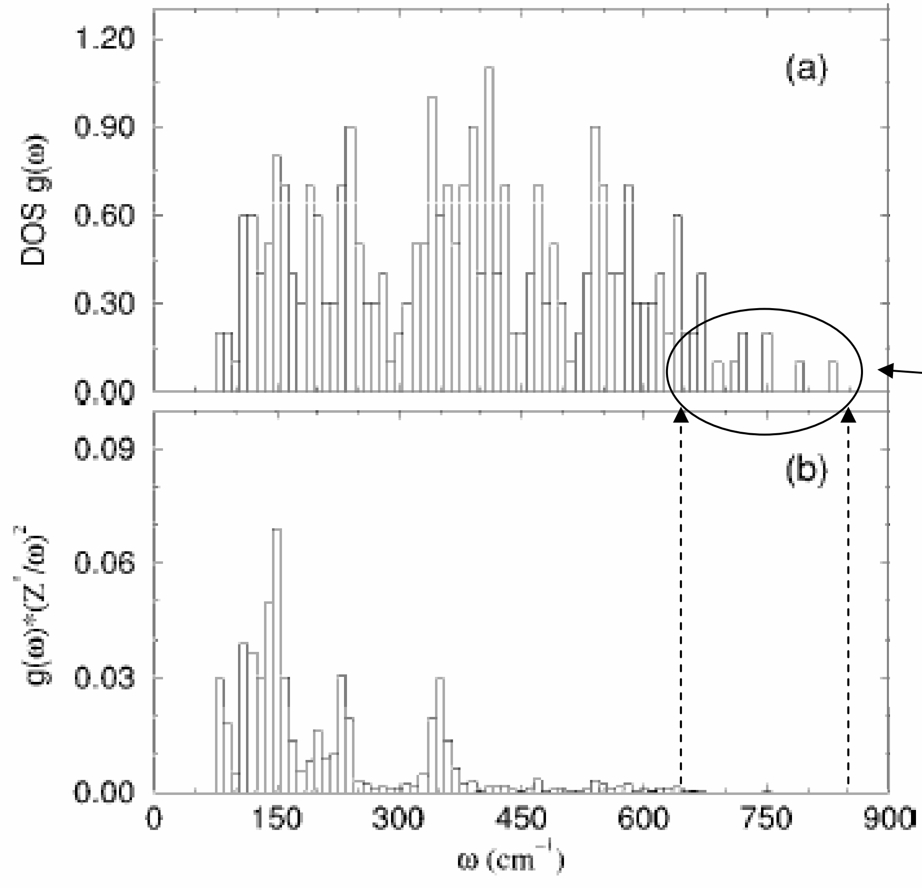
Difference in electronegativities

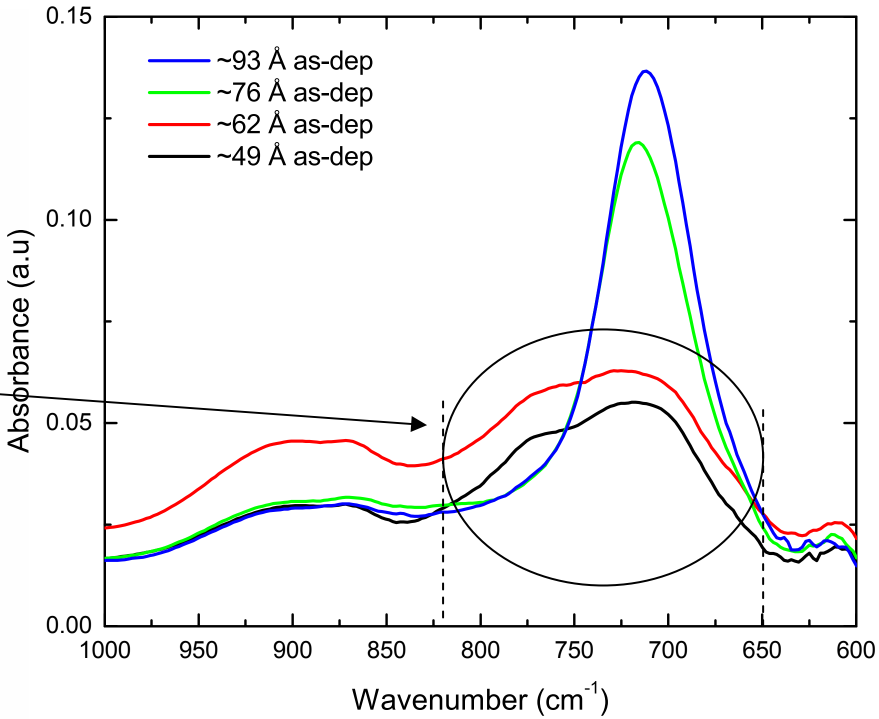


(After contact)

- Electrochemical potential equalization results in charge transfer to silicon, therefore band bending occurs to accommodate this charge

- If the local workfunction at the surface could be probed, we could learn about the changes in the electrostatical potential (e.g upon FGA)





Comparing black and red traces with theory in the range 650-850 cm^{-1}.

- The two thin films (49, 62 Å – black and red traces) were found to be amorphous by XRD and XAS whereas the two thicker ones (76, 93 Å – blue and green traces) were tetragonal.
- The features in the 850-1000 cm^{-1} are common to all spectra suggesting that these features not related to the phase of the film.
- The frequencies of the two main features are ~700 and ~750 cm^{-1} in FTIR spectra. Also seen two bars (more intense than others in this frequency range) approximately at these two frequencies (~700 and ~750 cm^{-1}) .