# *Nanoelectronics Beyond Si: Challenges and Opportunities*

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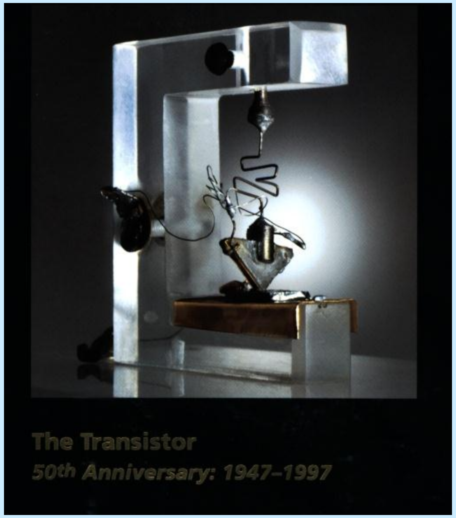
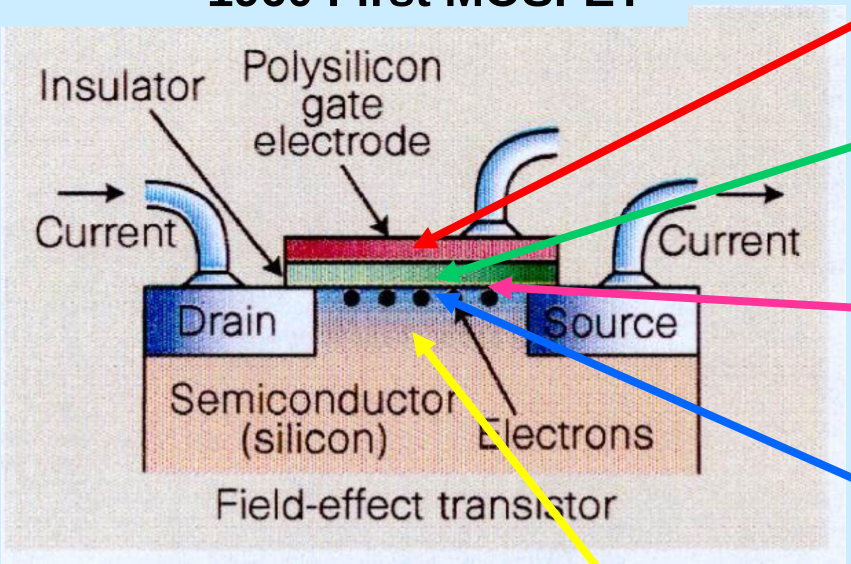
# Si CMOS Device Scaling – Beyond 22 nm node
# High κ, Metal gates, and High mobility channel

**1947 First Transistor**




**1960 First MOSFET**




*Metal Gate*

*High κ gate dielectric*

*Oxide/semiconductor interface*

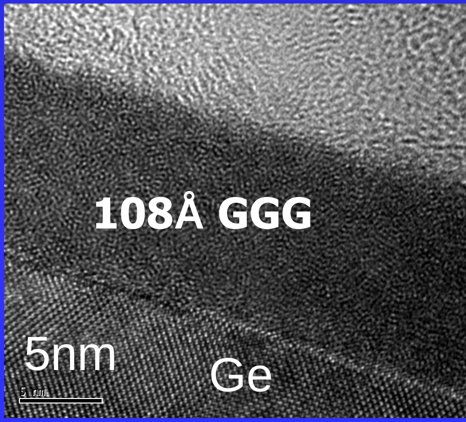
*High mobility channel*

*Integration of Ge, III-V with Si*

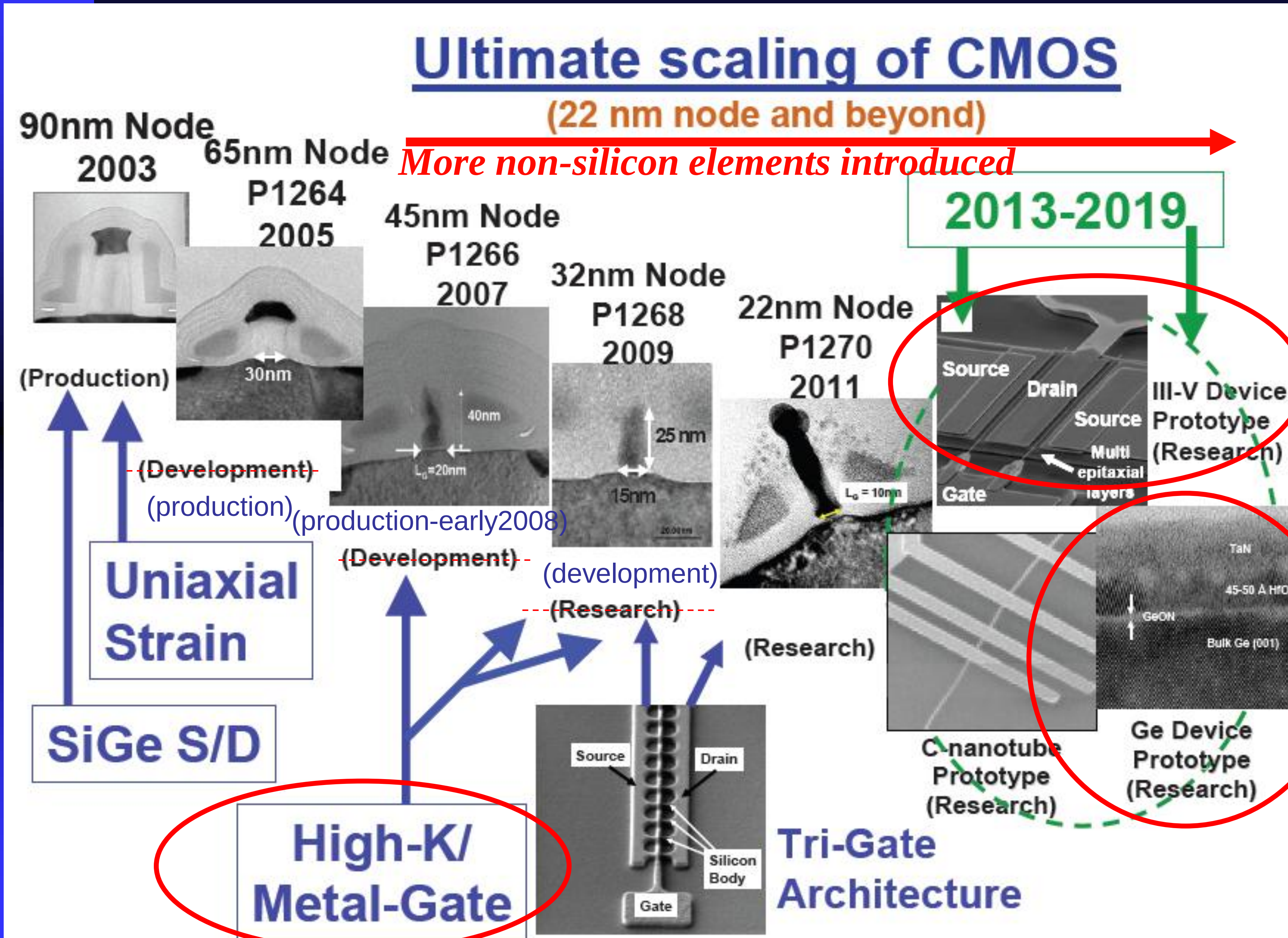
*Moore's Law: The number of transistors per square inch doubles every 18 months*

Shorter gate length *L*
Thinner gate dielectrics $t_{ox}$

*Driving force :*
*High speed*
*Low power consumption*
*High package density*



# Intel Transistor Scaling and Research Roadmap



# Major Research Subjects

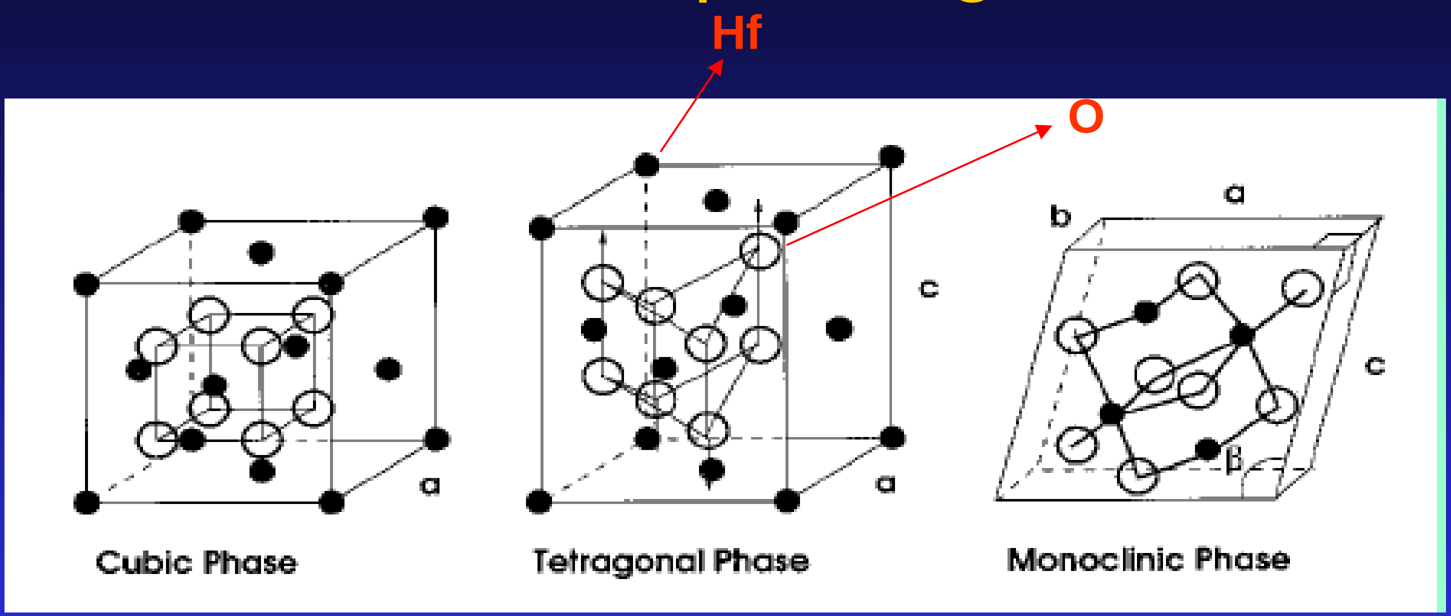
- Enhancement of κ in the new phase through epitaxy
- Fundamental study by IETS for detections of phonons and defects in high κ dielectrics
- Room temperature ferromagnetism in cluster free, Co doped $HfO_2$ films

*Can you make κ even higher ?*

*“ Phase Transition Engineering”*

---Enhancement of κ in the New Phase through Epitaxy

# Crystal structures of $HfO_2$ and the corresponding κ



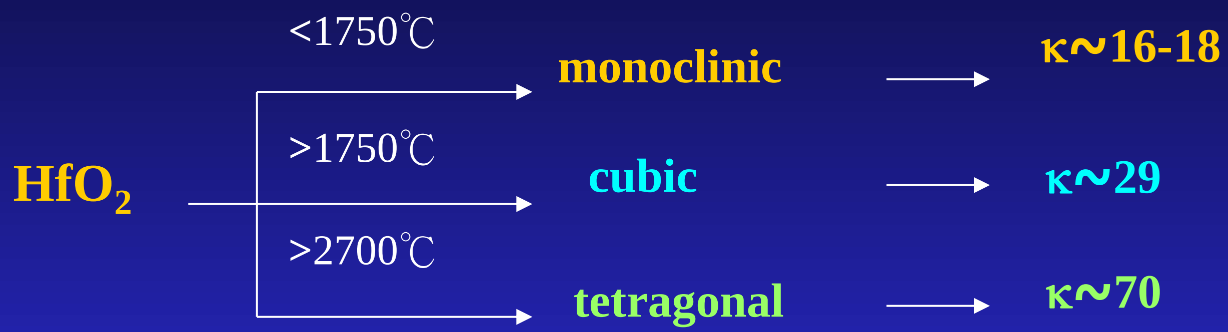

| | Cubic | Tetragonal | Monoclinic |
|---|---|---|---|
| *Dielectric constants* | *29* | *70* | *16 ** |
| *Stable phase temperature* | *>1750°C* | *>2700°C* | *<1750°C* |

**The dielectric constant increases when $HfO_2$ structure is changed from monoclinic to other symmetry**

* Xinyuan Zhao and David Vanderbrit, P.R.B. 65, 233106, (2002).

# Permittivity Increase of Yttrium-doped $HfO_2$ Through Structural Phase Transformation

by Koji Kita, Kentaro Kyuno, and Akira Toriumi, Tokyo Univ.




- Yttrium serves effectively as a dopant to induce a phase transformation from the ***monoclinic*** to the ***cubic*** phase even at 600 °C.
- Yttrium-doped $HfO_2$ films show higher permittivity than undoped $HfO_2$, and the permittivity as high as 27 is obtained by 4 at. % yttrium doping.
- The permittivity of undoped $HfO_2$ is reduced significantly at high temperature, whereas that of 17 at. % yttrium-doped film shows no change even at 1000 °C.

| | 2x position | 1x position |
|---|---|---|
| | | |

After deposition for 5mins

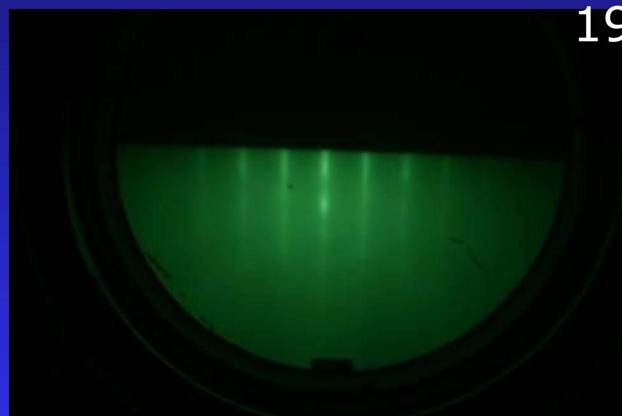
Dielectric film of 4 –fold symmetry in the plane

190 °

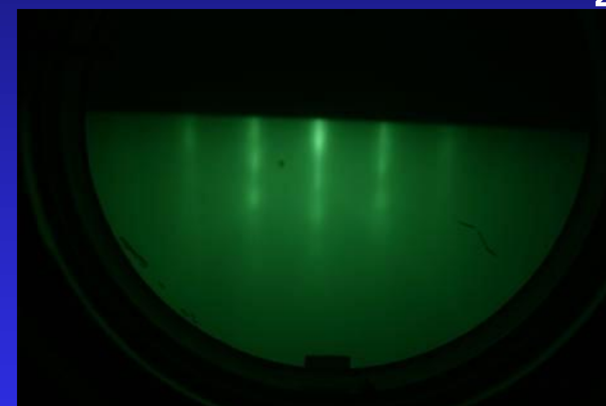
280 °

After deposition for 2mins

190 °



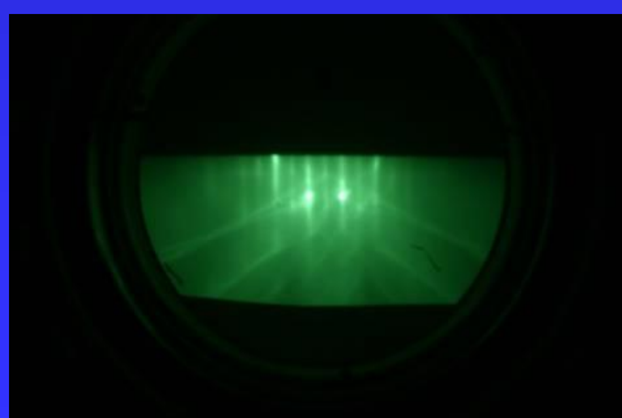
280 °



Wafer rotate22.5 °

After reconstruction

145 °

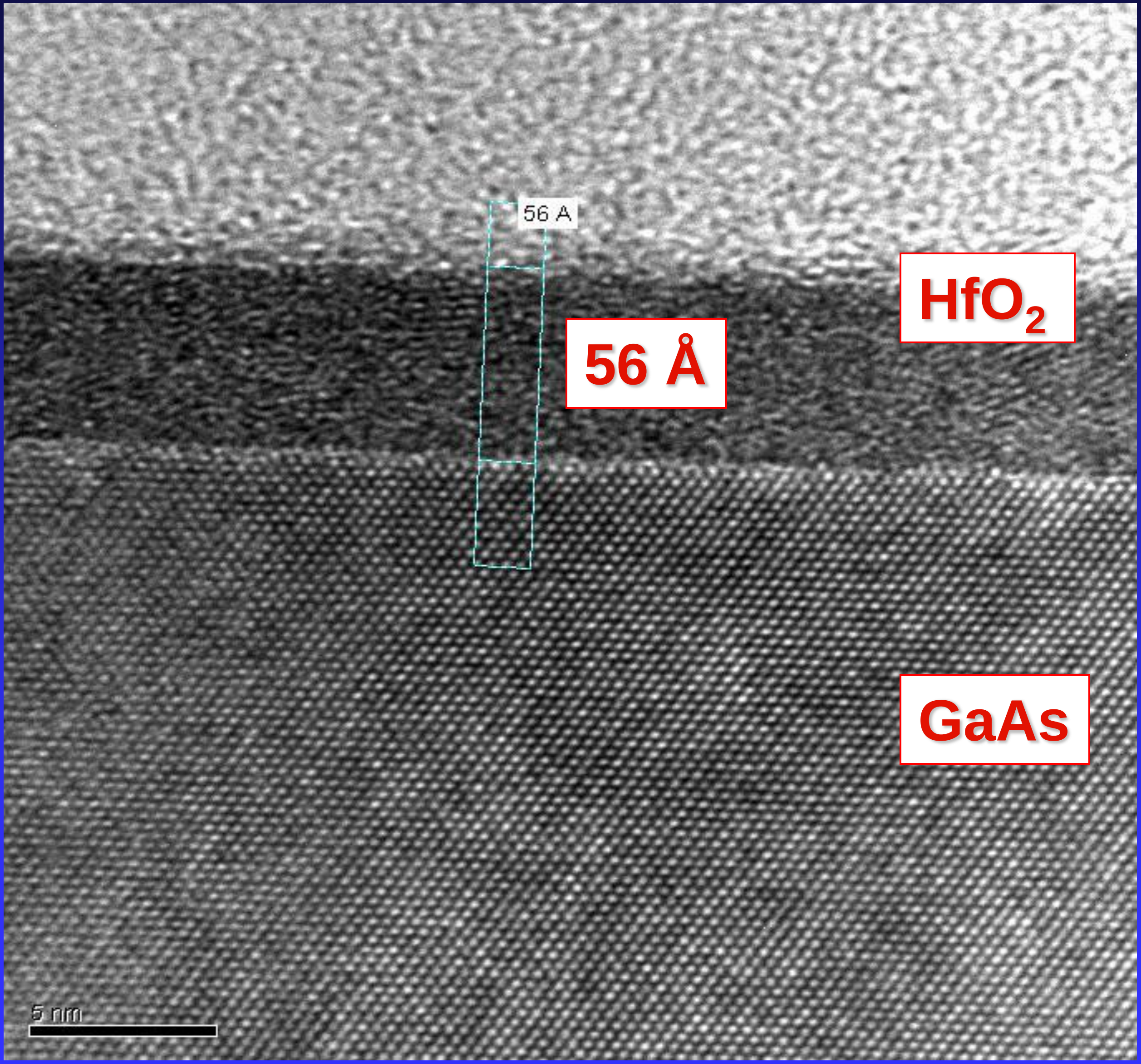


235 °

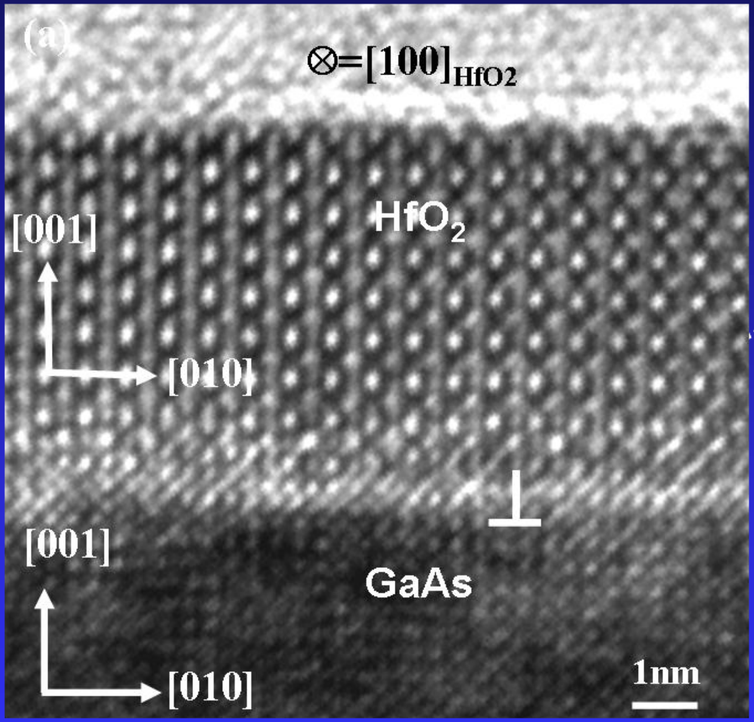
# HRTEM of Low Temp Growth

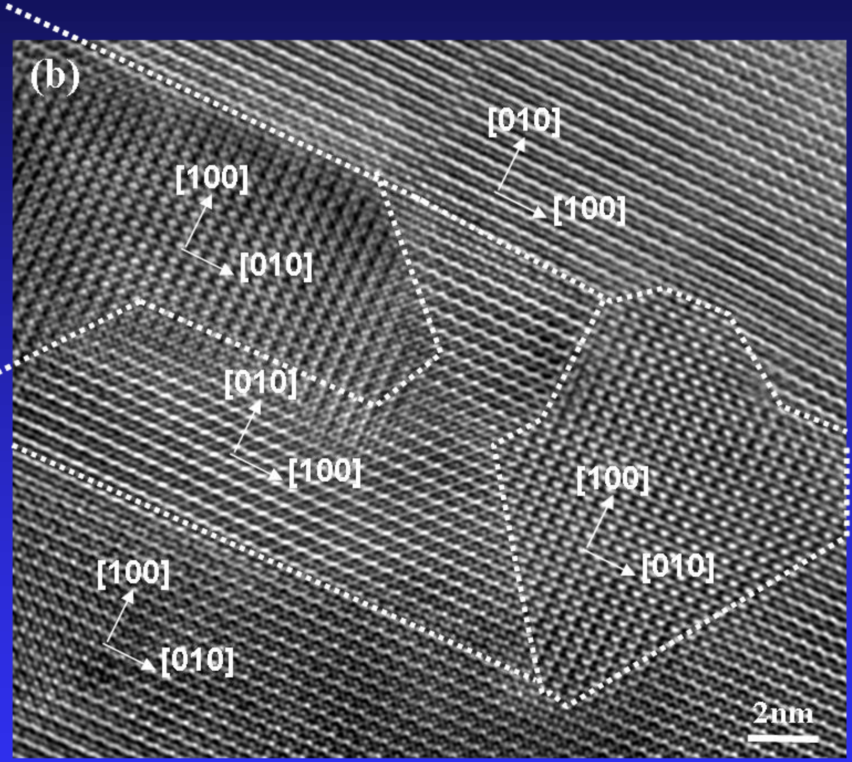
**Amorphous $HfO_2$ on GaAs (100)**

**A very abrupt transition from GaAs to $HfO_2$ over one atomic layer thickness was observed.**



# High Resolution TEM Images of Pure $HfO_2$ on GaAs (001)

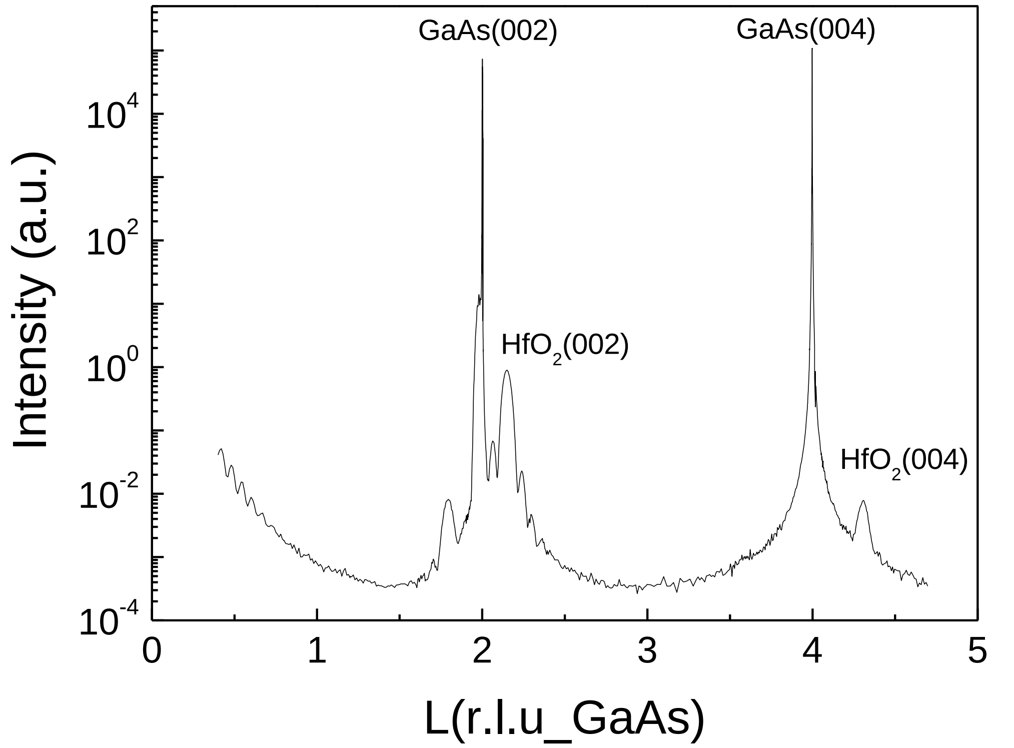


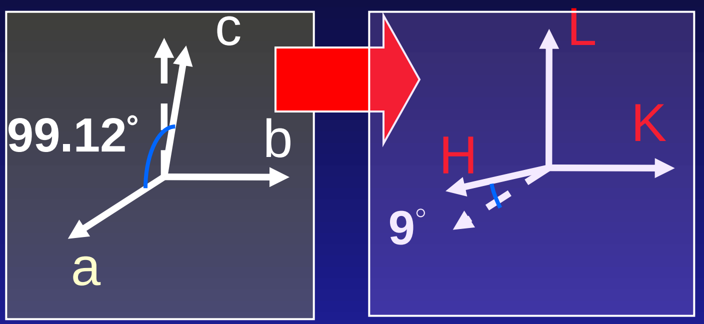




An abrupt transition from GaAs to $HfO_2$ and no interfacial layer

Coexistence of four monoclinic domains rotated by 90º.

# X-ray Diffraction of Epitaxial $HfO_2$ Films Recrystalized on GaAs




R space

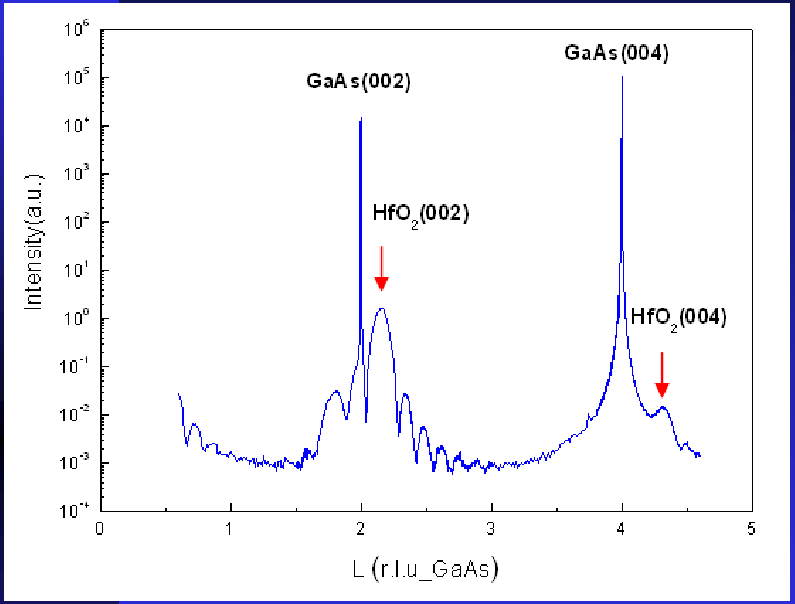
K space

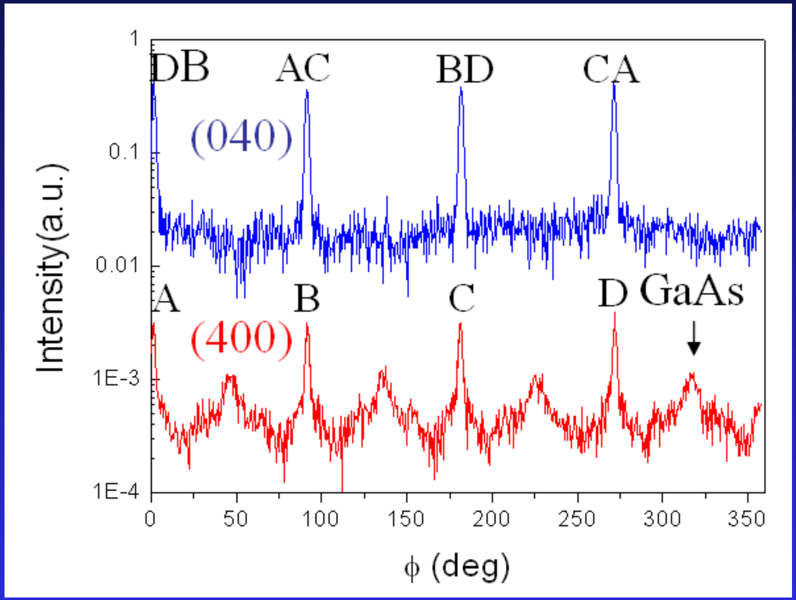
$HfO_2$(004) FWHM(L)=0.0578°
⇒ domain size 97.8 Å
⇒ close to film thickness

**--- Monoclinic $HfO_2$ in R space and K space**
**--- Forming four degenerate domains about the surface normal**

**With C. H. Hsu of NSRRC**

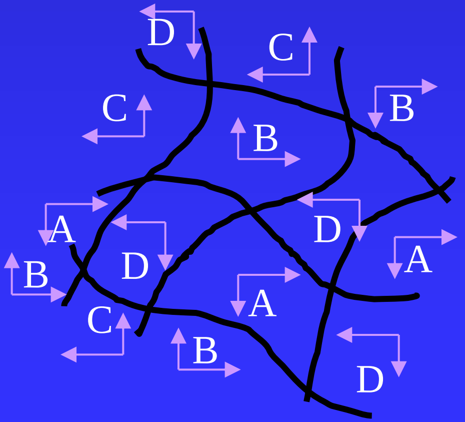
# The Structure of $HfO_2$ Grown on GaAs(001)



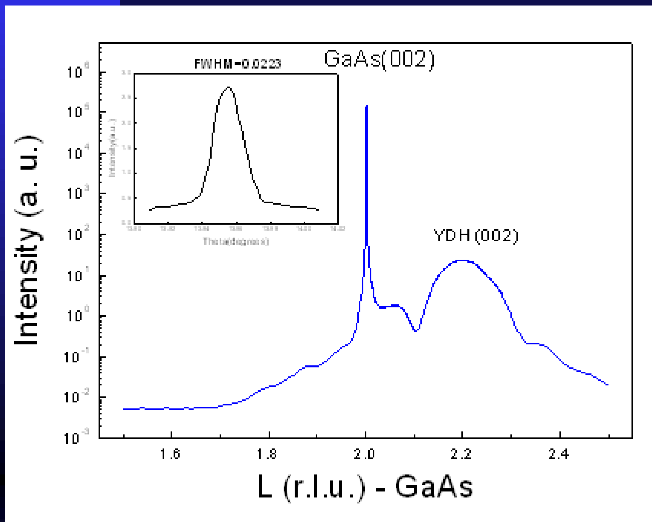

monoclinic phase

a=5.116A, b=5.172A, c=5.295A, β=99.18A




Coexistence of 4 domains rotated 90° from each other

# The Structure of $HfO_2$ doped with $Y_2O_3$ Grown on GaAs (100)




Surface normal scan

Find the peaks:

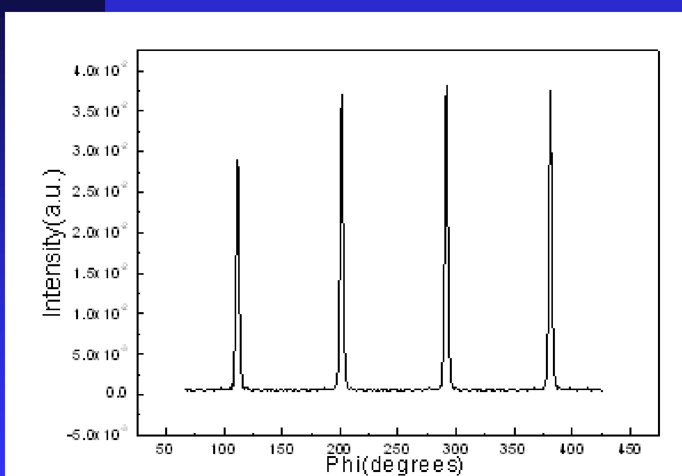
- (022)(400)(200)(311)(31-1)(113)(420)(133)(20-2)
- All peaks of film match the JCPDS of cubic phase $HfO_2$
- Use the d-spacing formula to fit the lattice parameters

→ $HfO_2$ doped with $Y_2O_3$ Grown on GaAs(001) is

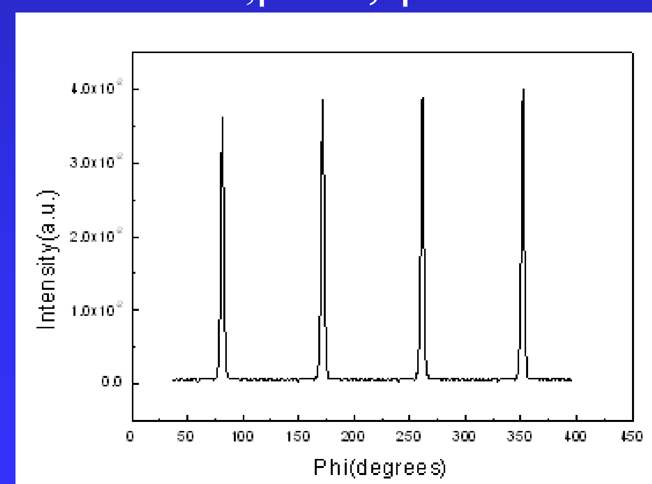
Cubic phase

a=5.126A, b=5.126A, c=5.126A

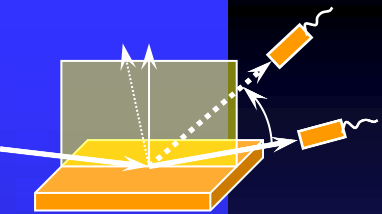
α=90,β=90, γ=90




(400)Phi scan

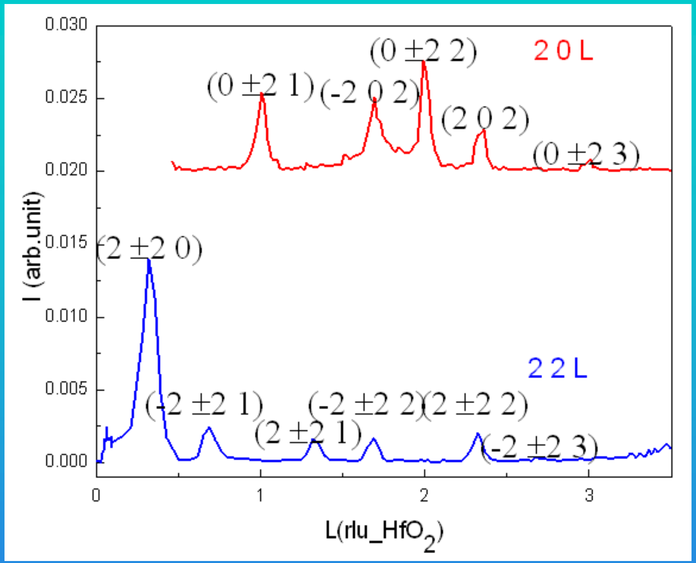



(040)Phi scan

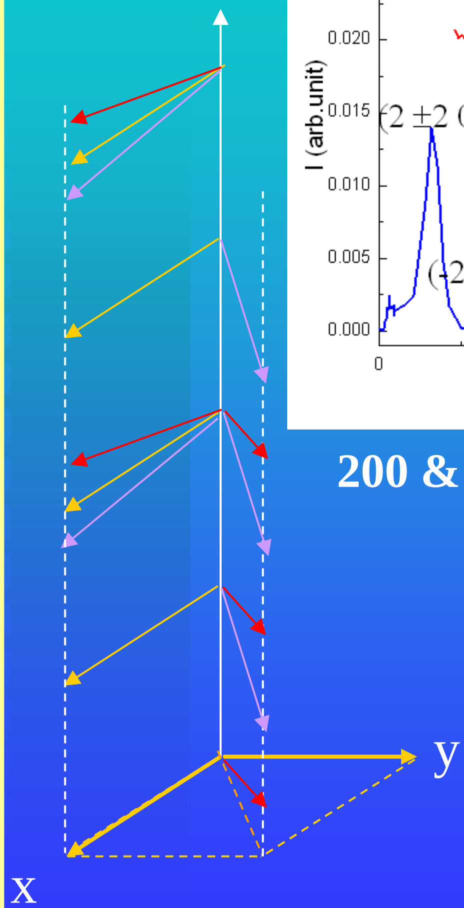


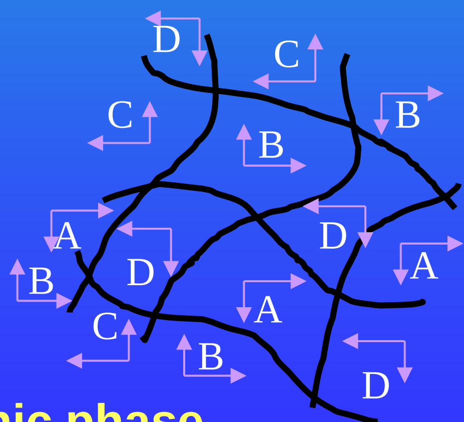
# Comparison between Monoclinic phase and Cubic phase of $HfO_2$

## Without doping $Y_2O_3$



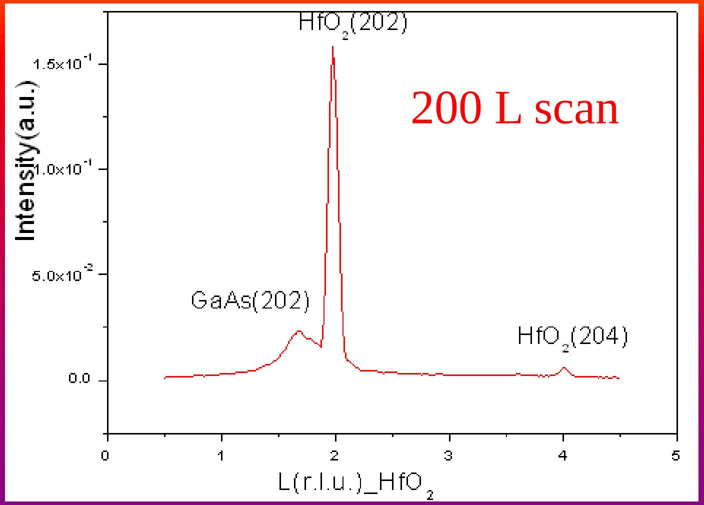

200 & 220 L scan

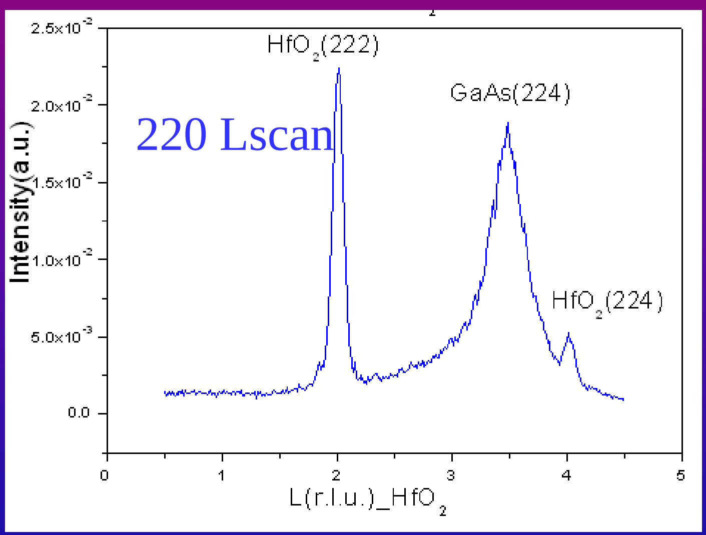



**Monoclinic phase**

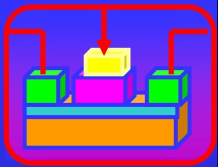
## With doping $Y_2O_3$




**Cubic phase**

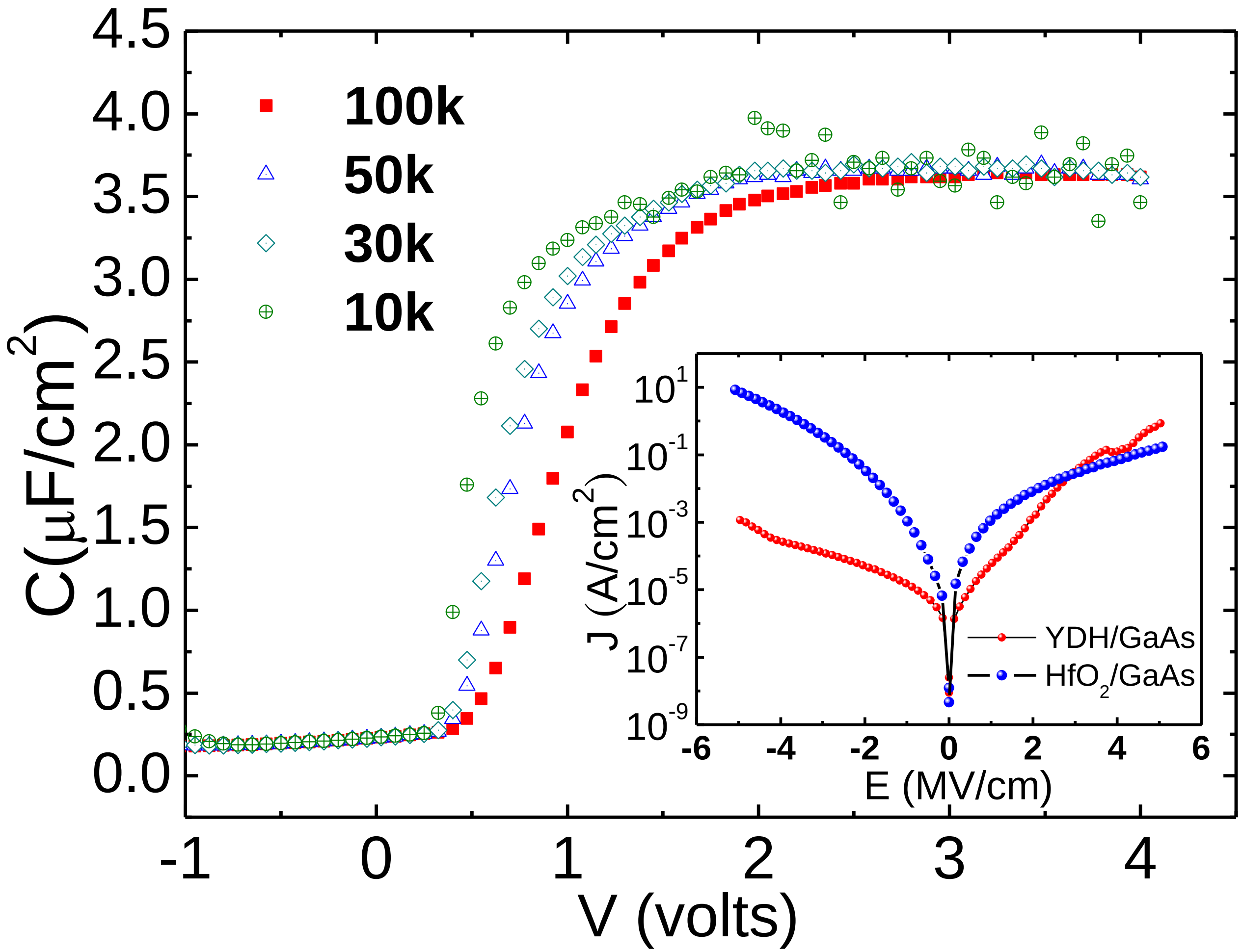
# The Electrical Property of $HfO_2$ doped with $Y_2O_3$ Grown on GaAs(001)



T=110A κ=32

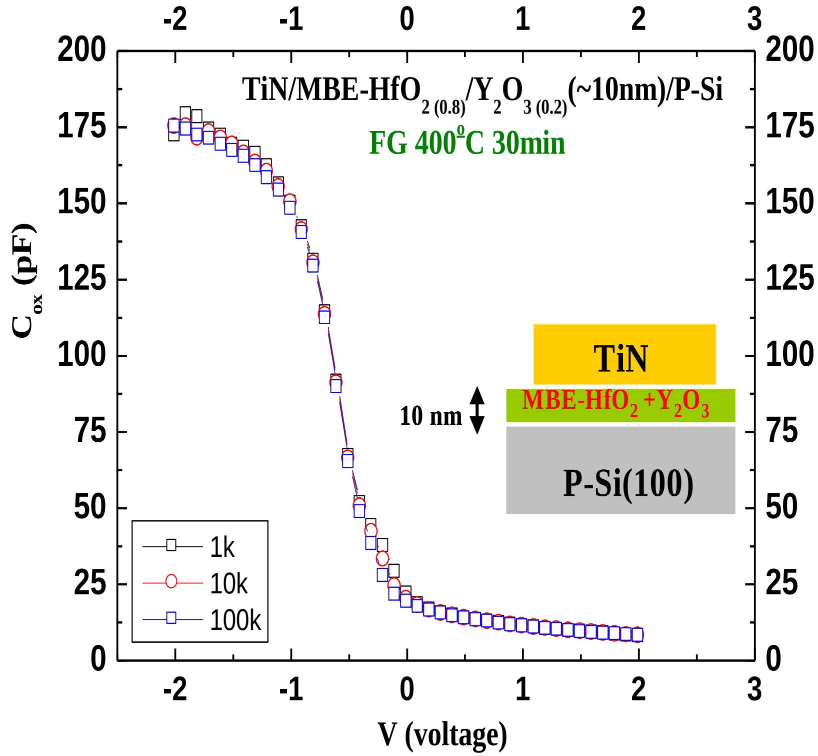
$Y_2O_3$+$HfO_2$

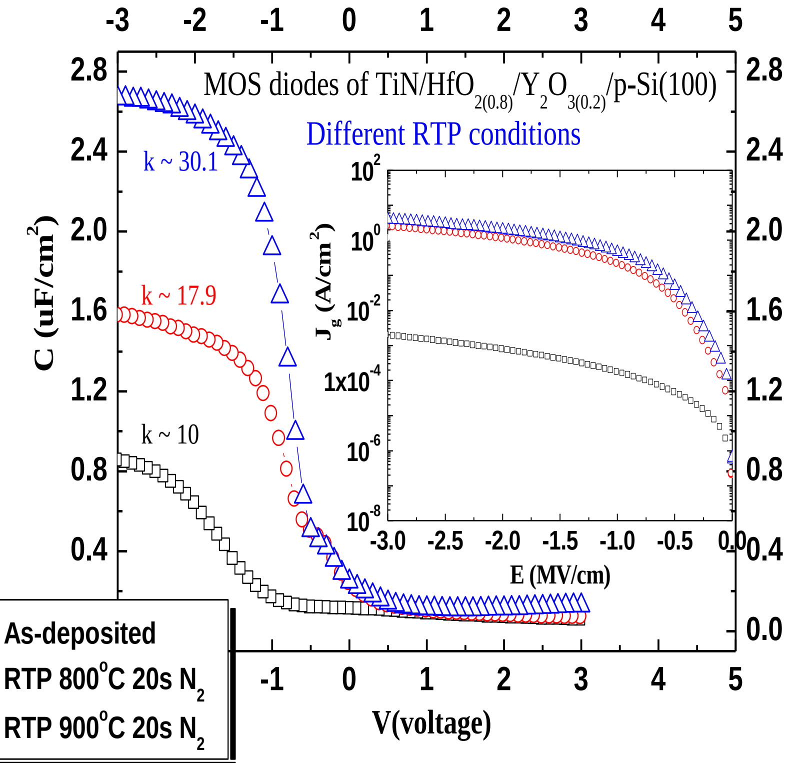
GaAs(001)



# Electrical properties - MBE-$HfO_{2\,(0.8)}$ $Y_2O_{3\,(0.2)}$

## MBE-$HfO_{2\,(0.8)}$ $Y_2O_{3\,(0.2)}$

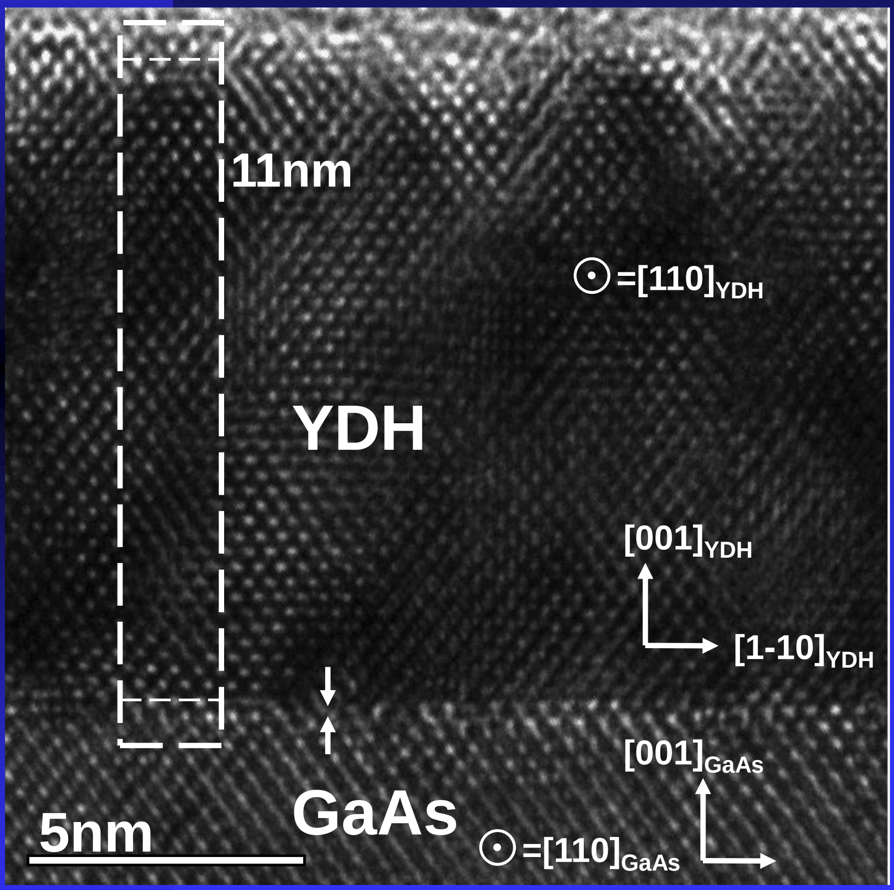


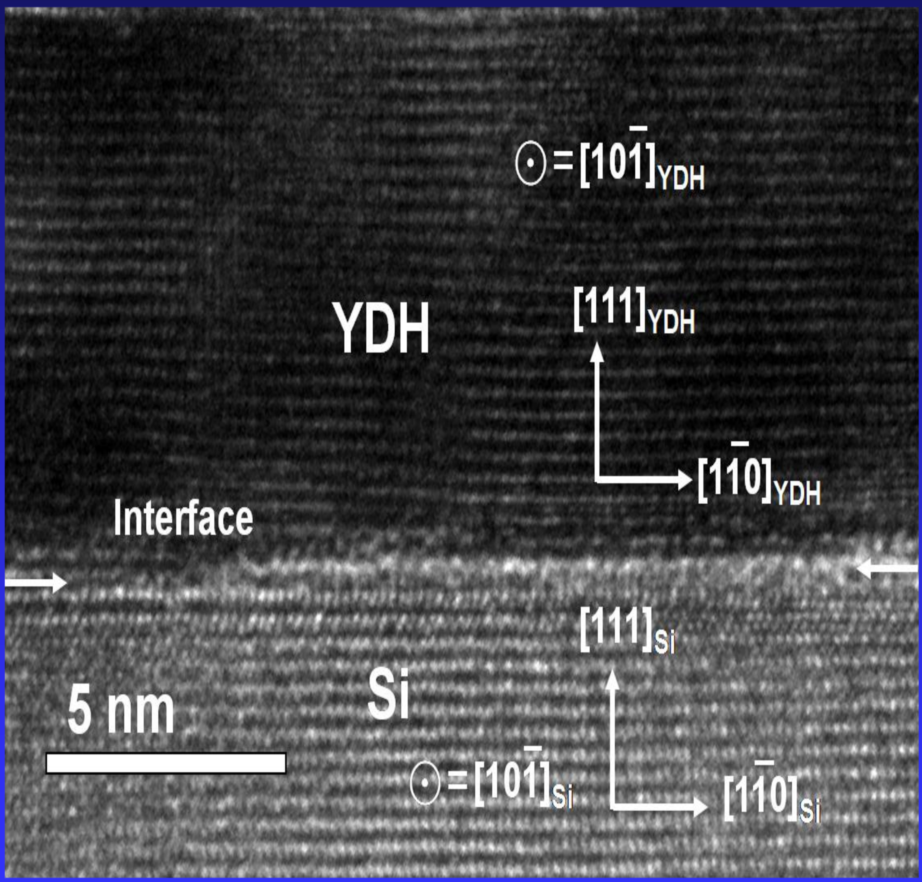

**Increase of κ from 15 to over 30 in cubic phase !**

# Cross Sectional HRTEM Study of The Y-doped $HfO_2$ Films in Cubic Phase

**Interfaces of YDH(100)/GaAs, and YDH(111)/Si are atomically sharp**

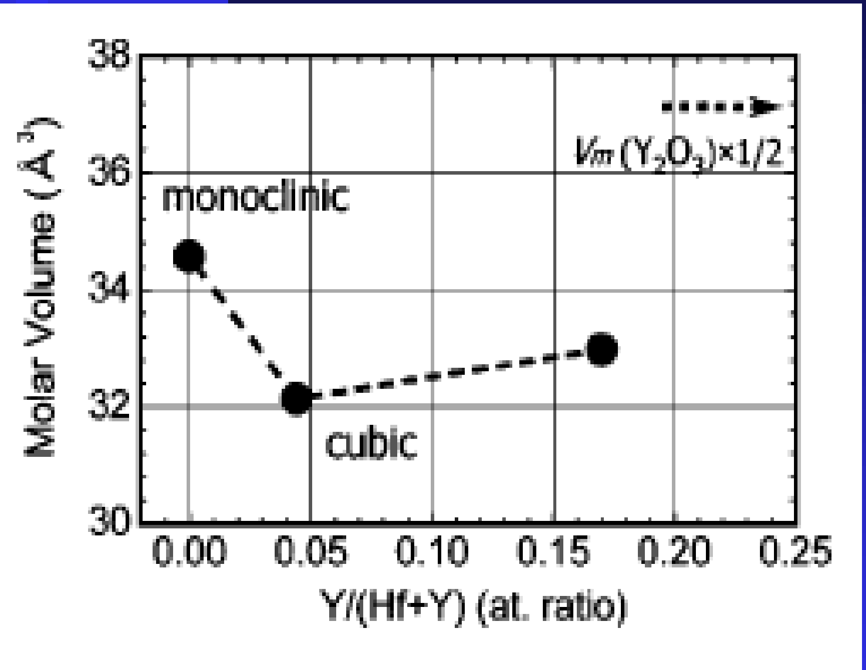



HRTEM image of yttrium-doped $HfO_2$ films 11 nm thick on GaAs (001).




HRTEM image of yitturm-doped $HfO_2$ films 7.5 nm thick on Si (111).

# The Enhancement of κ through "Phase Transition Engineering"




$$\kappa = (1 + 8\pi\,\alpha_m/3V_m)\,/\,(1 - 4\pi\alpha_m/3V_m)$$

Clausius-Mossotti Relation

***Change of molar volume in Y doped $HfO_2$***

- Many high κ materials, such as $HfO_2$, $ZrO_2$, $TiO_2$, $Ta_2O_5$, commonly have high temperature phases with a higher κ.
- Achieve the enhancement through ***phase transition engineering*** by additions of dopants such as lower valence cations, followed by proper post high temperature anneals.

# *IETS Study to Detect Phonons and Defects in High $\kappa$ Dielectrics*

*But what is inside of high $\kappa$ ?*

# Electrical characterization / optimization

## -- Good News !!

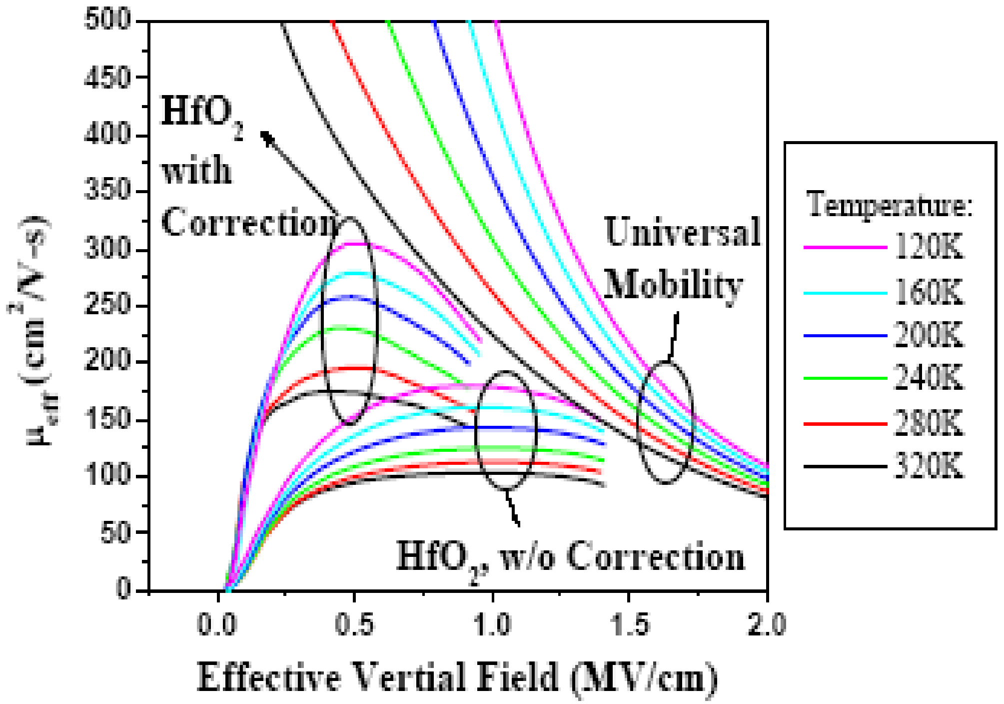
- **Low electrical leakage is common .**
- **Have Attained an EOT under 1.0-1.4 nm .**

## -- Major problems are :

- High interfacial state density
- Large trapped charge
- Low channel mobility
- Electrical stability and reliability

# Degradation of Mobility in High κ Gate Stack

## Temperature dependence of mobility



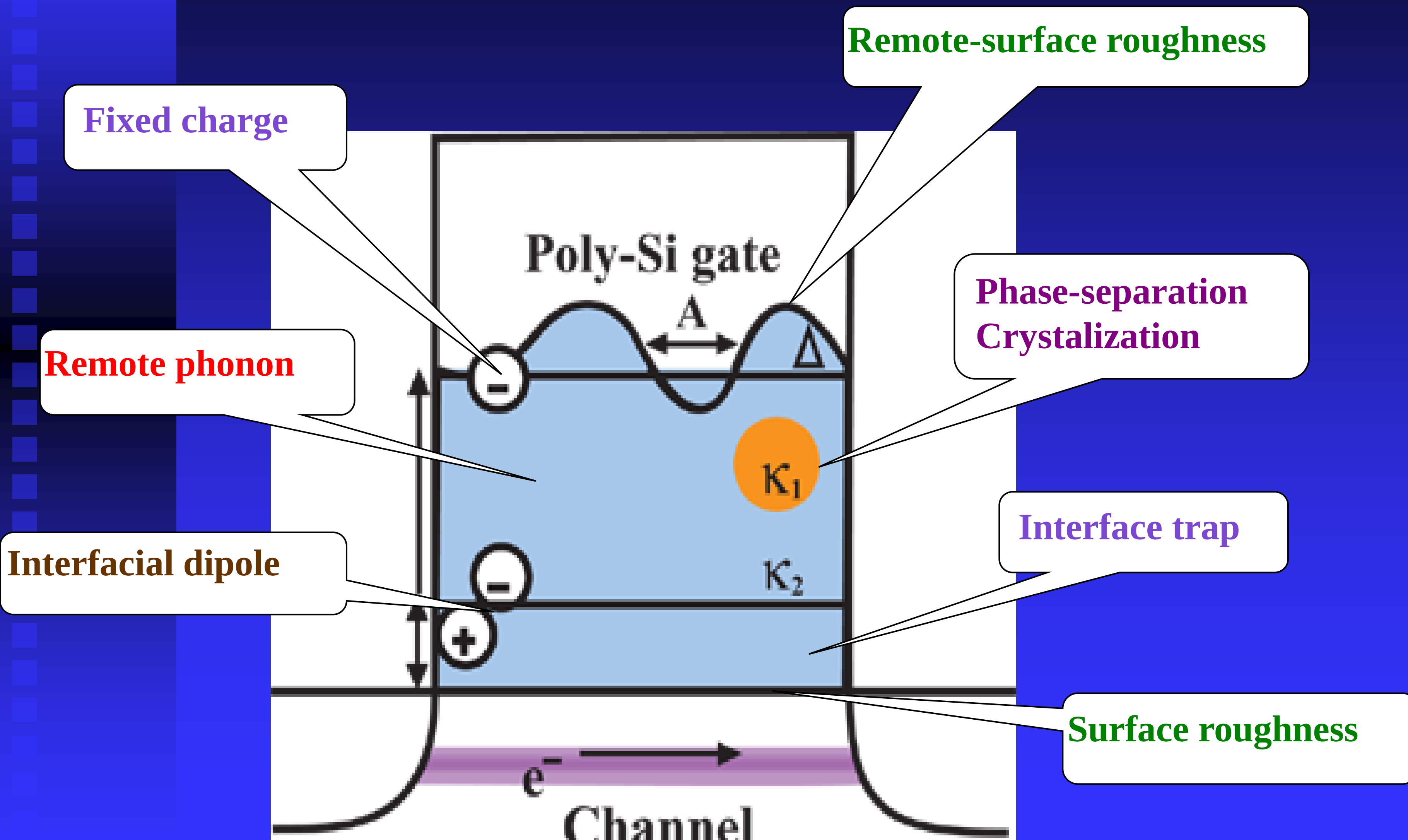

**Correction from the charge trapping effect**

- Effective mobility for $HfO_2$ is lower than universal mobility even after interface correction.

*Phonons may have reduced mobility seriously !*

Fechetti et al, JAP **90**, 4587, (2001).

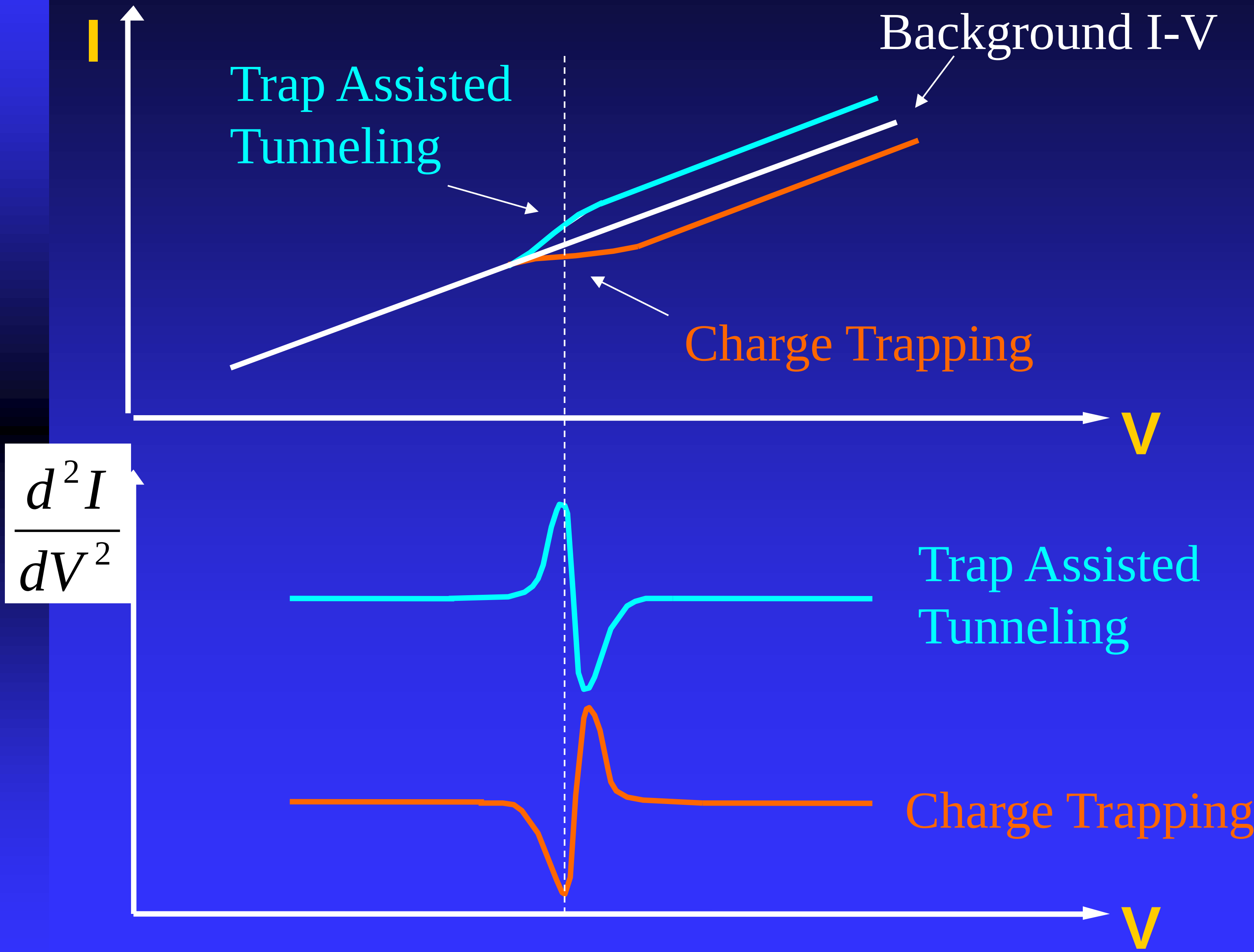
# Possible Source of Mobility Degradation



# Interactions Detectable by IETS

- Substrate Silicon Phonons
- Gate Electrode Phonons
- Dielectric Phonons
- Chemical Bonding
- Interfacial Structures
- Defects (Trap States)

# Trap-Related Signatures in IETS

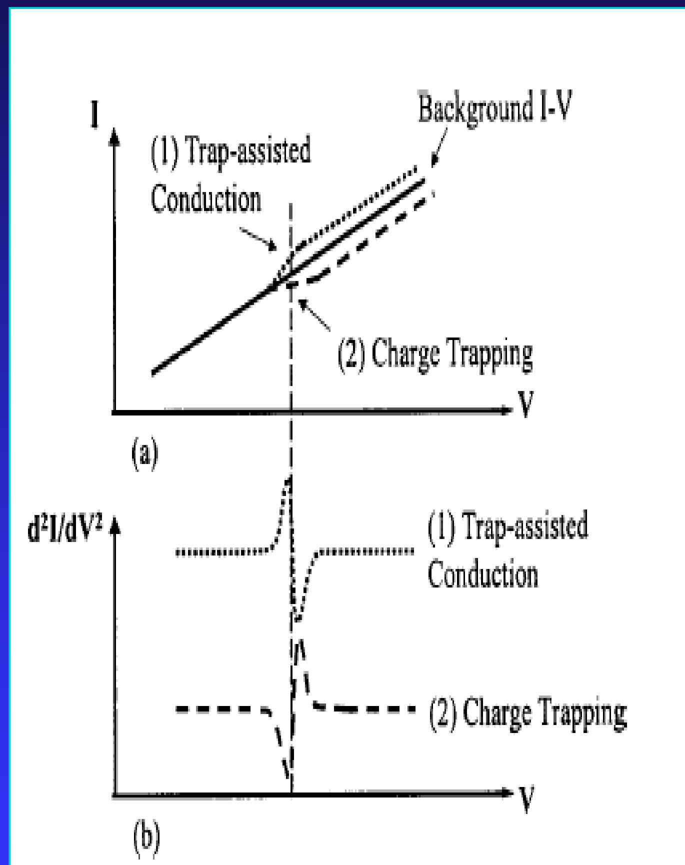


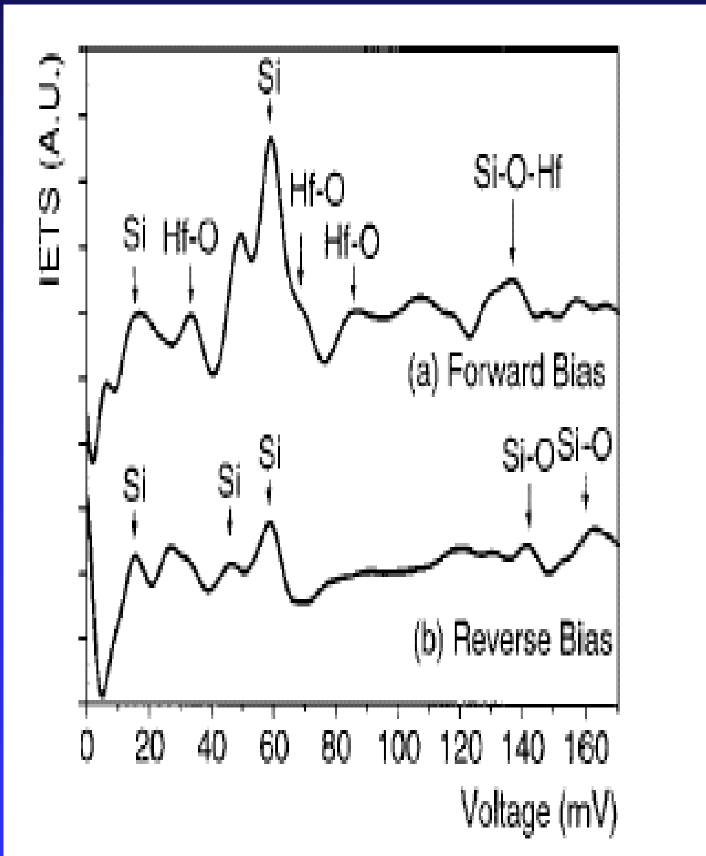

Wei He and T.P.Ma, APL **83**,2605, (2003) ; APL **83**, 5461, (2003).

# Inelastic Electron Tunneling Spectroscopy (IETS)

Charge trapping will cause shift in the threshold voltage.

Trap-assisted conduction will cause increased leakage current.

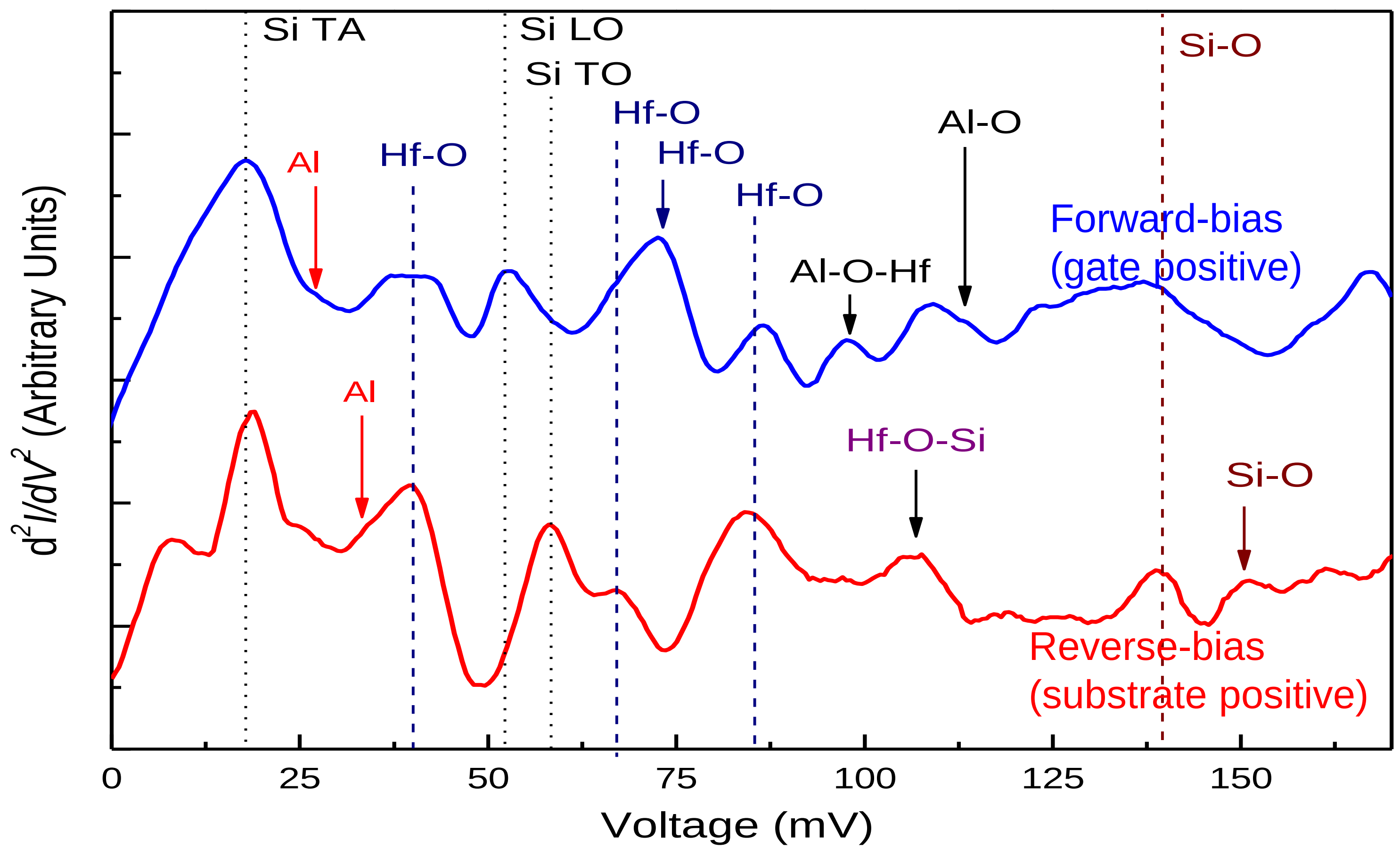


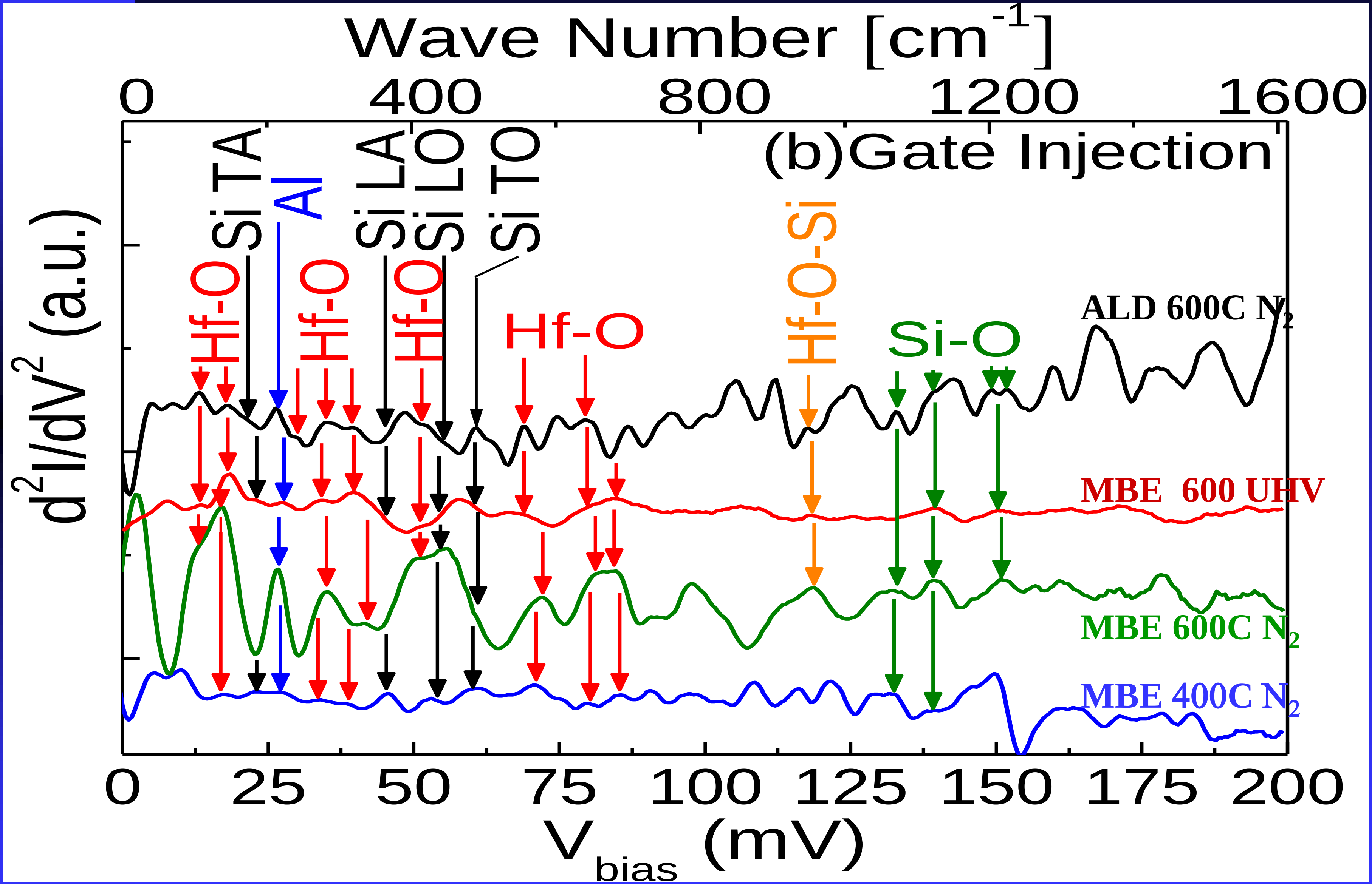

Wei He and T.P.Ma, APL **83**,2605, (2003) ; APL **83**, 5461, (2003)

# IET spectrum of Al/$HfO_2$/Si MOS structure

Al/$HfO_2$/Si, vacuum 600℃ annealing for 3 minutes

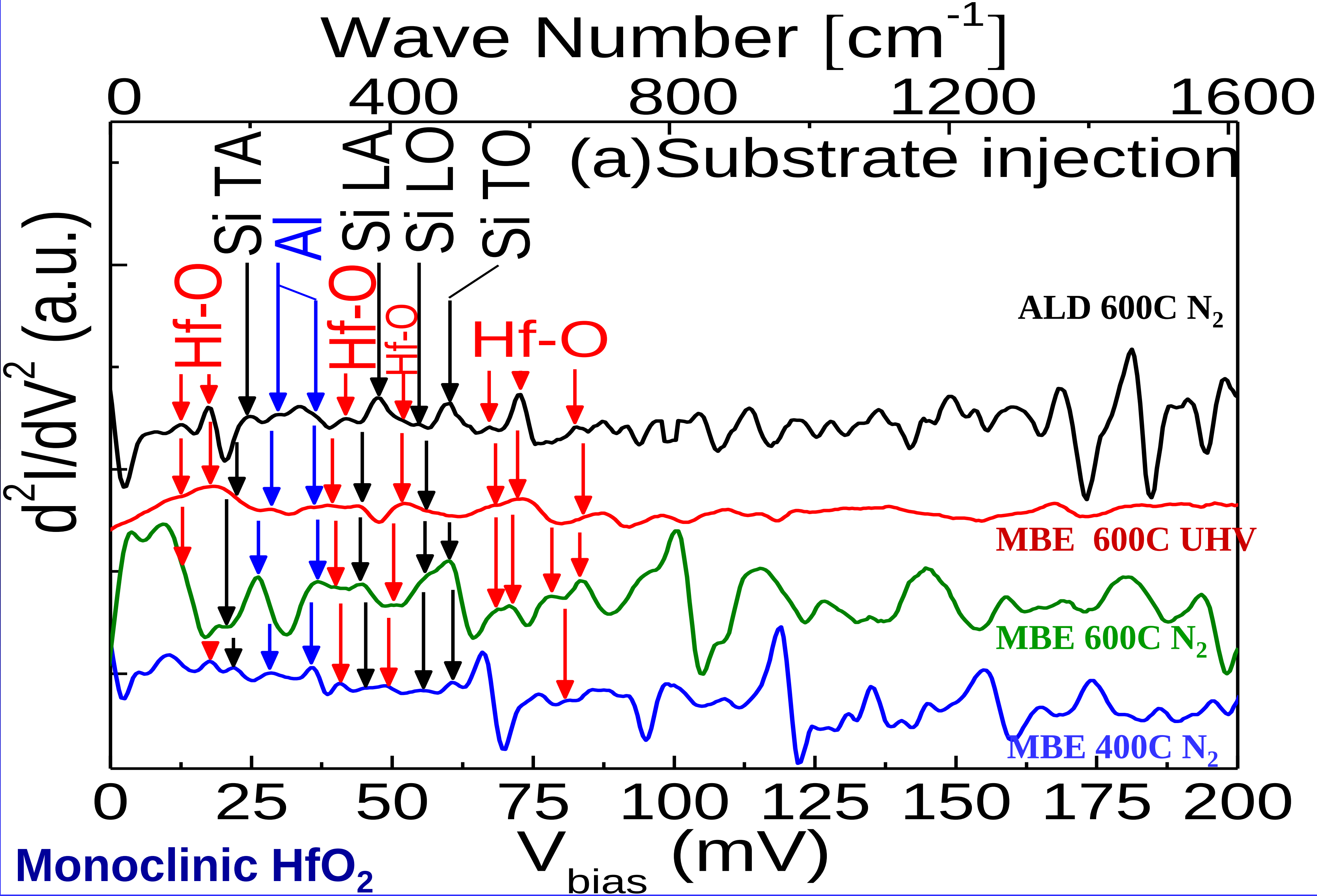


# IET spectrum of Al/$HfO_2$/Si MOS structure



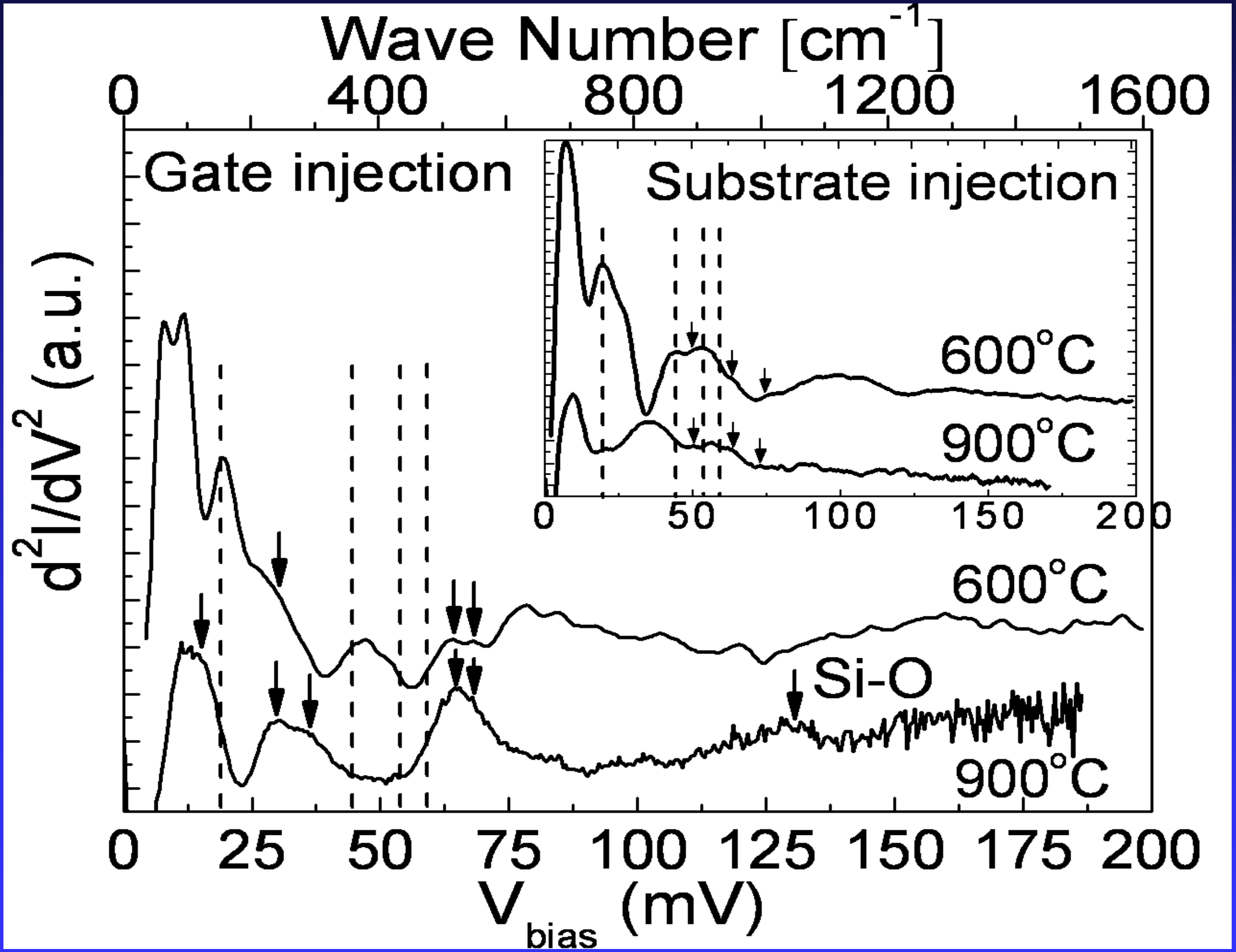

**Monoclinic $HfO_2$**

# IET spectrum of Al/HfO2/Si MOS structure



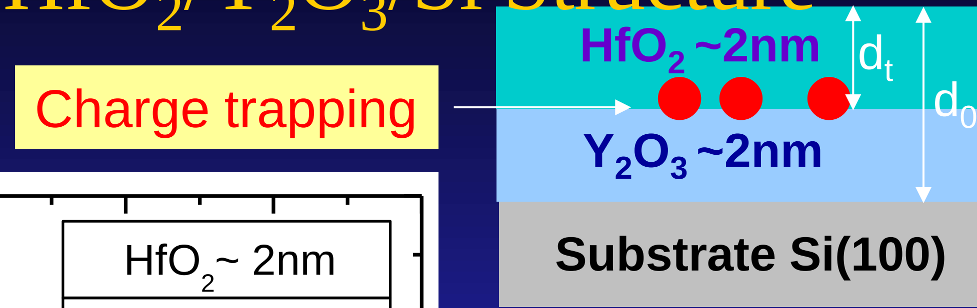

**Monoclinic $HfO_2$**

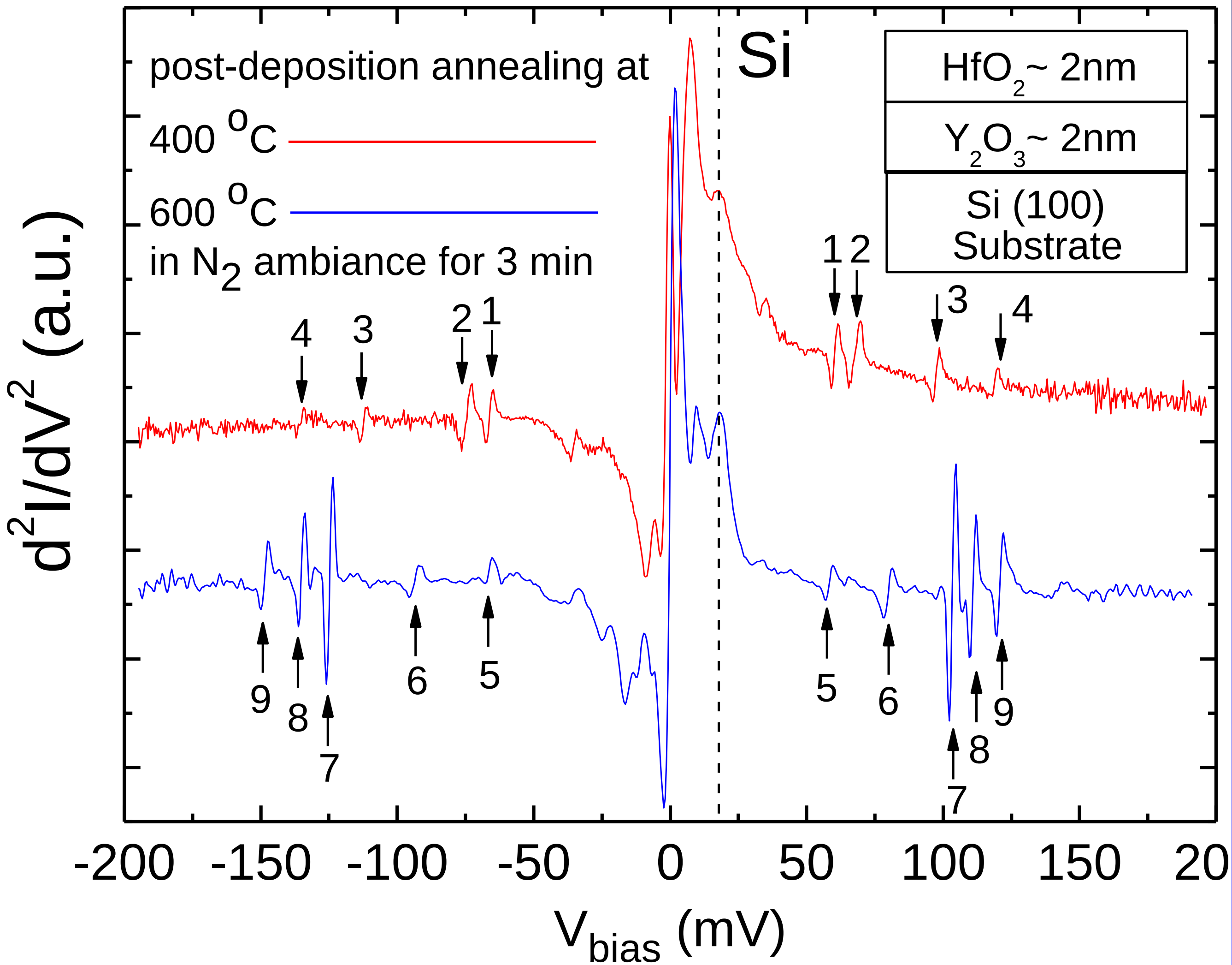
# IET Spectrum of Al/$Y_2O_3$/Si MOS Diode




**Cubic $Y_2O_3$**

# Determination of Physical Locations and Energy Levels of Trap in Stacked $HfO_2/Y_2O_3/Si$ Structure



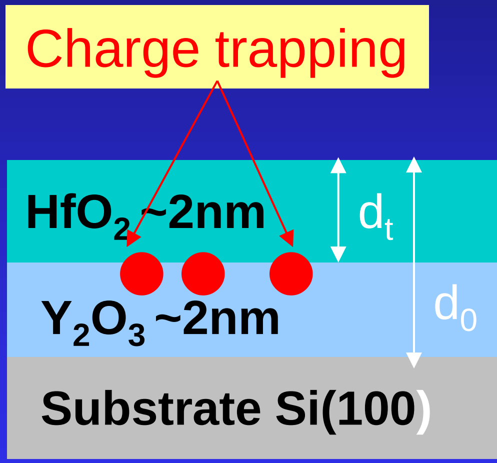

$$\begin{cases} V_t = V_f V_r / (V_f + V_r) \\ d_t = d_0 V_f / (V_f + V_r) \end{cases}$$

$V_f$ and $V_r$ are the voltages where the charge trapping features occur in forward bias and reverse bias.


M. Wang et al,
APL. **86**, 192113 (2005)
APL, **90**, 053502 (2007)

# Determination of Physical Locations and Energy Levels of Trap in Stacked $HfO_2/Y_2O_3/Si$ Structure

| Bilayer Sample | Trap label | $V_f$ (mV) | $V_r$ (mV) | $V_t$ (mV) | $d_t/d_0$ |
|---|---|---|---|---|---|
| $HfO_2$(1.7nm) /$Y_2O_3$(1.4nm) 400°C | 1 | 60 | 66 | 31 | 0.47 |
| | 2 | 67 | 75 | 35 | 0.47 |
| | 3 | 97 | 112 | 52 | 0.46 |
| | 4 | 118 | 135 | 63 | 0.46 |
| $HfO_2$(1.7nm) /$Y_2O_3$(1.4nm) 600°C | 5 | 58 | 66 | 31 | 0.46 |
| | 6 | 78 | 93 | 42 | 0.45 |
| | 7 | 103 | 124 | 56 | 0.45 |
| | 8 | 111 | 135 | 61 | 0.45 |
| | 9 | 120 | 148 | 66 | 0.45 |
| $HfO_2$(1.2nm) /$Y_2O_3$(1.5nm) 600°C | 1 | 26 | 32 | 14.3 | 0.45 |
| | 2 | 87 | 94 | 45.2 | 0.48 |
| | 3 | 99 | 108 | 51.7 | 0.48 |



# *Can you make $HfO_2$ magnetic ?*

## Diluted Magnetic Oxides

*"Observation of Room Temperature Ferromagnetic Behavior in Cluster Free, Co doped $HfO_2$ Films"*

*Appl. Phys. Lett. 91, 082504 (2007)*

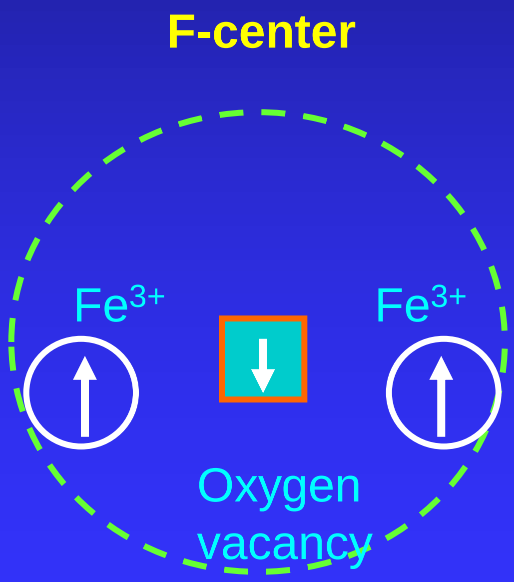
# Introduction and motivation

- Both injection and transport of spin-polarized carriers are necessary for the spintronic devices. Using diluted magnetic semiconductor (DMS) as the ferromagnetic contact is one way to achieve this goal.

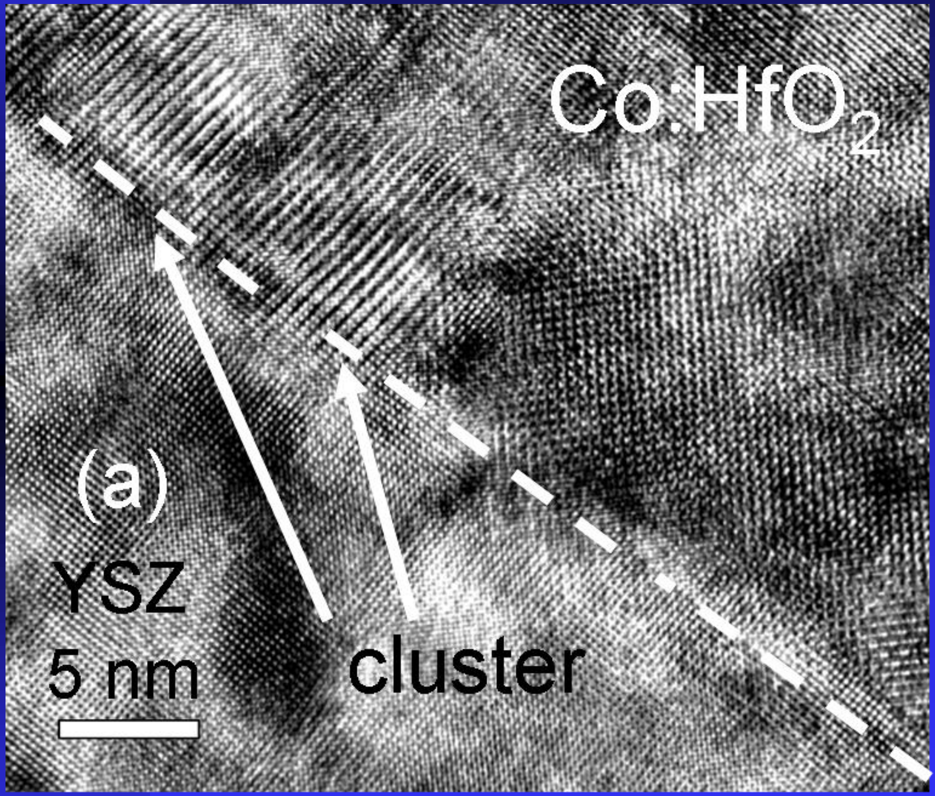
- Several models such as Zener's model , bound magnetic polaron, and F-center theory were used to describe the ferromagnetism.

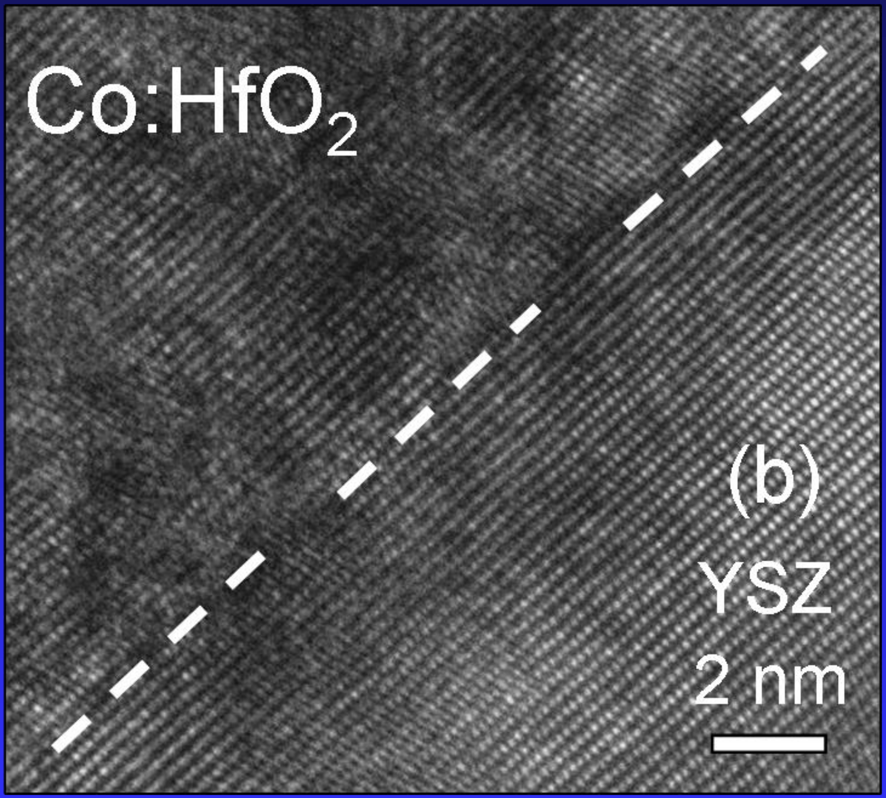
- The potential usage of $HfO_2$ as alternative high-κ gate dielectrics in replacing $SiO_2$ for nano CMOS.

- Giant magnetic moment in Co doped $HfO_2$ as reported recently.



# HR-TEM Images of High-T and Low-T Grown Films

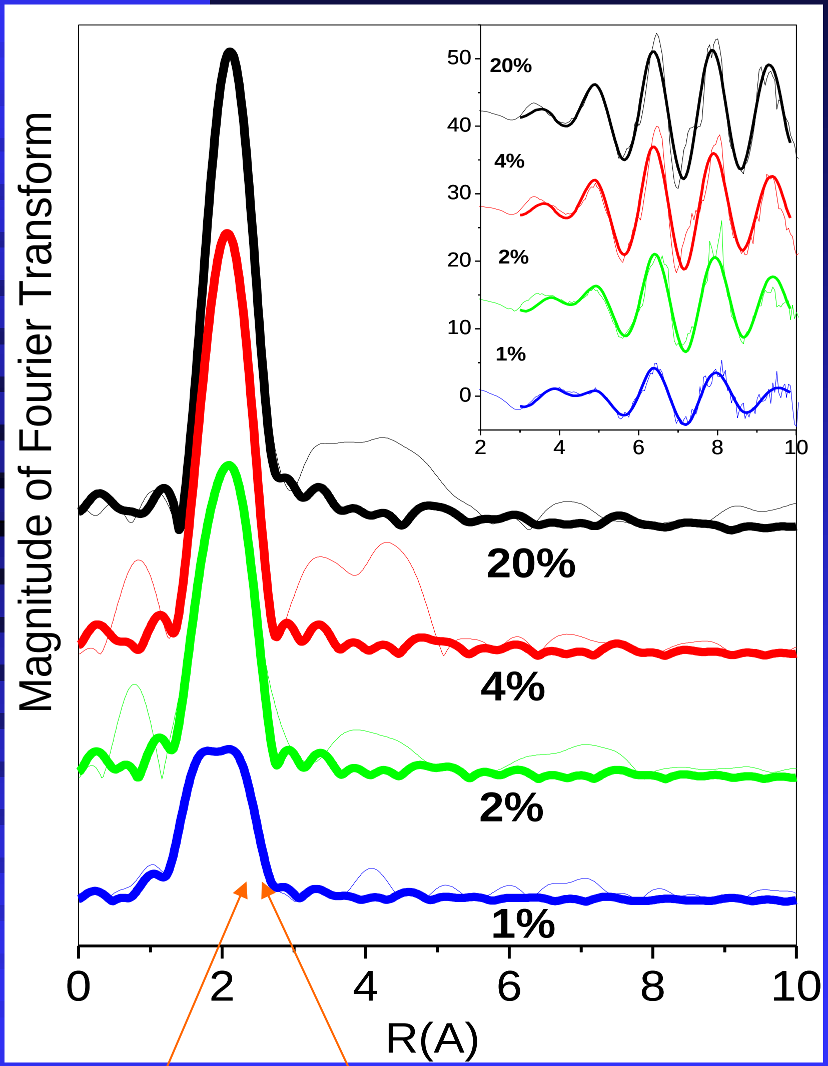


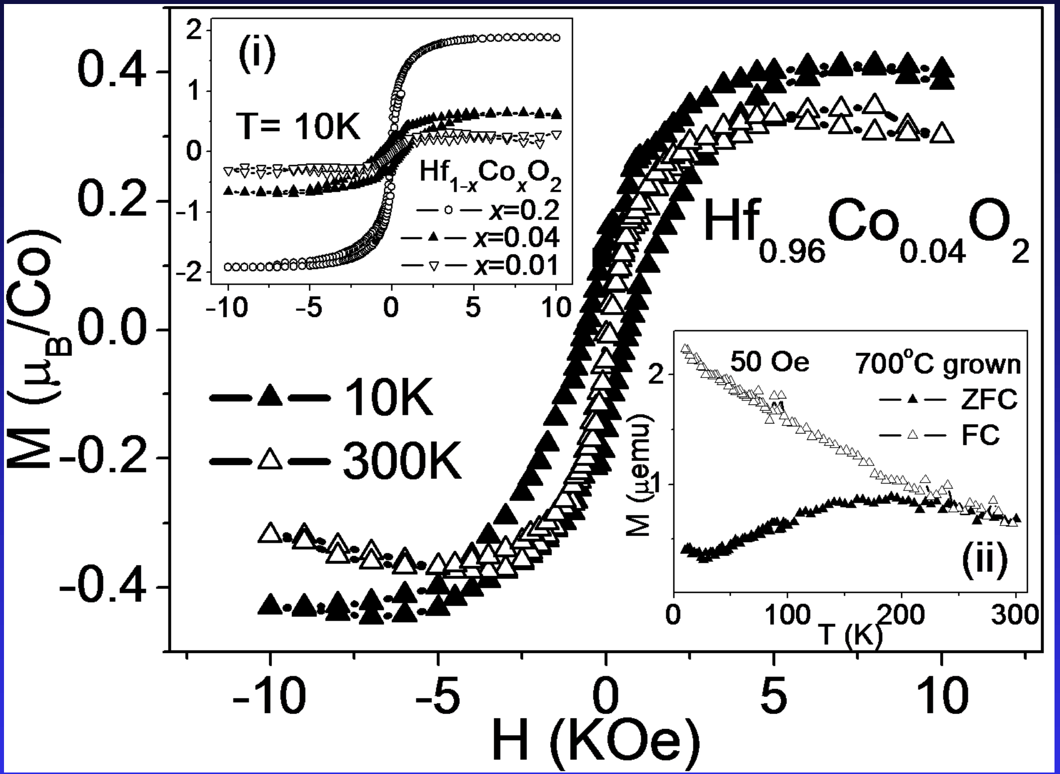

**High-T (700˚C) grown film**
**Monoclinic phase**

**Low-T (100˚C) grown,**
**Polycrstalline film**

# EXAFS and Magnetic Characterization of High-T (700℃) Grown Films

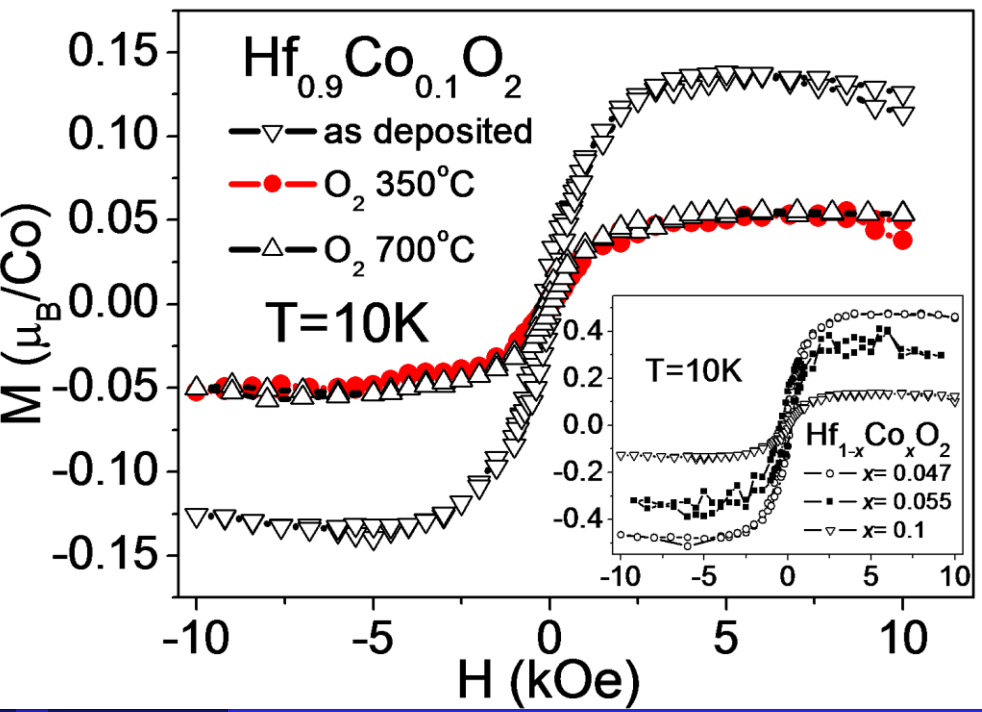



**1st O shell + 2nd Co shell**
**2.04A 2.49A**




- **EXAFS** of the high-T grown samples showed a progressive formation of Co clusters in the film (Co = 1-20 at.%).
- **Superparramagnetic** temperature dependence.
- Saturation moment increases with increasing Co doping concentration.

# Magnetic Property of Low-T Grown Films




| Substrate Temperature (℃) | 40~100 | 40~100 | 40~100 |
|---|---|---|---|
| Doping concentration (at.%) | 4.7 | 5.5 | 10 |
| Ms at 10K ($\mu_B$/Co) | 0.47 | 0.36 | 0.13 |
| Ms at 300K($\mu_B$/Co) | 0.43 | 0.29 | 0.1 |

- Ferromagnetic behavior was observed at both 10K and 300K.
- The magnetic moment decreases with increasing Co doping due to enhanced dopant dopant associations.
- The magnetic properties are stable after annealing in $O_2$ at 350°C.
- Correlation between saturation magnetization with concentrations of **oxygen vacancies**

# F-center Exchange Mechanism:

--An electron orbital created by an **oxygen vacancy** with trapped electrons is expected to correlate with magnetic spins dispersed inside the oxides.

# Impurity-band Exchange Model :

--The hydrogenic orbital formed by **donor defect (like oxygen vacancy)** associated with an electron overlaps to create delocalized impurity bands.

-- If the donor concentration is large enough and interacts with the magnetic cations with their 3d orbitals to form **bound magnetic polarons** leading to ferromagnetism.

**$\gamma^3\delta_p \approx 4.3$, where $\gamma = \varepsilon(m/m^*)$**

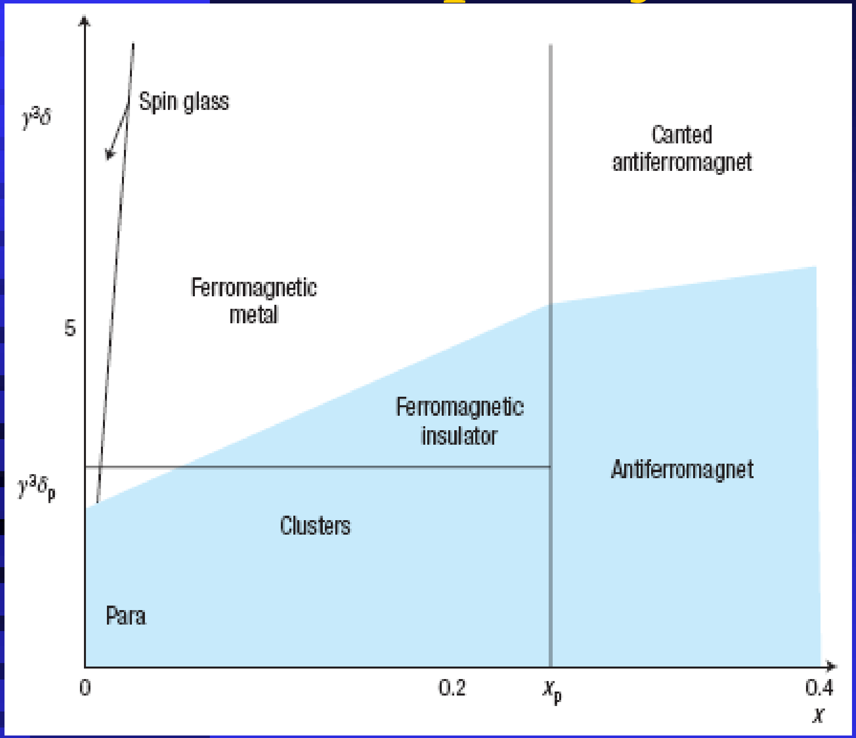
**$\delta_p$ : polaron percolation threshold**

**$x_p$ : cation percolation threshold**

**$\gamma_H$ : hydrogenic radius**

M. Coey et al, *Nature Materials*, 2005.

# Theoretical Analysis Using Impurity Band Exchange Model




| Material | ε | $m^*/m$ | γ | $\gamma_H$ (nm) | $\delta_P$ ($10^{-6}$) |
|---|---|---|---|---|---|
| ZnO | 4 | 0.28 | 14 | 0.76 | 1500 |
| $TiO_2$ | 9 | 1 | 9 | 0.48 | 5900 |
| $SnO_2$ | 3.9 | 0.24 | 16 | 0.86 | 1000 |
| $HfO_2$ | 15 | 0.1 | 150 | 7.95 | 1.27 |
| $Al_2O_3$ | 9 | 0.23 | 39 | 2.07 | 72 |

$\delta_p$ : Polaron percolation threshold
$X_p$ : Cation percolation threshold
$\gamma_H$ : Hydrogenic orbital radius

- $\delta_p$ and $\boldsymbol{x_p}$ are two landmarks on magnetic phase diagram.
- Ferromagnetism occurs when $\boldsymbol{\delta > \delta_p}$ and $\boldsymbol{x < x_p}$.
- $\boldsymbol{\delta_p}$ of **$HfO_2$** based DMO is about **$1.27\times10^{-6}$ - $8.15\times10^{-5}$**
- Appearance of ferromagnetic insulator behavior in **$HfO_2$** is more likely than **ZnO, $TiO_2$** and **$SnO_2$** .
- Will try $Y_2O_3$, $ZrO_2$, and $Al_2O_3$ etc.

# Major Research Topics

- Novel MBE template approach for ALD growth
- Enhancement of κ in the new phase through epitaxy
- Fundamental study by IETS for detections of phonons and defects in high κ dielectrics
- Room temperature ferromagnetism in cluster free, Co doped $HfO_2$ films