Nanoelectronics Beyond Si: Challenges and Opportunities

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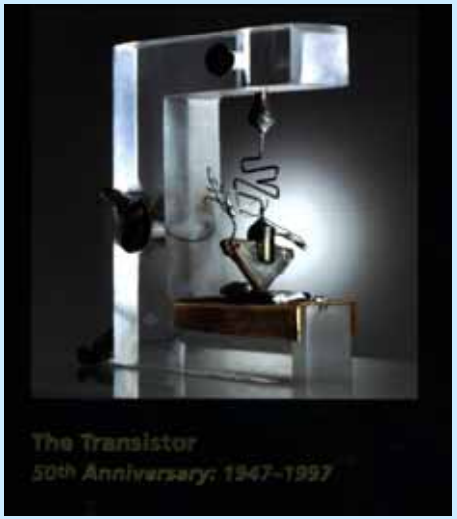
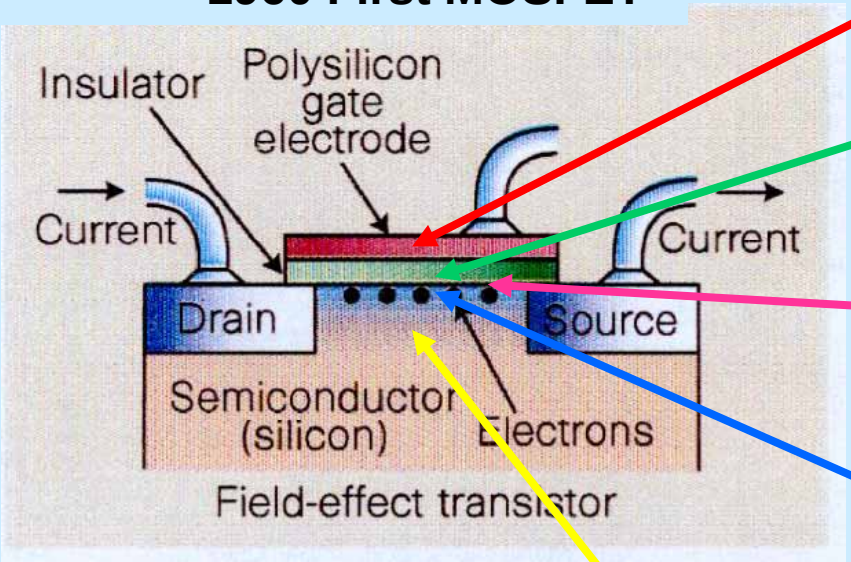
Si CMOS Device Scaling – Beyond 22 nm node
High κ, Metal gates, and High mobility channel

1947 First Transistor



1960 First MOSFET



Metal Gate

High κ gate dielectric

Oxide/semiconductor interface

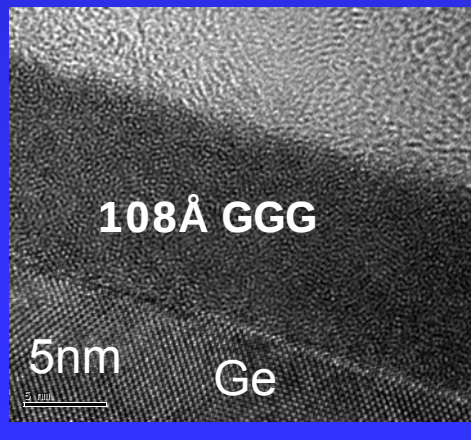
High mobility channel

Integration of Ge, III-V with Si

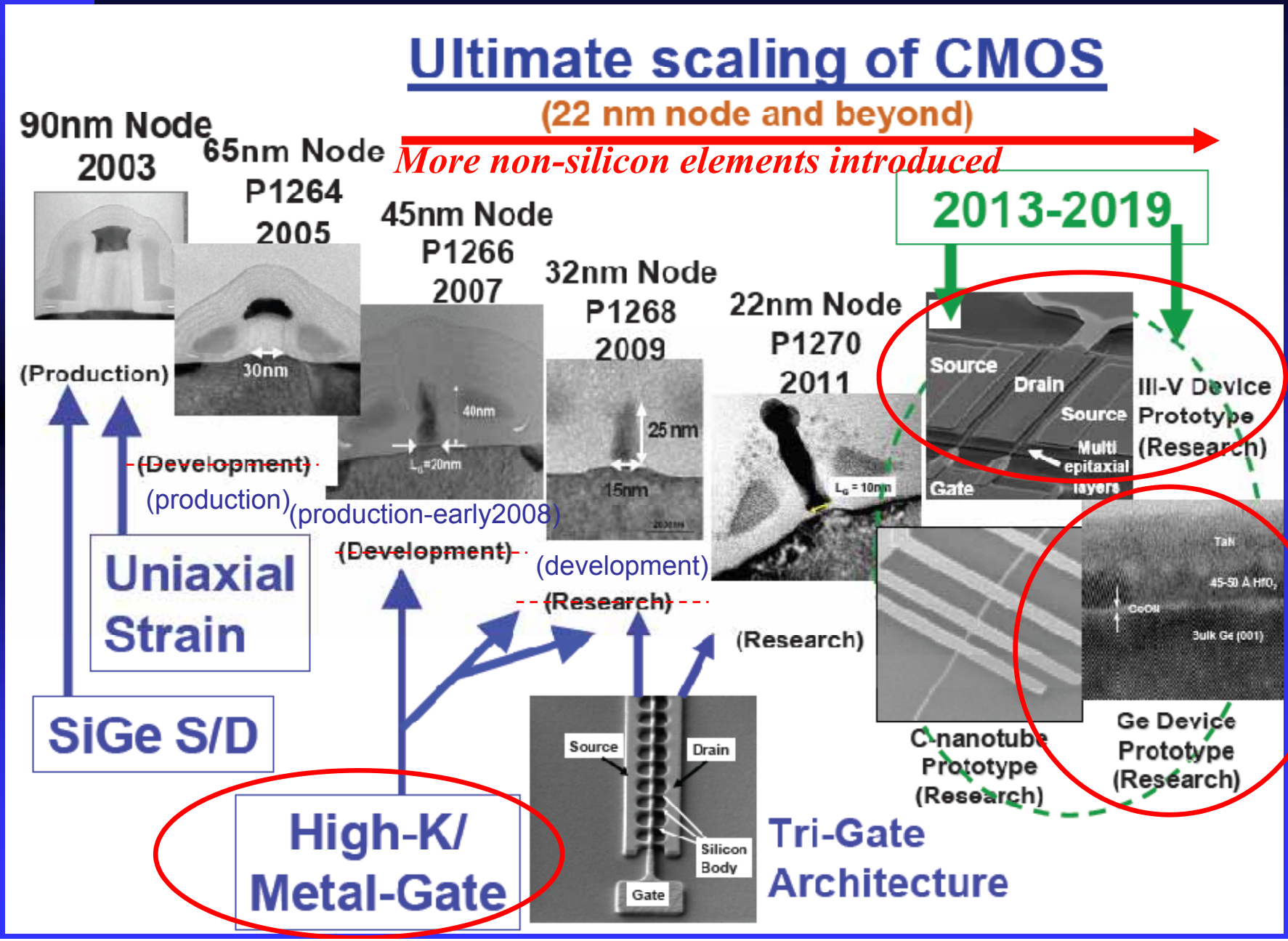
Moore's Law: The number of transistors per square inch doubles every 18 months

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

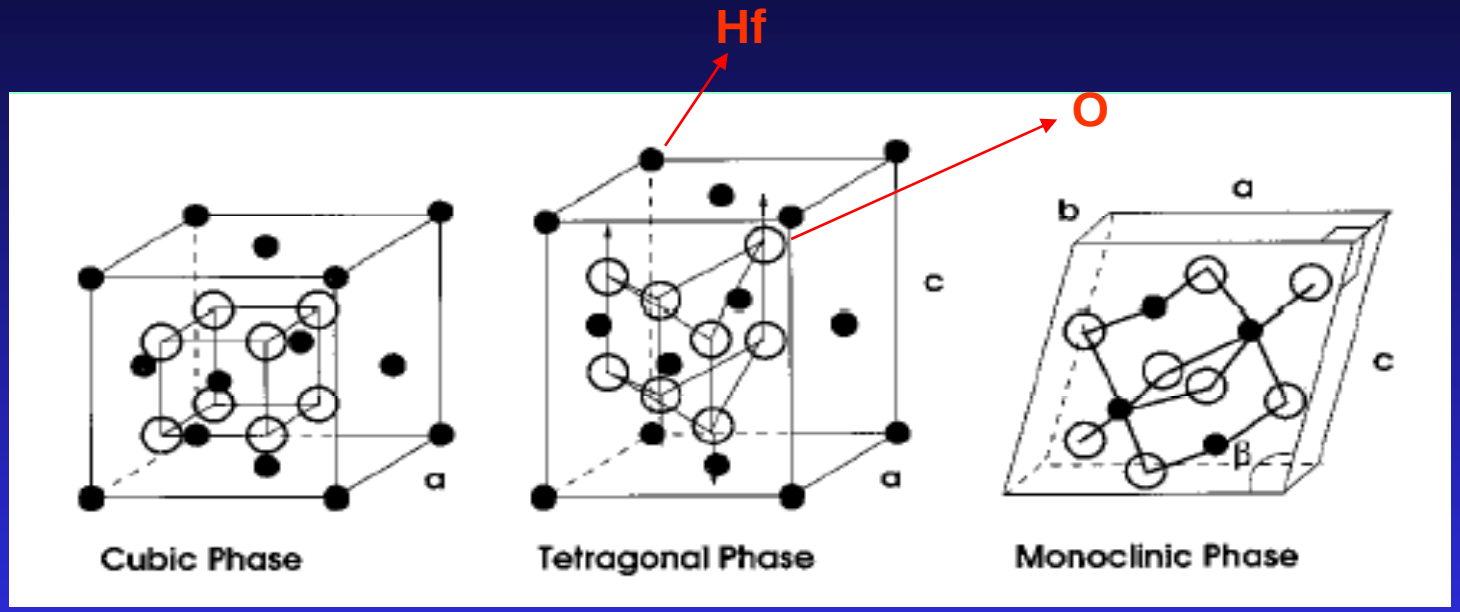
- Enhancement of κ in the new phase through epitaxy
- Fundamental study by IETS for detections of phonons and defects in high κ dielectrics
- Room temperature ferromagnetism in cluster free, Co doped HfO_2 films

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



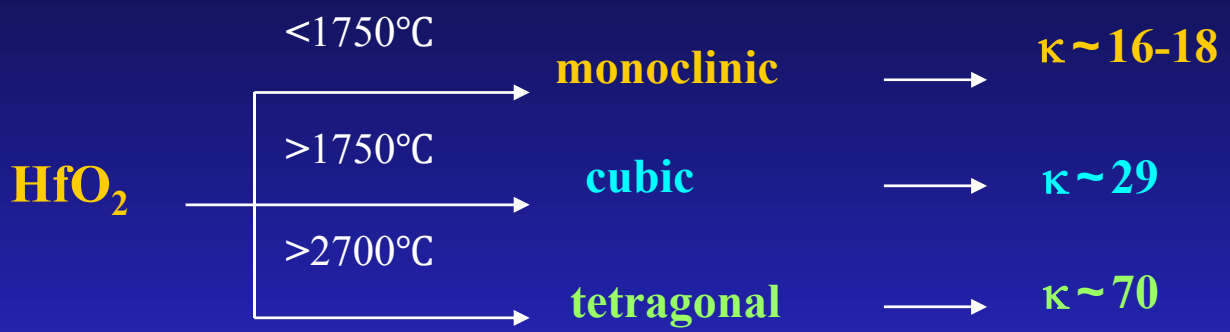
Dielectric constants	*29*	*70*	*16 **
Stable phase temperature	*>2700°C*	*>1750°C*	*<1750°C*

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

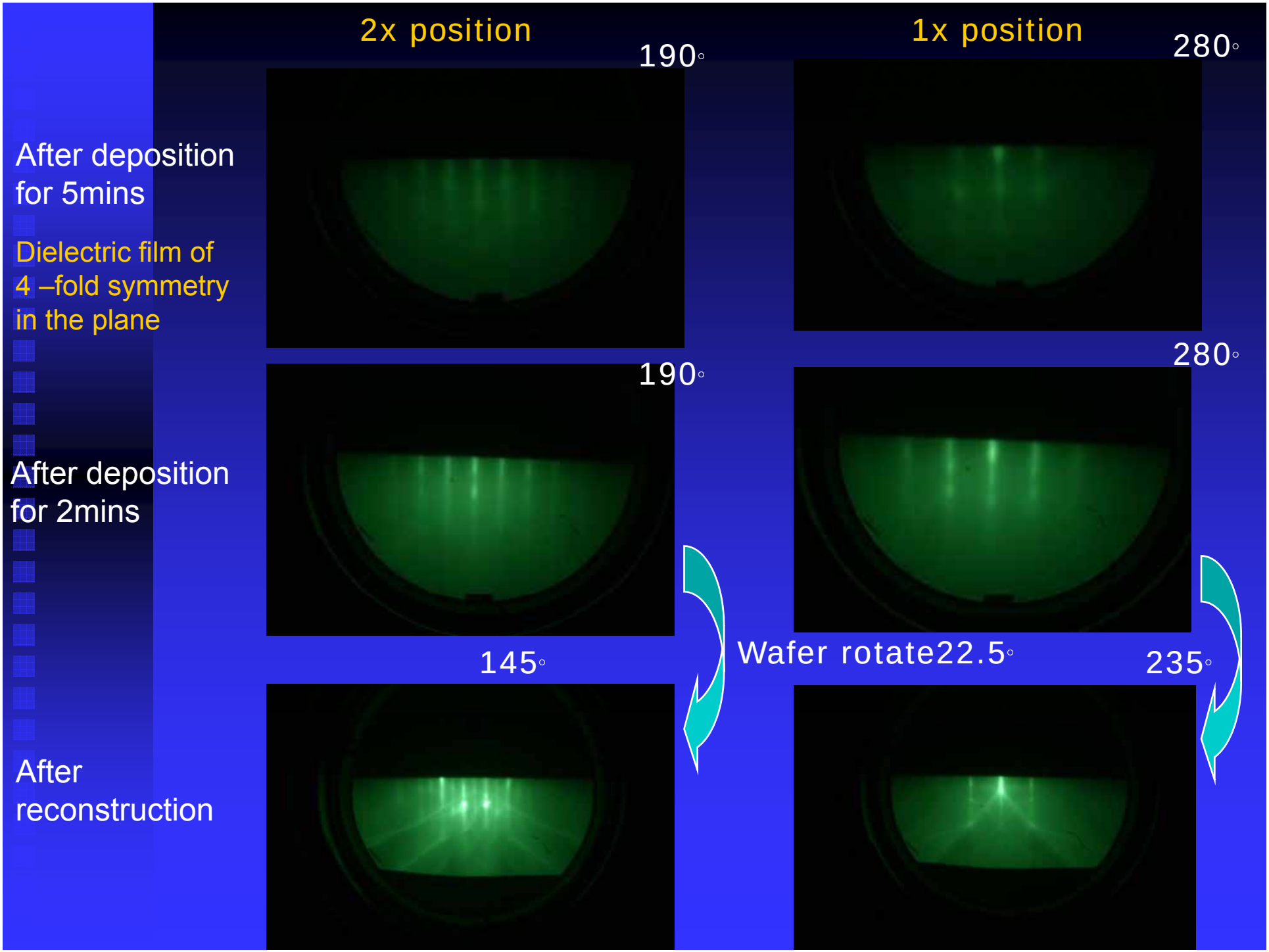
* Xinyuan Zhao and David Vanderbrit, P.R.B. 65, 233106, (2002).

Permittivity Increase of Yttrium-doped HfO_2 Through Structural Phase Transformation

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



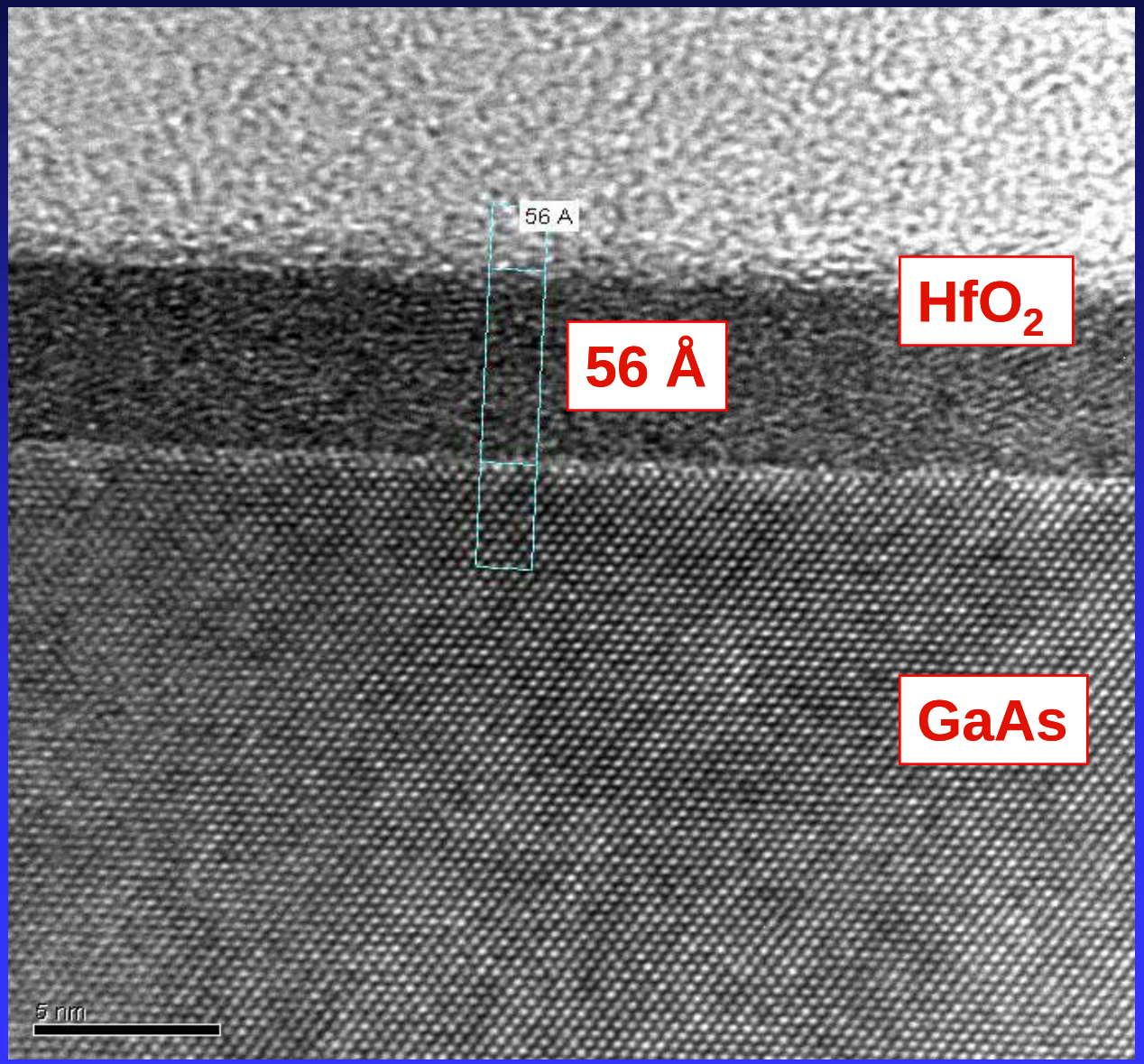
- Yttrium serves effectively as a dopant to induce a phase transformation from the ***monoclinic*** to the ***cubic*** phase even at 600 ℃.
- Yttrium-doped HfO_2 films show higher permittivity than undoped HfO_2, and the permittivity as high as 27 is obtained by 4 at. % yttrium doping.
- The permittivity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


2x position
1x position
190°
280°
After deposition for 5mins
Dielectric film of 4 –fold symmetry in the plane
190°
280°
After deposition for 2mins
Wafer rotate22.5°
145°
235°
After reconstruction

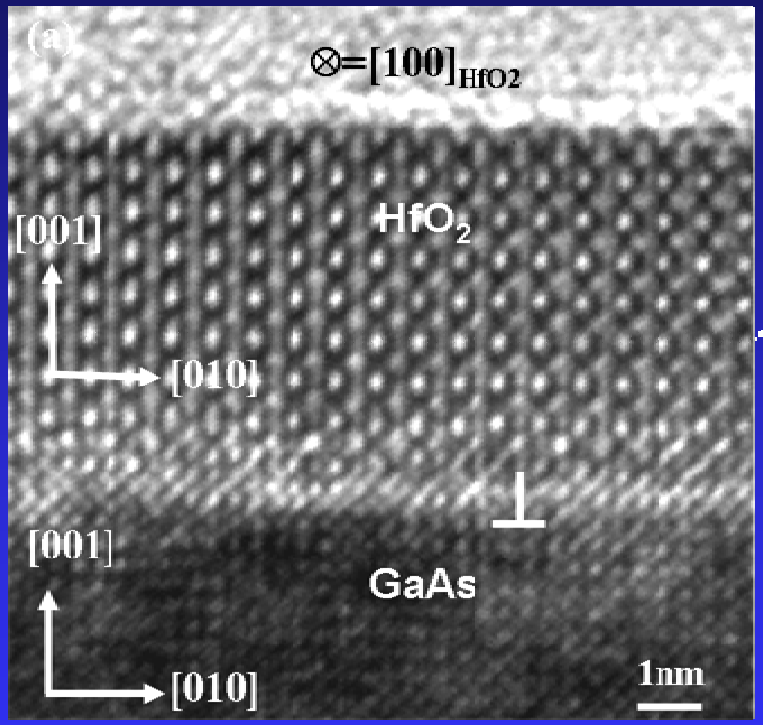
HRTEM of Low Temp Growth

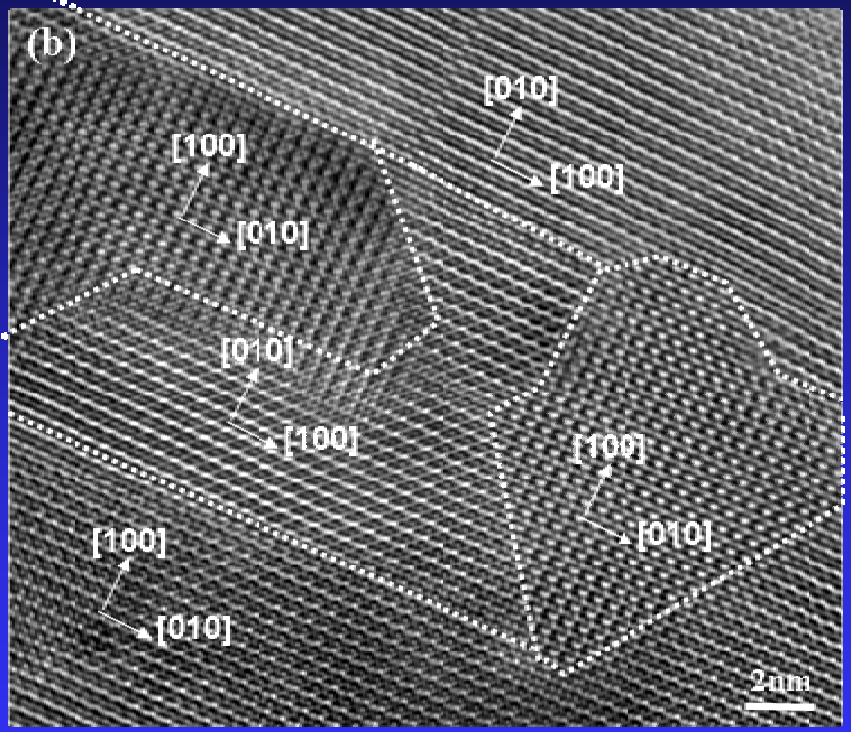
Amorphous HfO_2 on GaAs (100)

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)

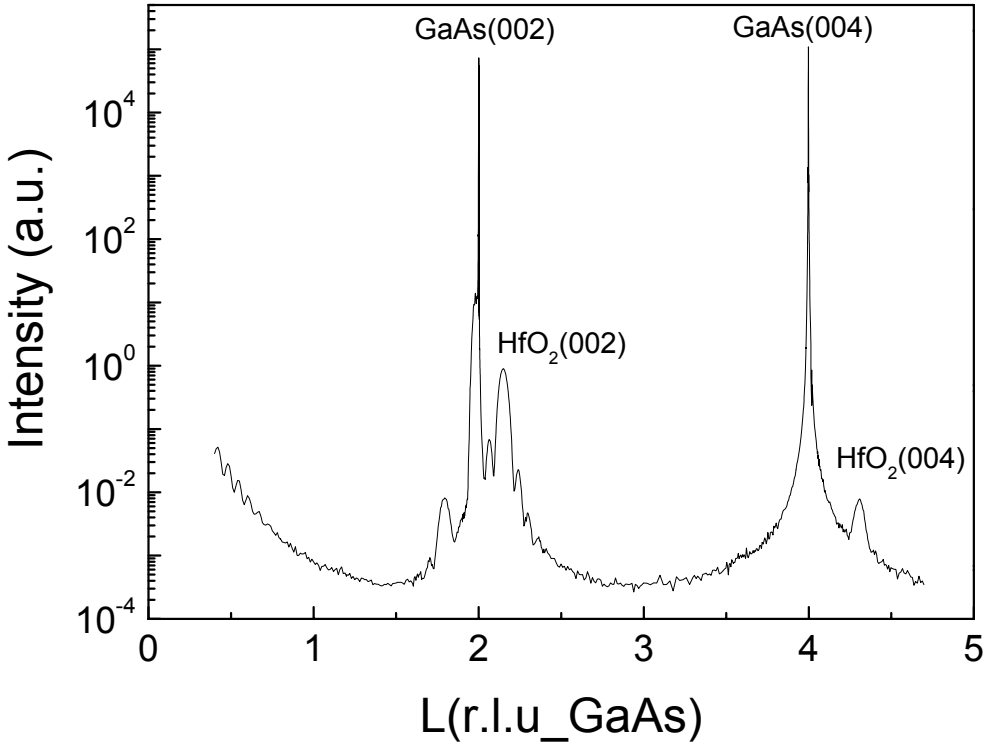


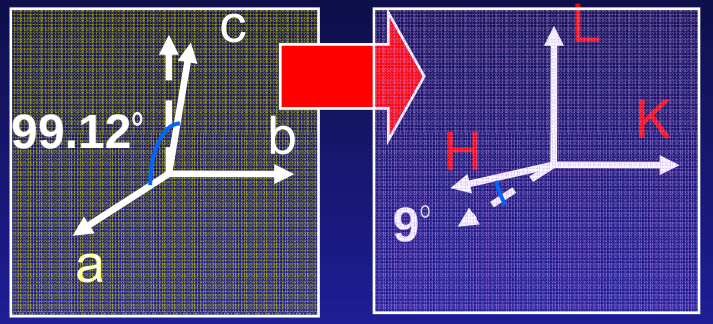


An abrupt transition from GaAs to HfO_2 and no interfacial layer

Coexistence of four monoclinic domains rotated by 90º.

X-ray Diffraction of Epitaxial HfO_2 Films Recrystalized on GaAs





R space

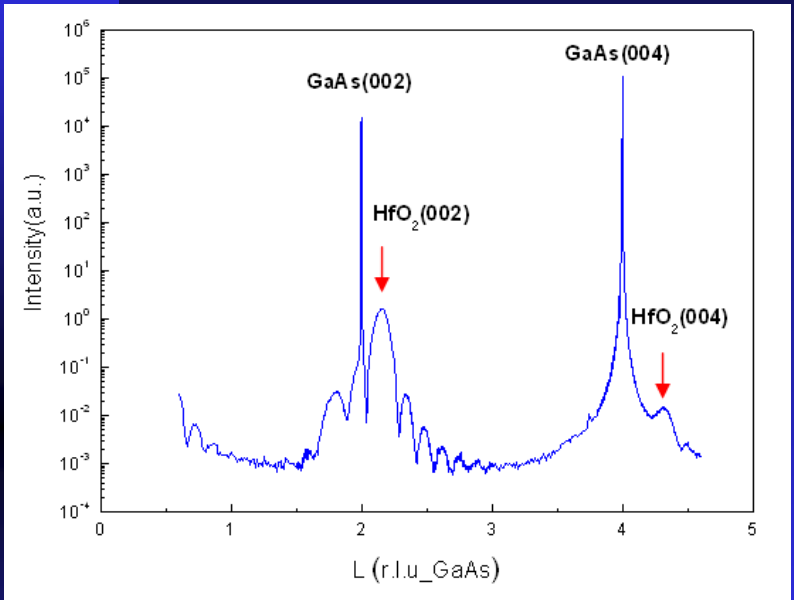
K space

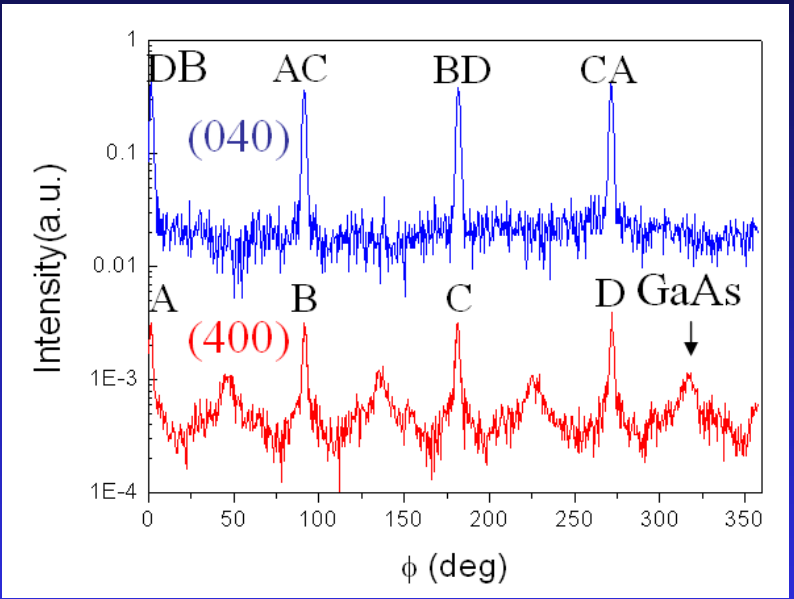
--- Monoclinic HfO_2 in R space and K space
--- Forming four degenerate domains about the surface normal

With C. H. Hsu of NSRRC

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

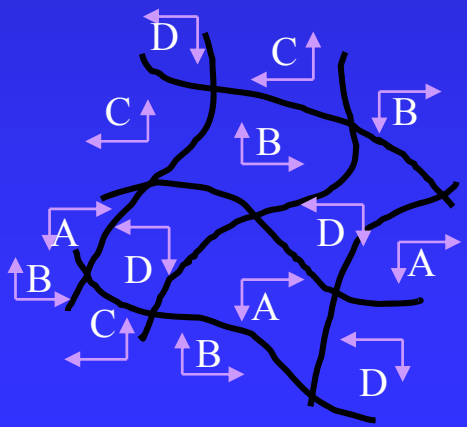
The Structure of HfO_2 Grown on GaAs(001)



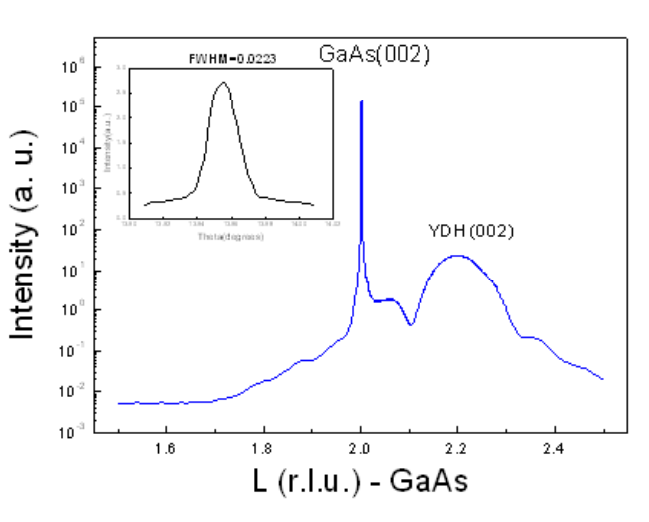


monoclinic phase
a=5.116A, b=5.172A, c=5.295A, β=99.18A

Coexistence of 4 domains rotated 90º from each other



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



Surface normal scan

Find the peaks:

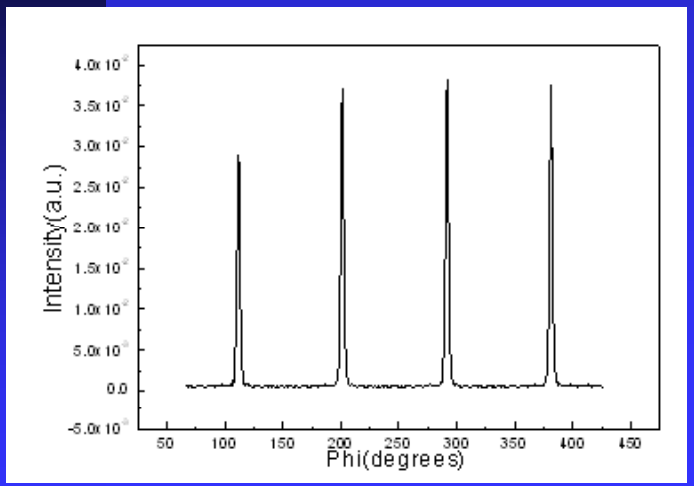
- (022)(400)(200)(311)(31-1)(113)(420)(133)(20-2)
- All peaks of film match the JCPDS of cubic phase HfO_2
- Use the d-spacing formula to fit the lattice parameters

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

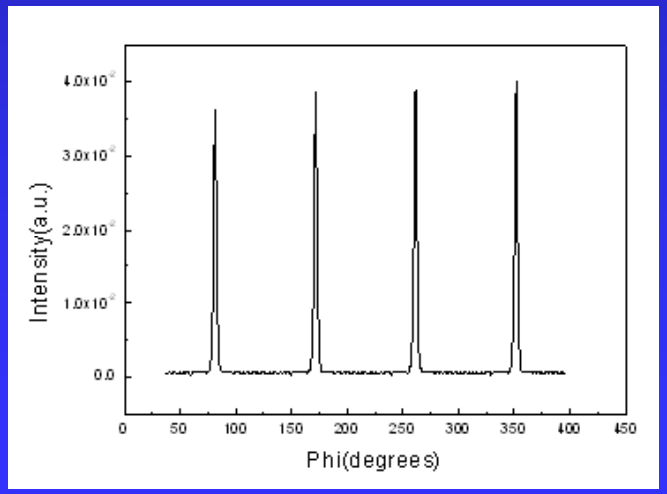
Cubic phase

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

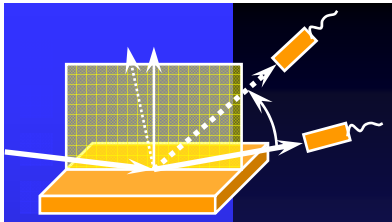
α=90,β=90, γ=90



(400)Phi scan

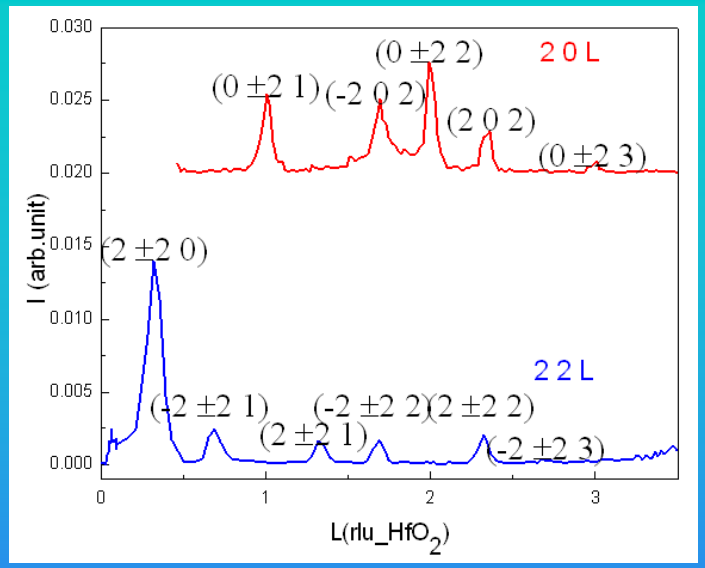


(040)Phi scan

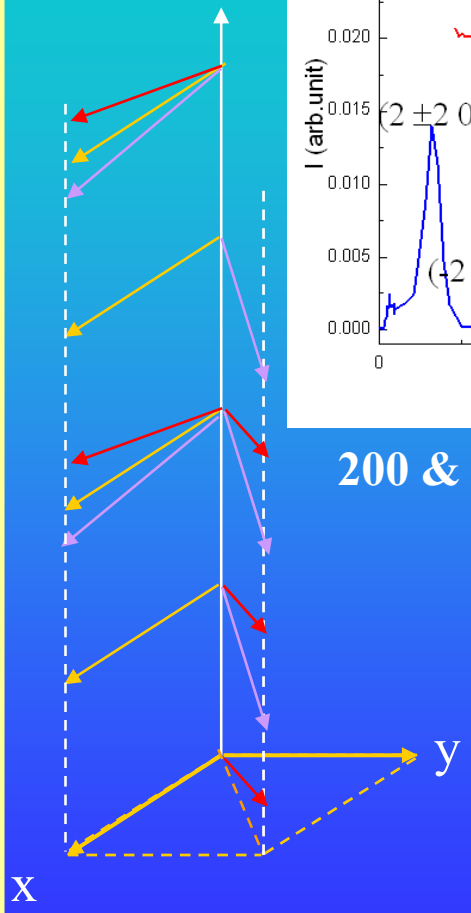


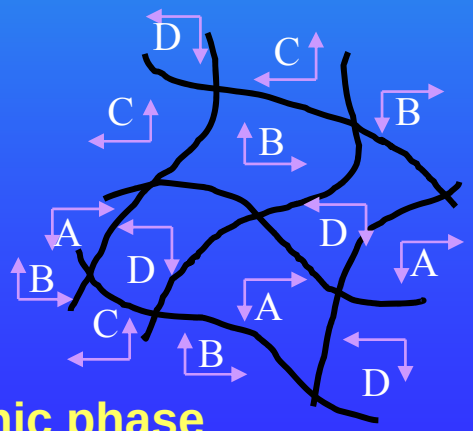
Comparison between Monoclinic phase and Cubic phase of HfO_2

Without doping Y_2O_3



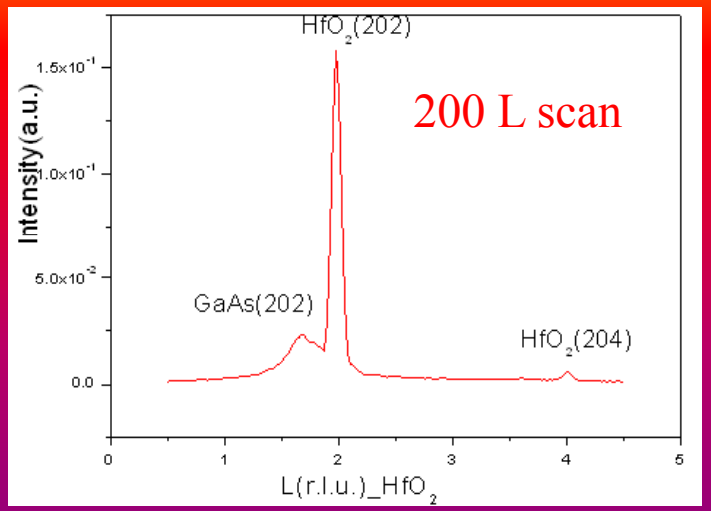
200 & 220 L scan

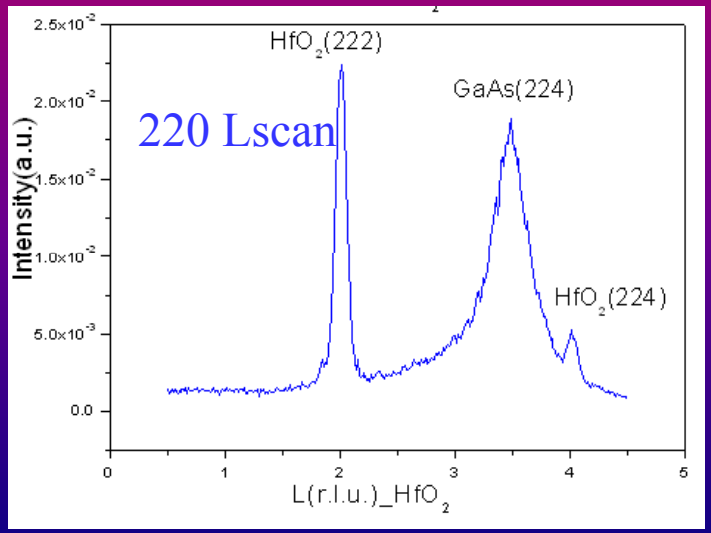




Monoclinic phase

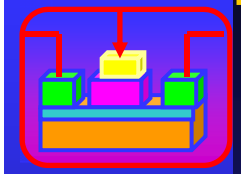
With doping Y_2O_3

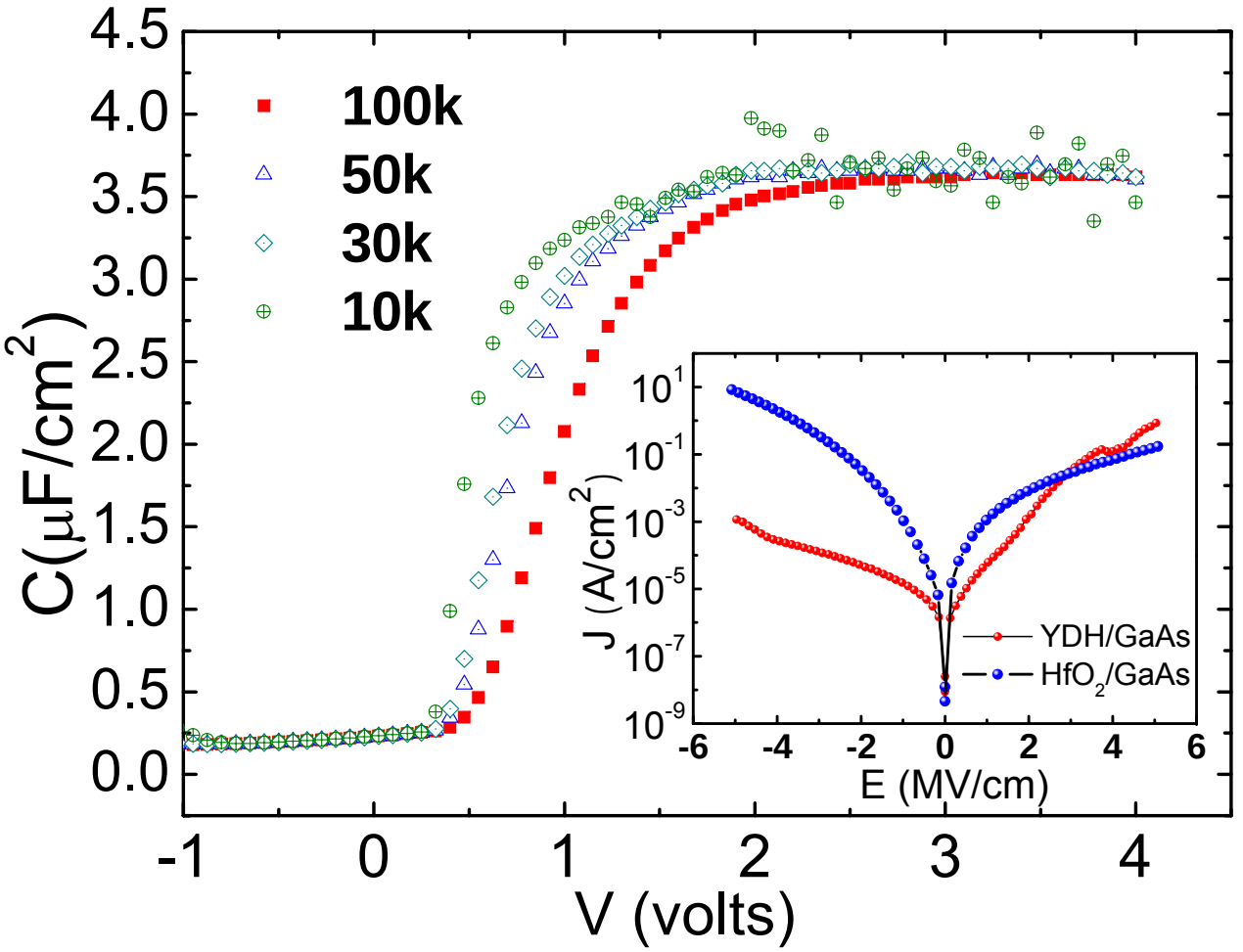




Cubic phase

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





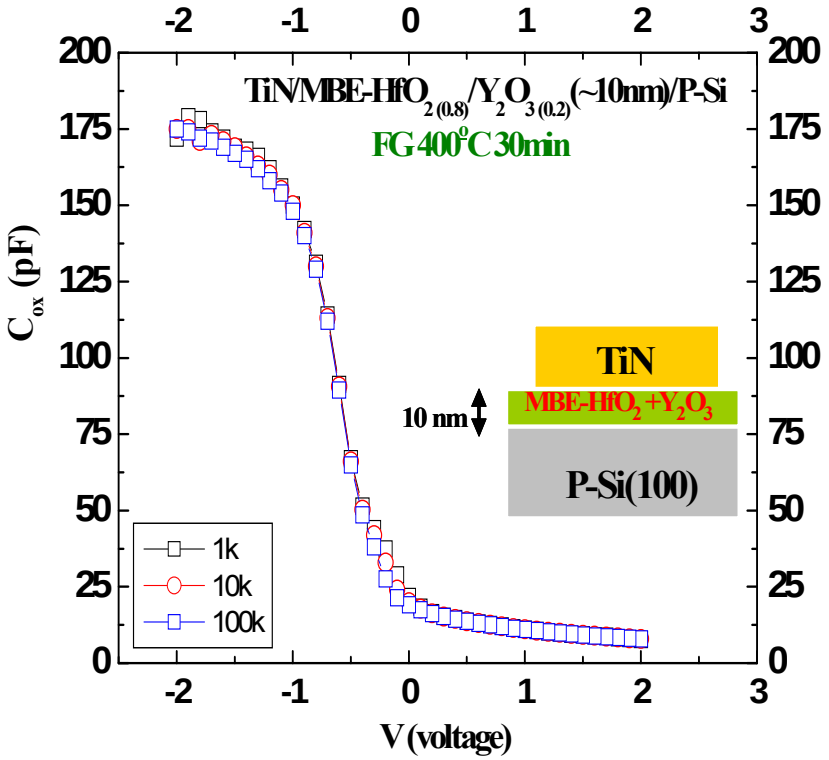
T=110A κ=32

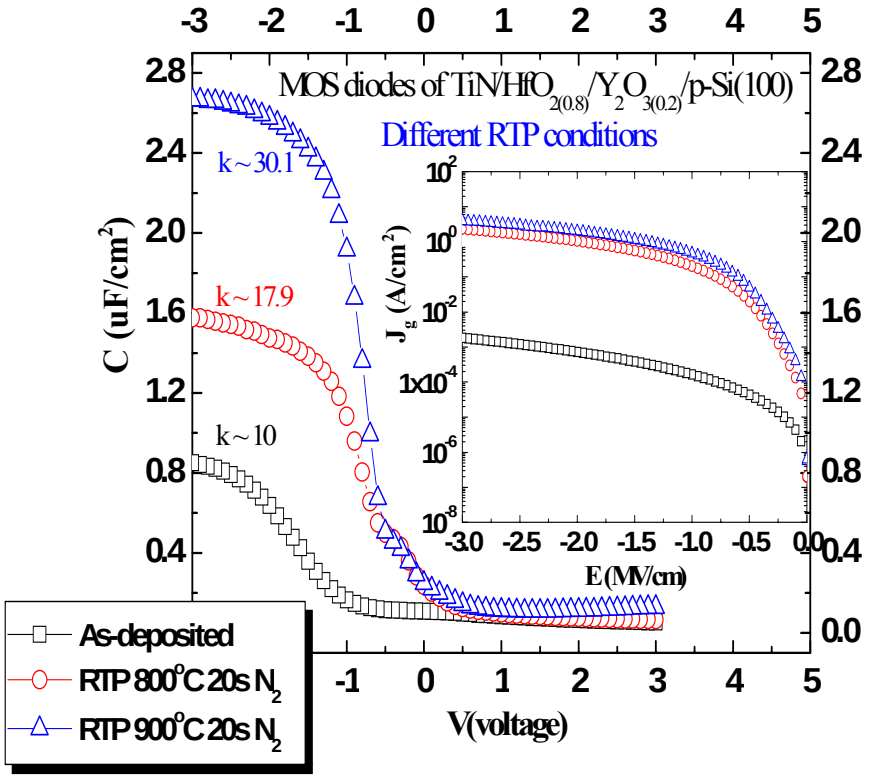
Y_2O_3+HfO_2

GaAs(001)

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

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

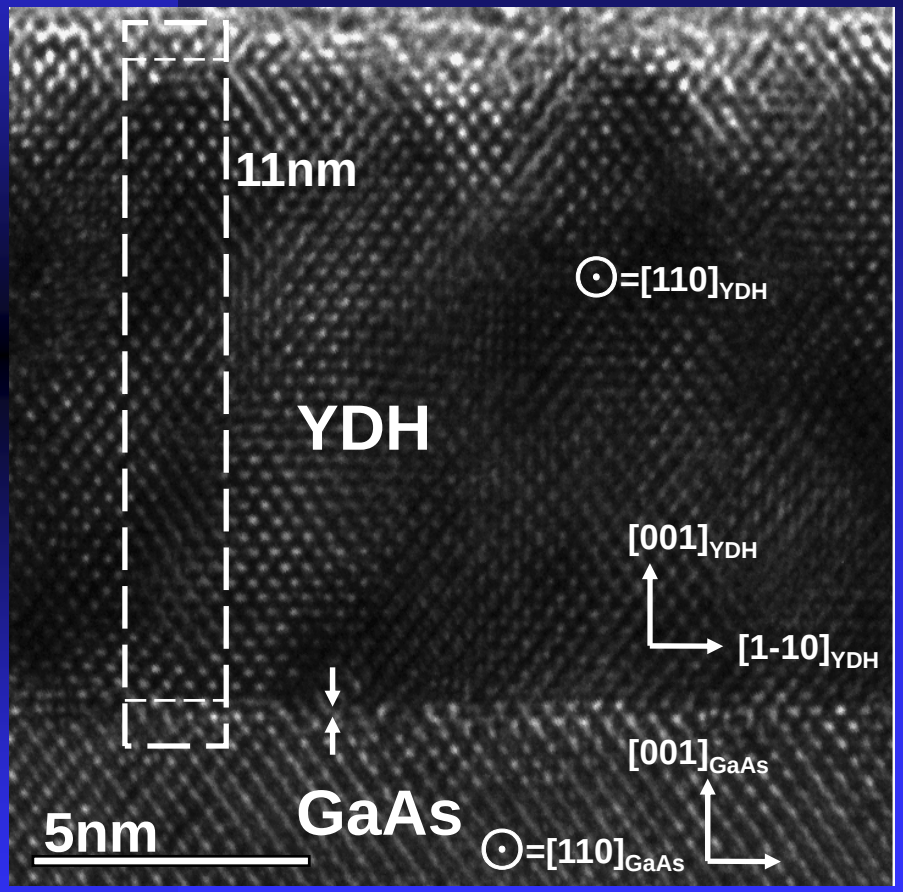




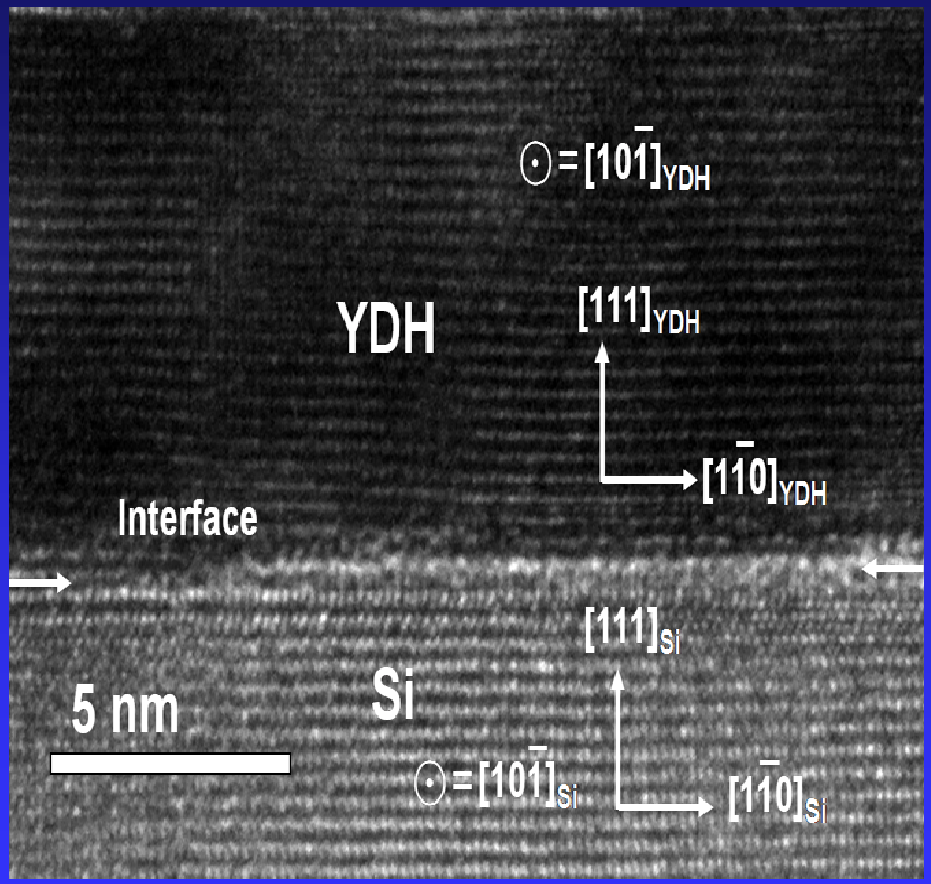
Increase of κ from 15 to over 30 in cubic phase !

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

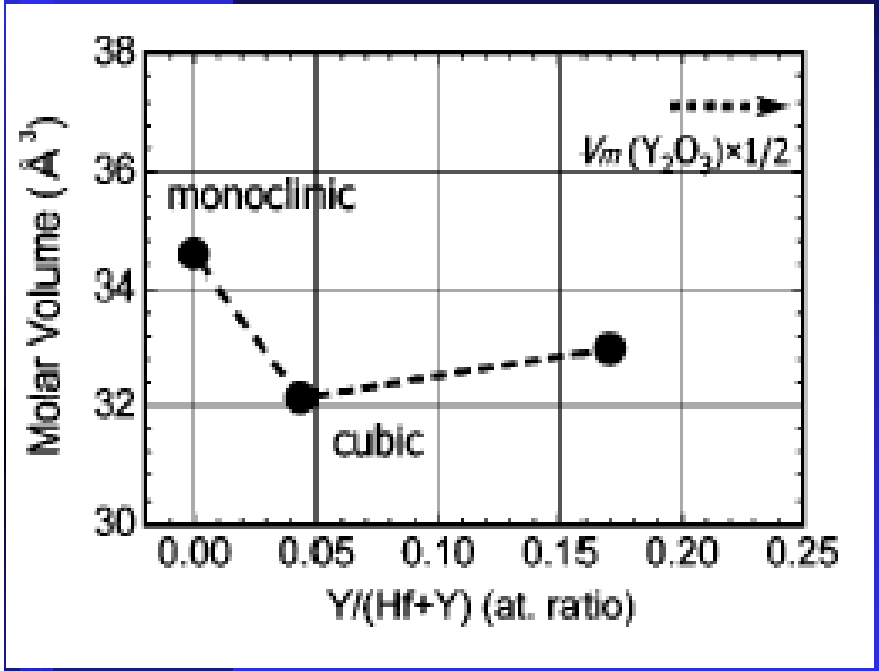


HRTEM image of yttrium-doped HfO_2 films 11 nm thick on GaAs (001).



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 κ Dielectrics

But what is inside of high κ ?

Electrical characterization / optimization

-- Good News !!

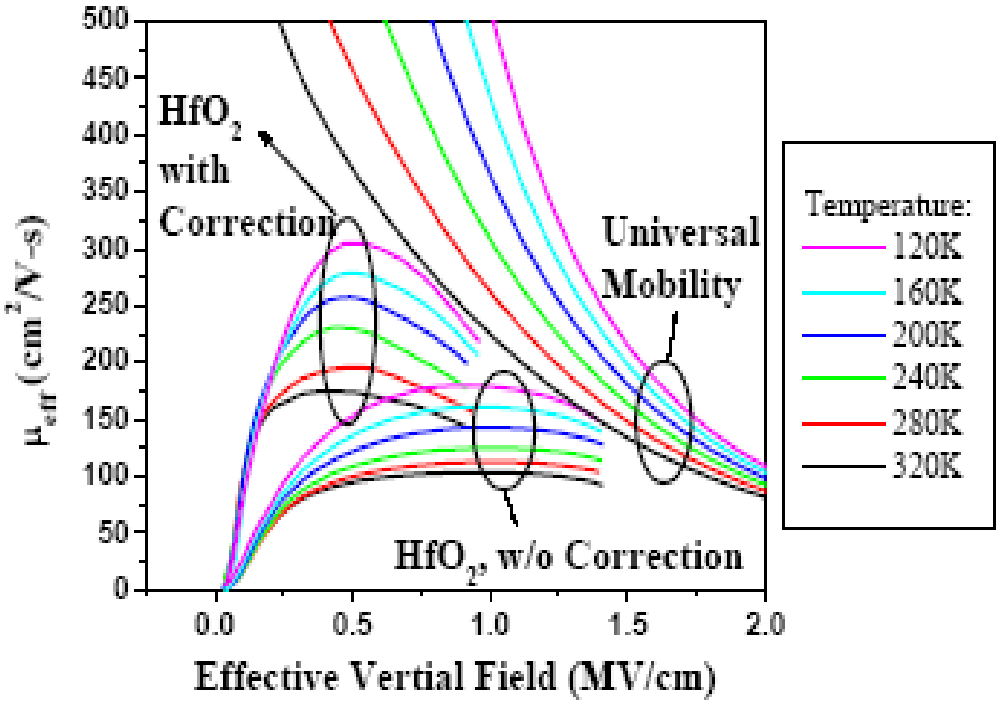
- **Low electrical leakage is common .**
- **Have Attained an EOT under 1.0-1.4 nm .**

-- 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



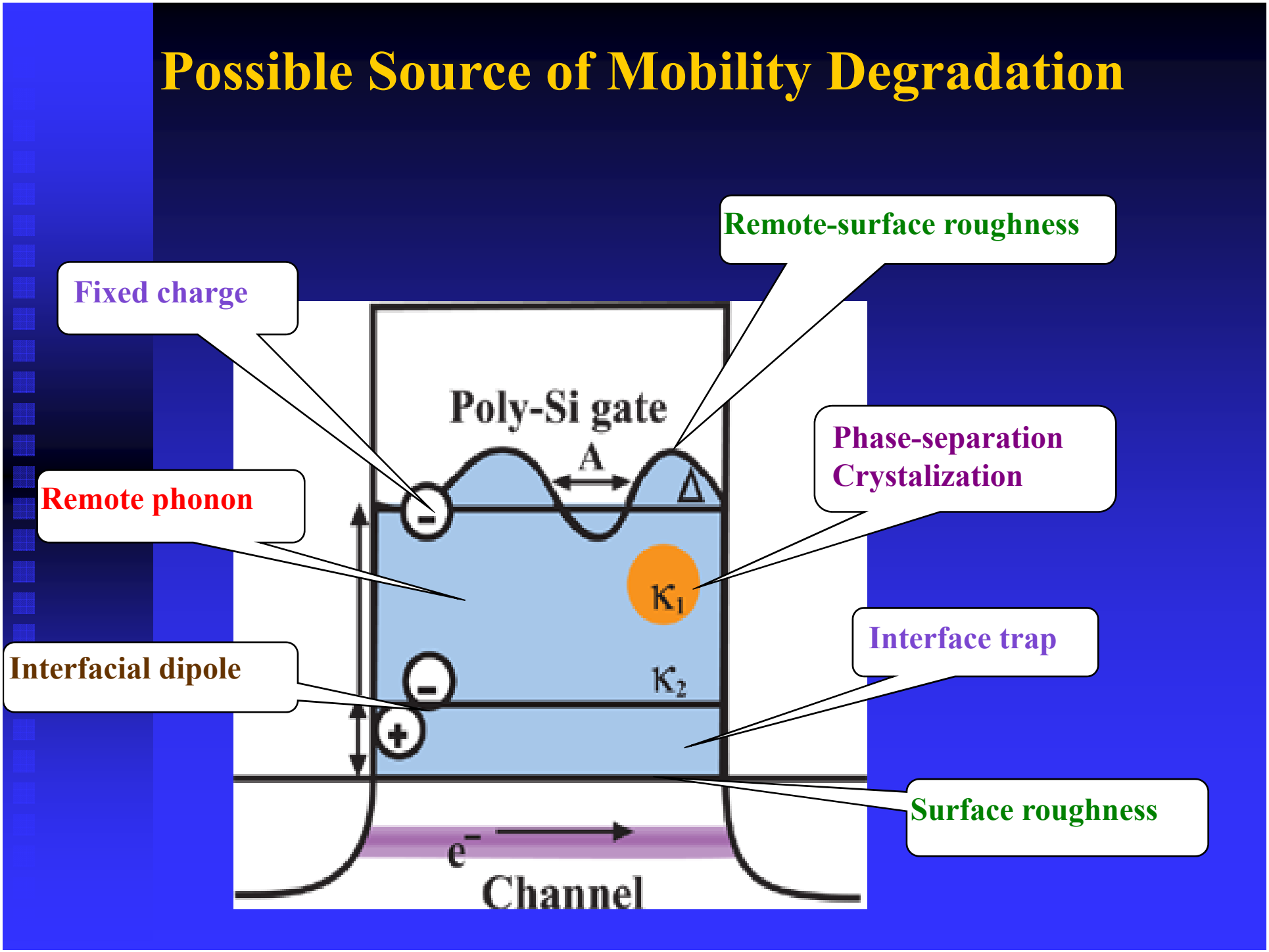
Correction from the charge trapping effect

- 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).

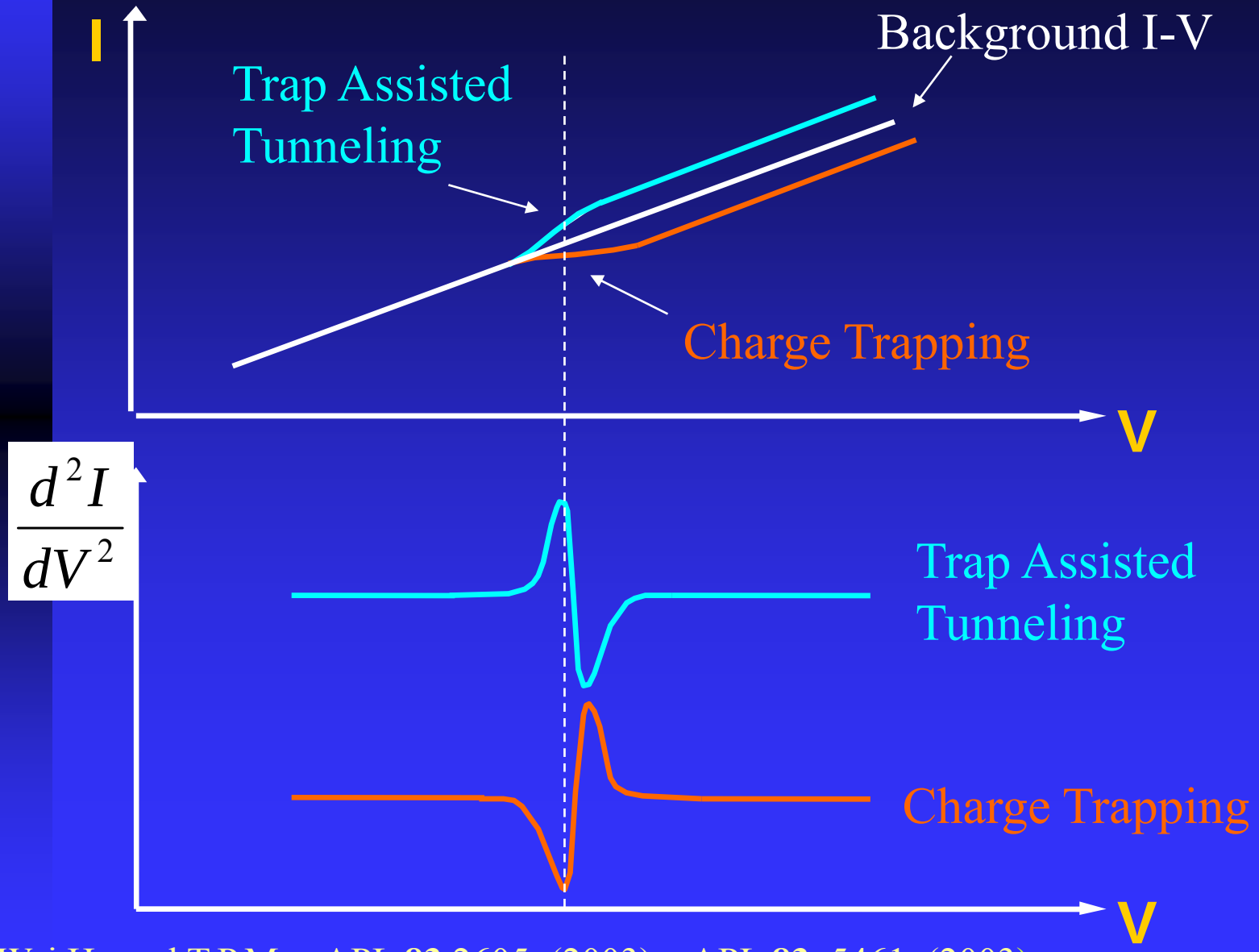
Possible Source of Mobility Degradation



Interactions Detectable by IETS

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

Trap-Related Signatures in IETS

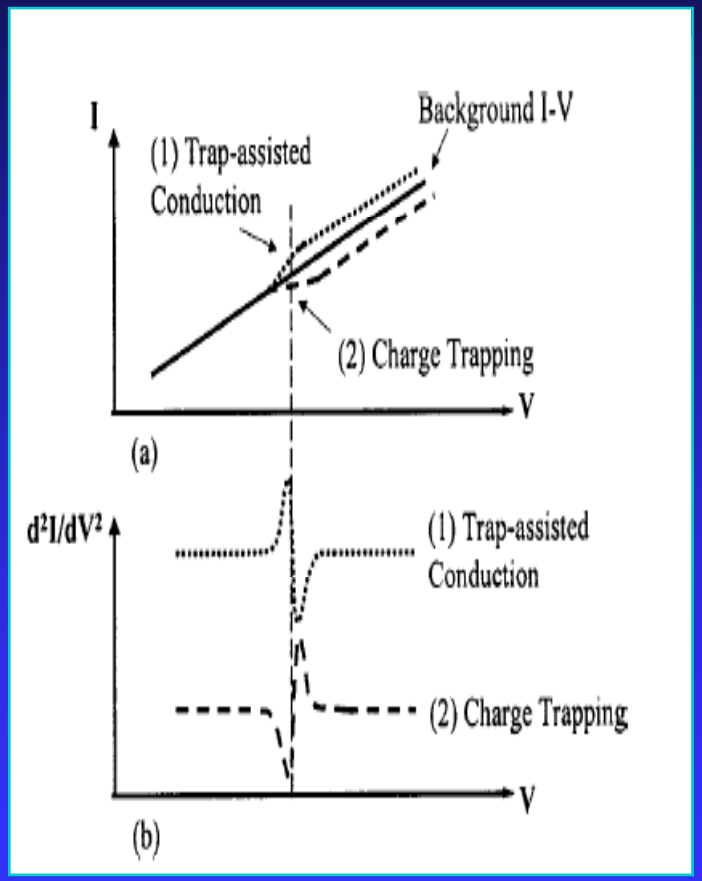


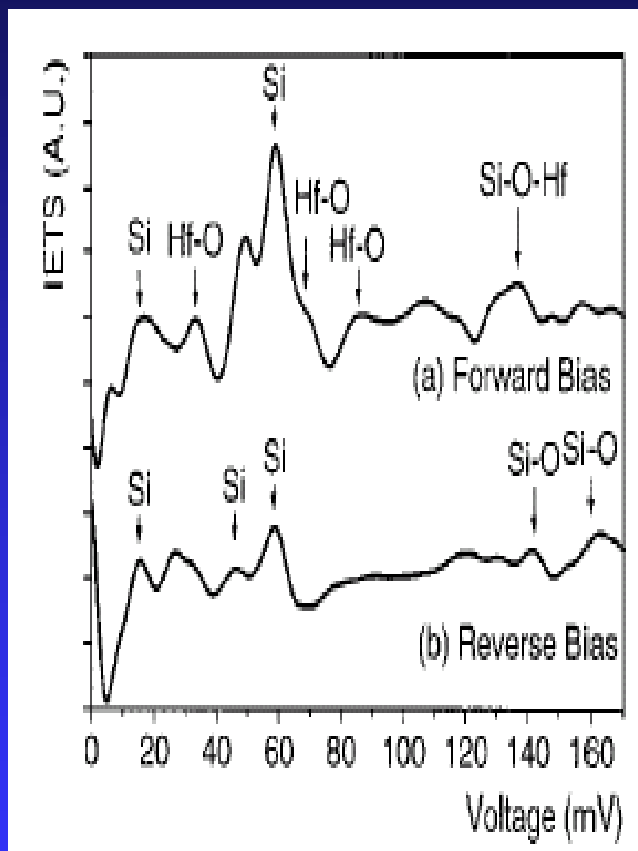
Wei He and T.P.Ma, APL **83**,2605, (2003) ; APL **83**, 5461, (2003).

Inelastic Electron Tunneling Spectroscopy (IETS)

Charge trapping will cause shift in the threshold voltage.

Trap-assisted conduction will cause increased leakage current.

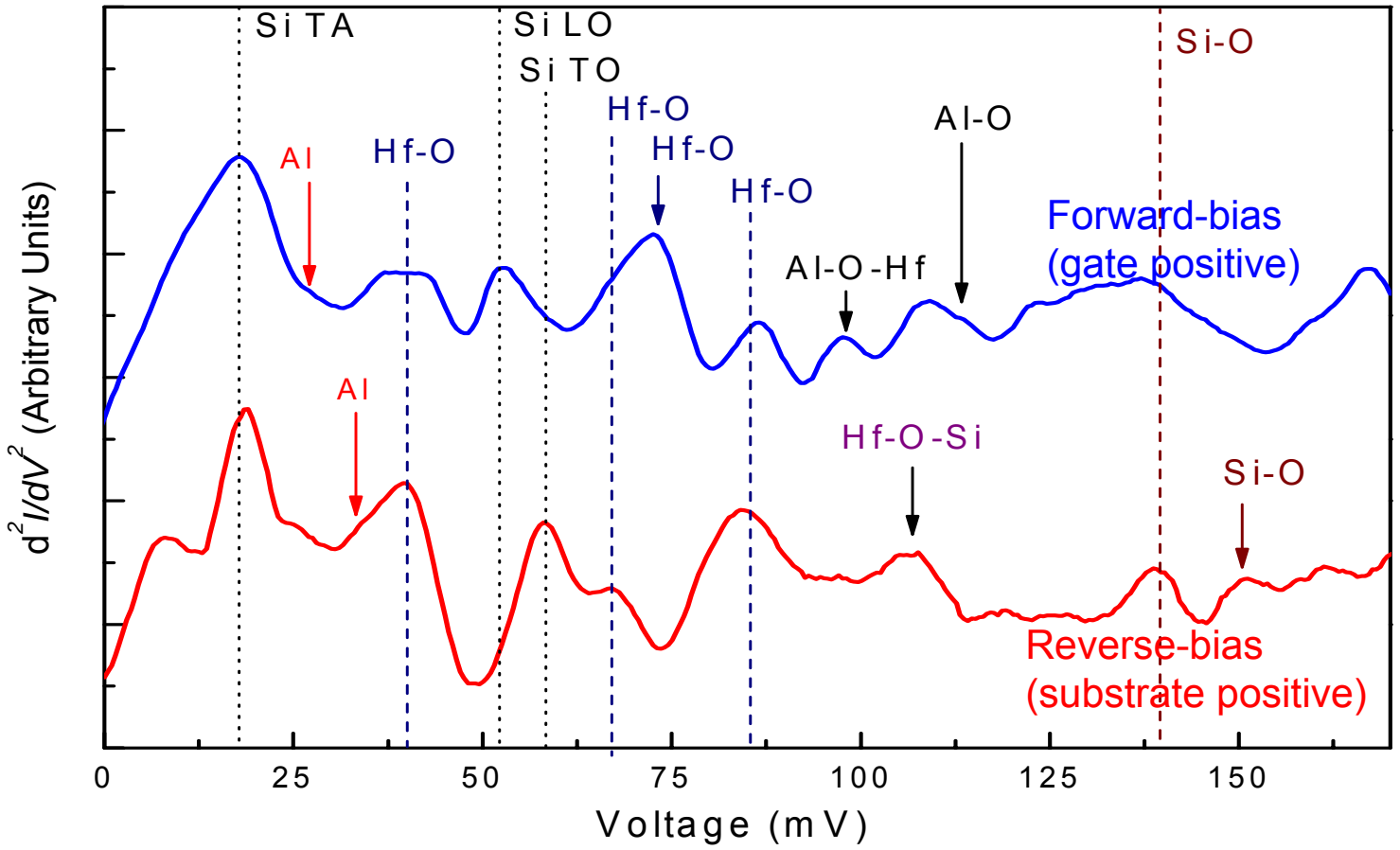




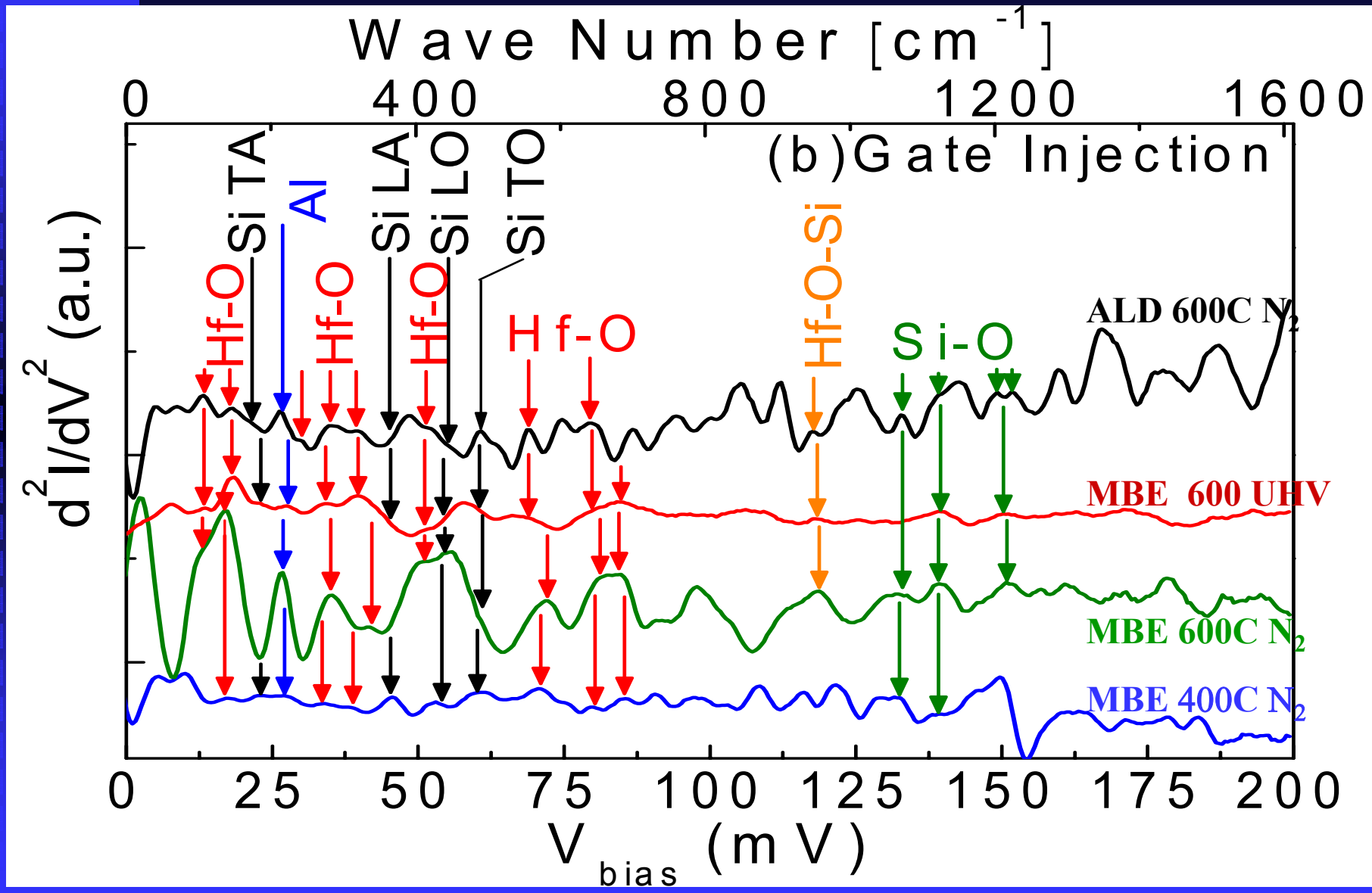
Wei He and T.P.Ma, APL **83**,2605, (2003) ; APL **83**, 5461, (2003)

IET spectrum of Al/HfO_2/Si MOS structure

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

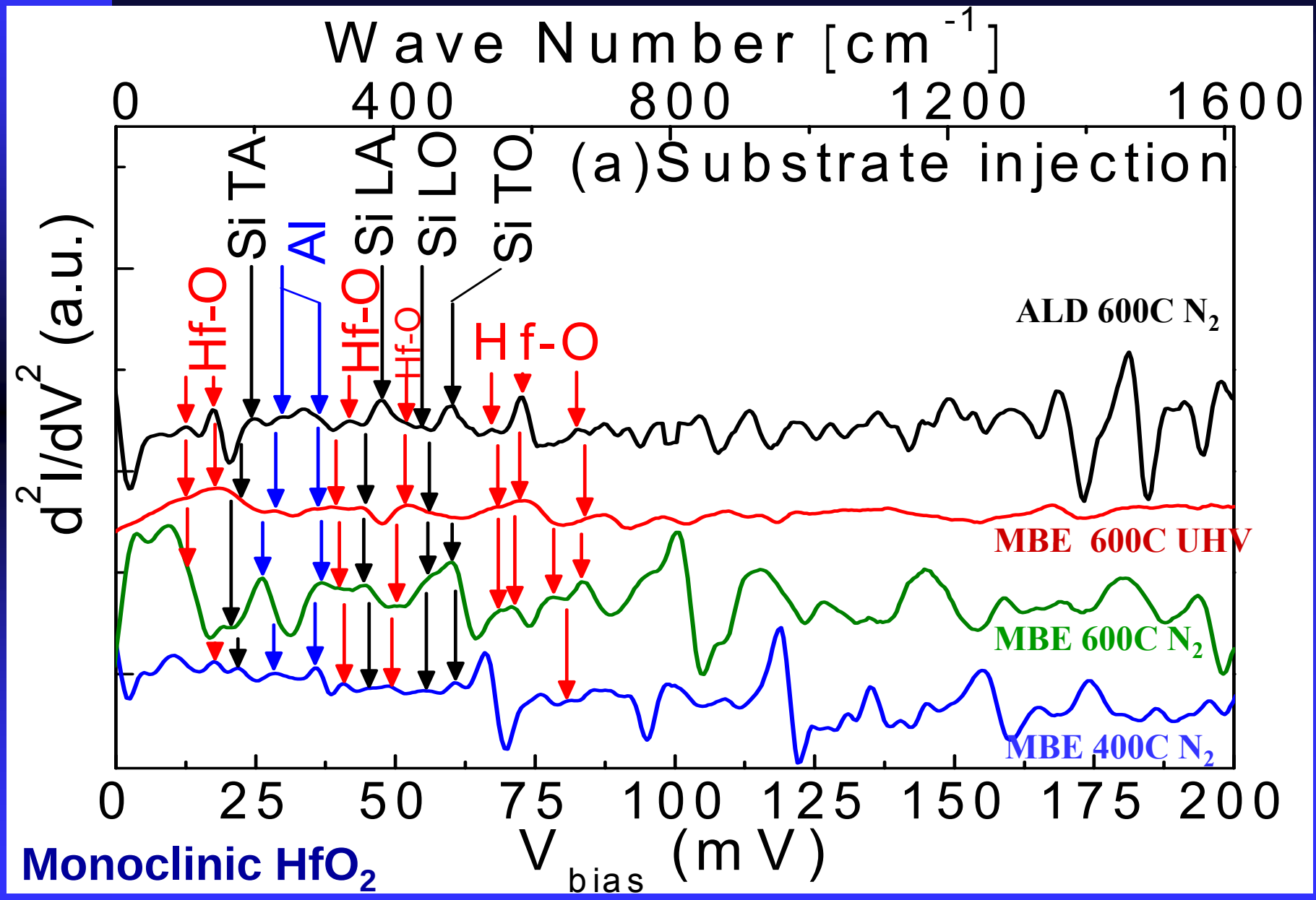


IET spectrum of Al/HfO_2/Si MOS structure

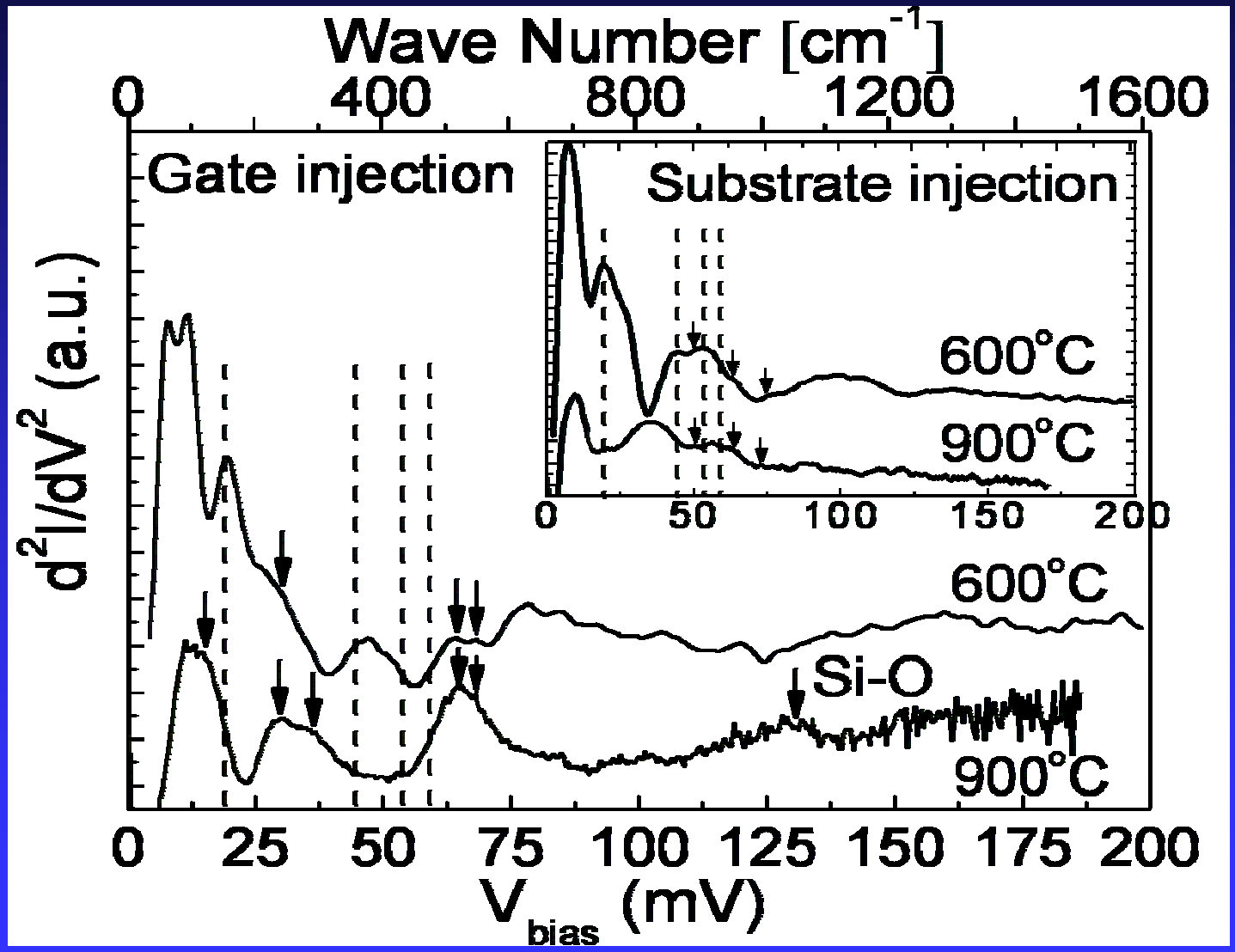


Monoclinic HfO_2

IET spectrum of Al/HfO2/Si MOS structure



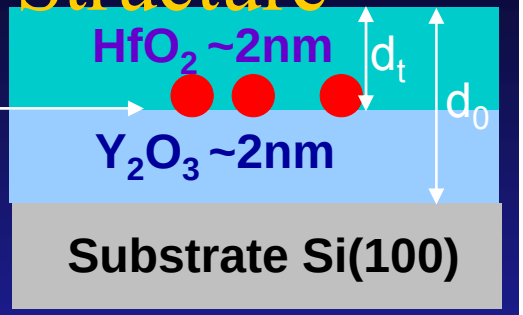
IET Spectrum of $Al/Y_2O_3/Si$ MOS Diode

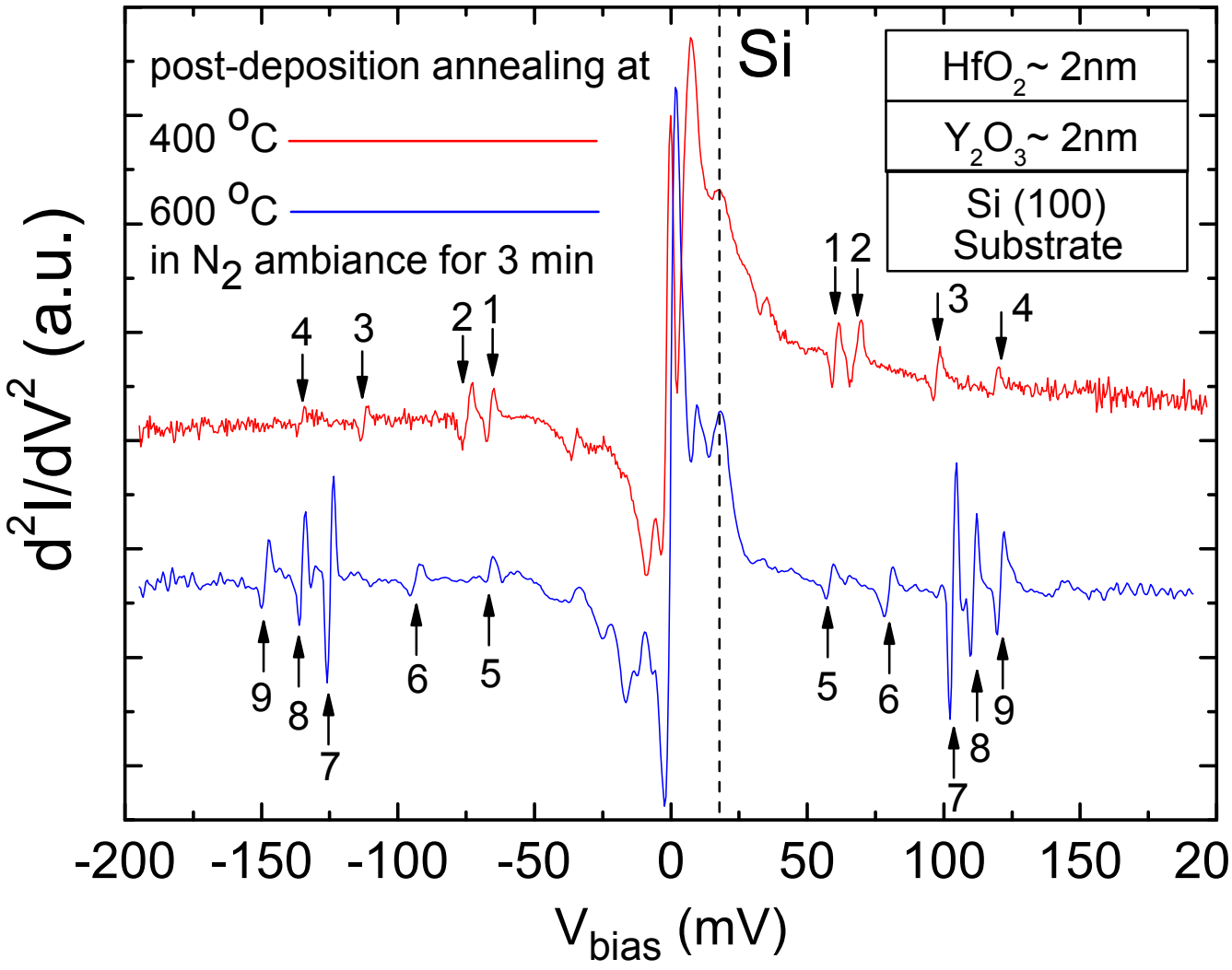


Cubic Y_2O_3

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

Charge trapping





$$V_t = V_f V_r / (V_f + V_r)$$

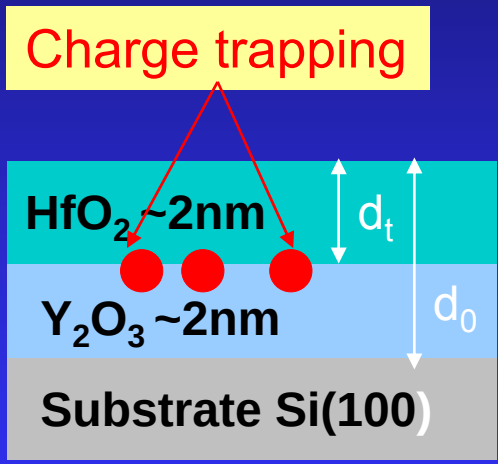
$$d_t = d_0 V_f / (V_f + V_r)$$

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 ?

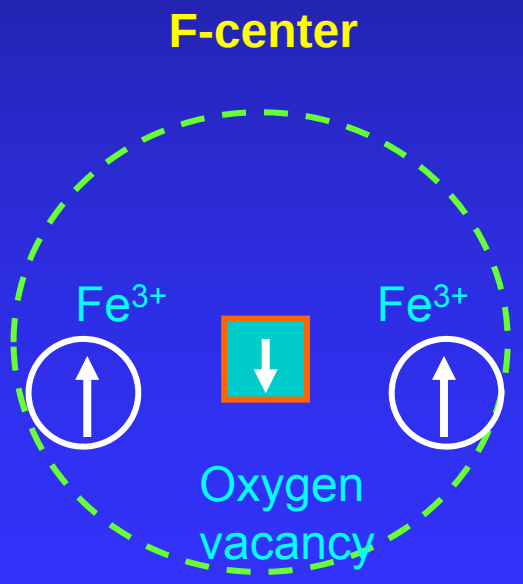
Diluted Magnetic Oxides

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

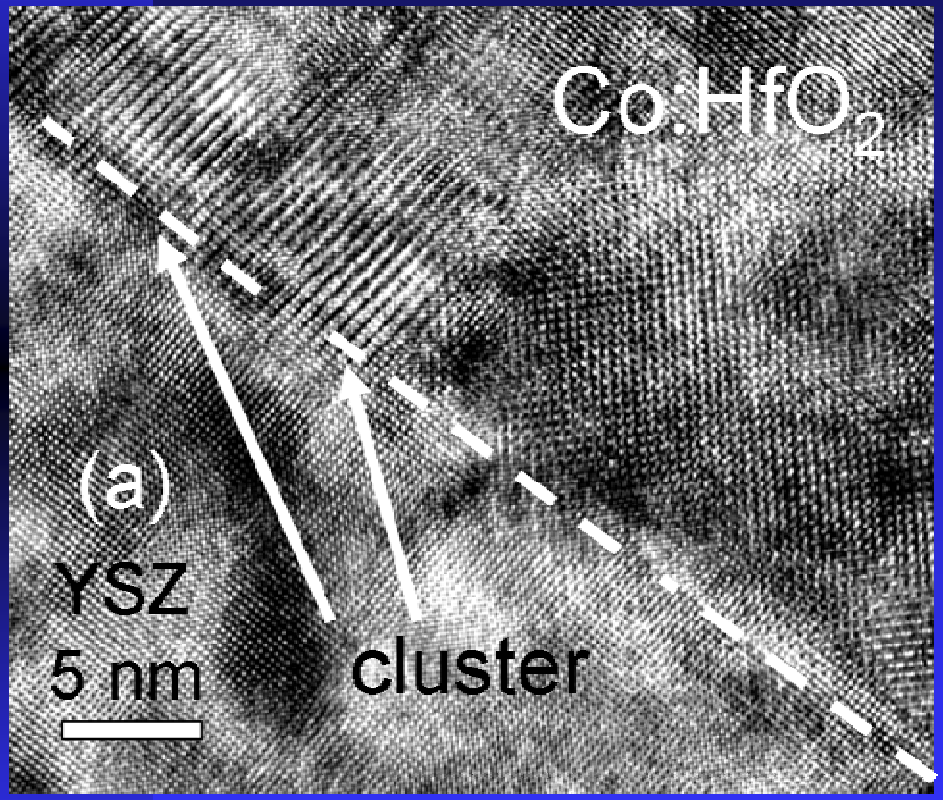
Appl. Phys. Lett. 91, 082504 (2007)

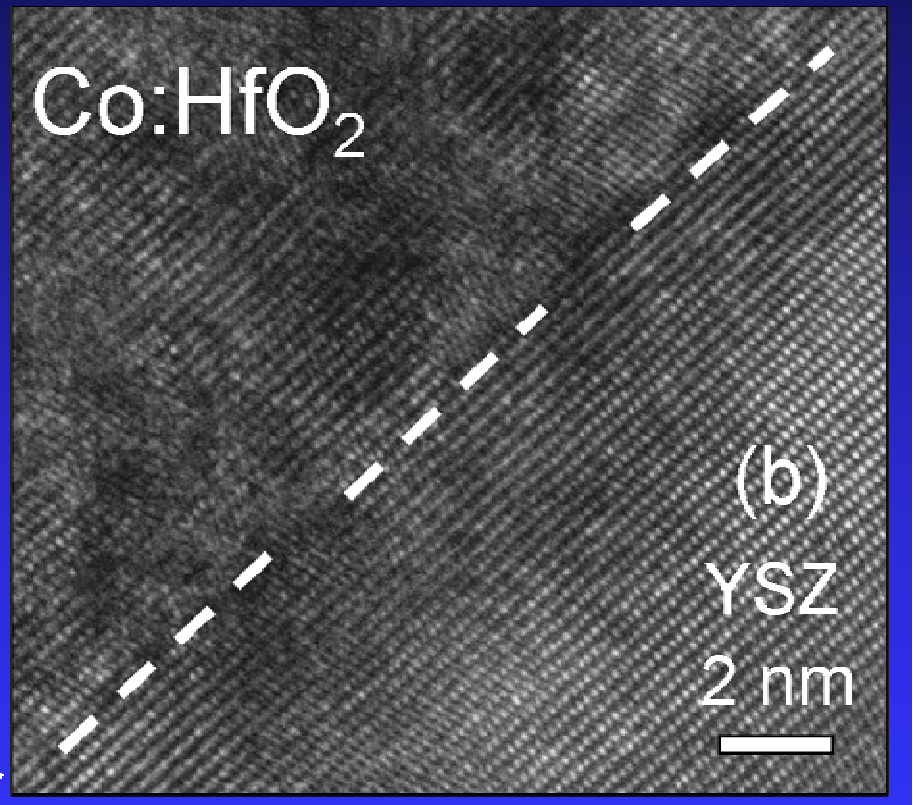
Introduction and motivation

- 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

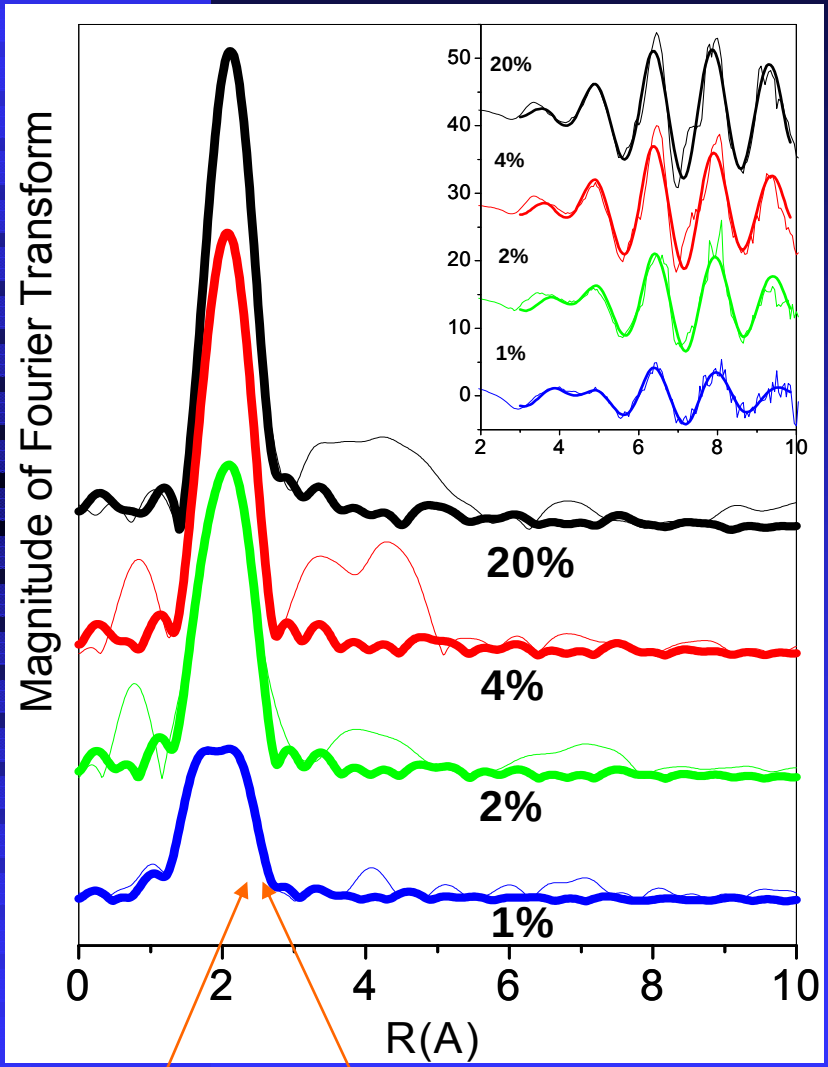




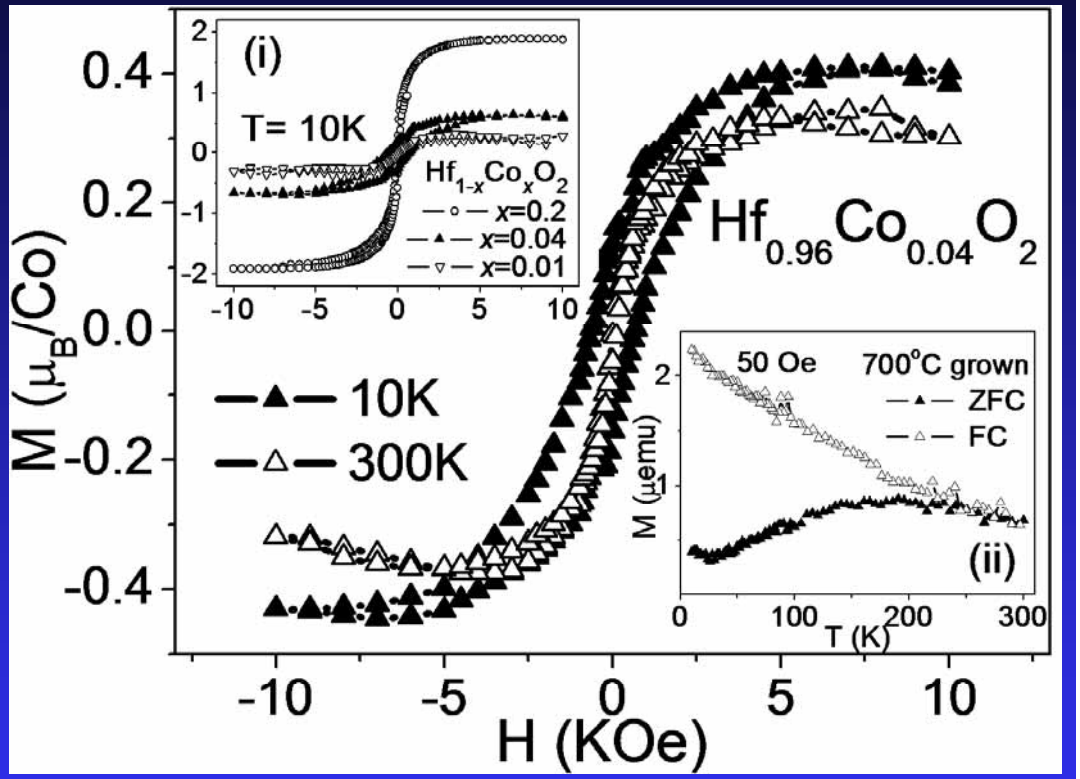
High-T (700°C) grown film
Monoclinic phase

Low-T (100°C) grown,
Polycrstalline film

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

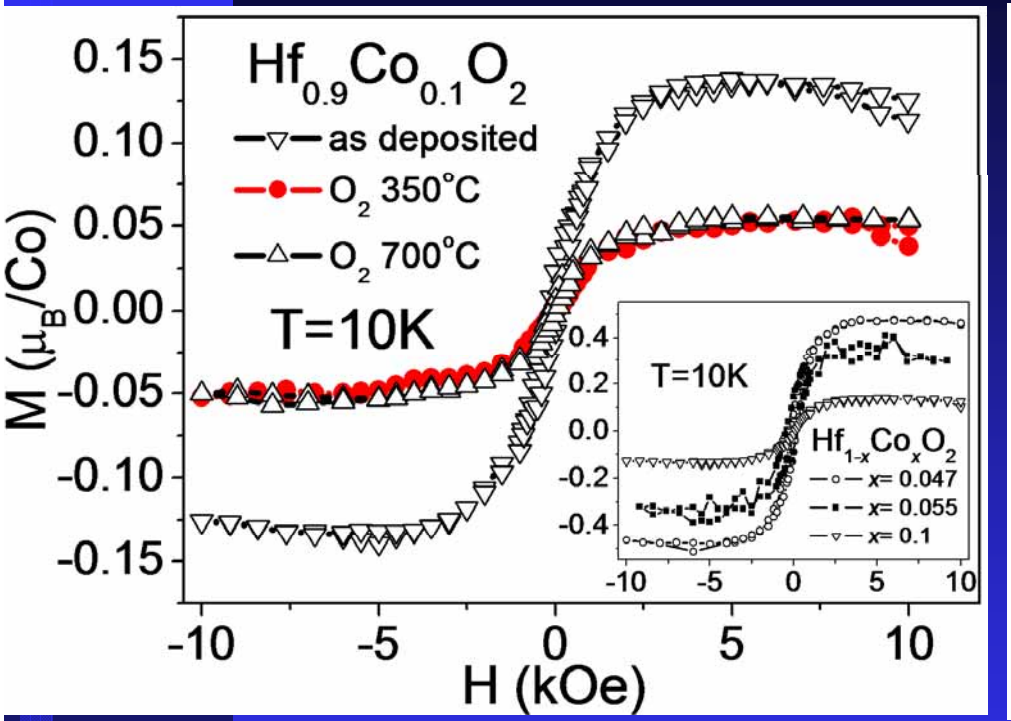


1st O shell + 2nd Co shell
2.04A 2.49A



- 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 (μ_B/Co)	**0.47**	**0.36**	**0.13**
Ms at 300K(μ_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** $\gamma = \varepsilon(m/m^*)$

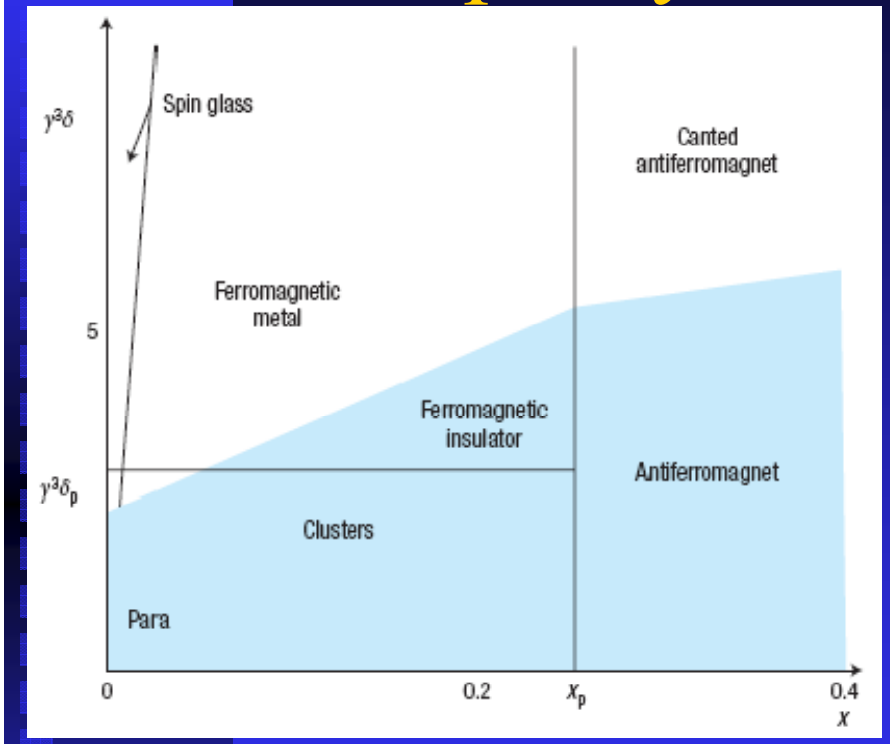
δ_p **: polaron percolation threshold**

X_p **: cation percolation threshold**

γ_H **: hydrogenic radius**

M. Coey et al,
Nature Materials, 2005.

Theoretical Analysis Using Impurity Band Exchange Model



Material	ε	m^*/m	γ	γ_H (nm)	δ_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

δ_p : Polaron percolation threshold

X_p : Cation percolation threshold

γ_H : Hydrogenic orbital radius

- T_{Mp} and x_p are two landmarks on magnetic phase diagram.
- Ferromagnetism occurs when $\delta > \delta_p$ and $x < x_p$.
- δ_p of HfO_2 based DMO is about 1.27×10^{-6} - 8.15×10^{-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