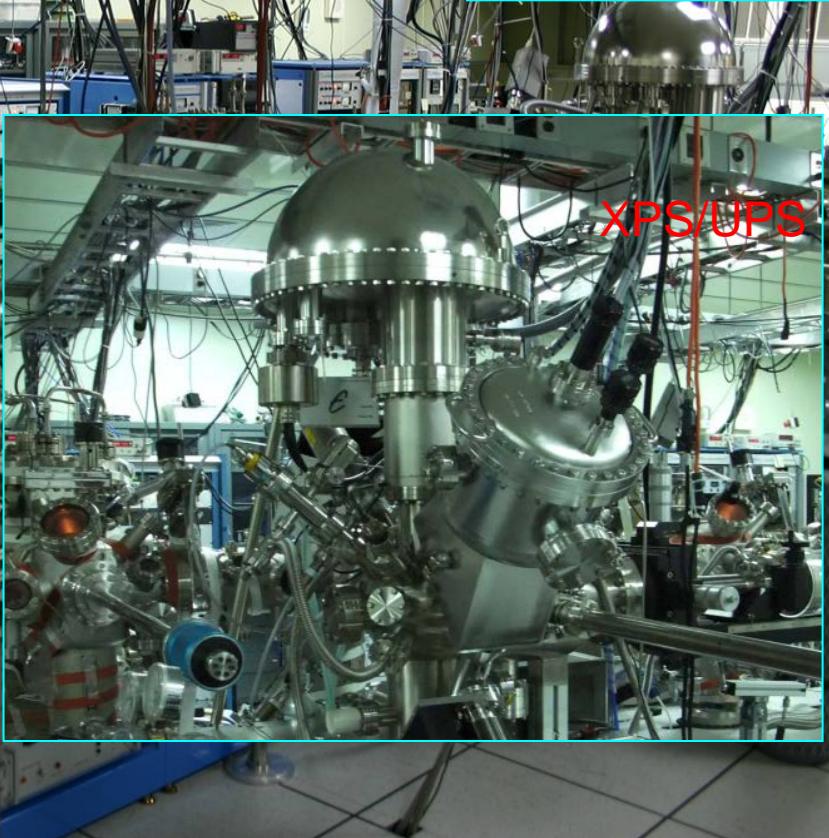
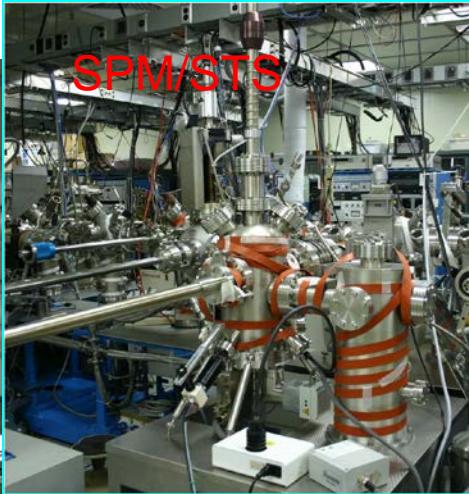
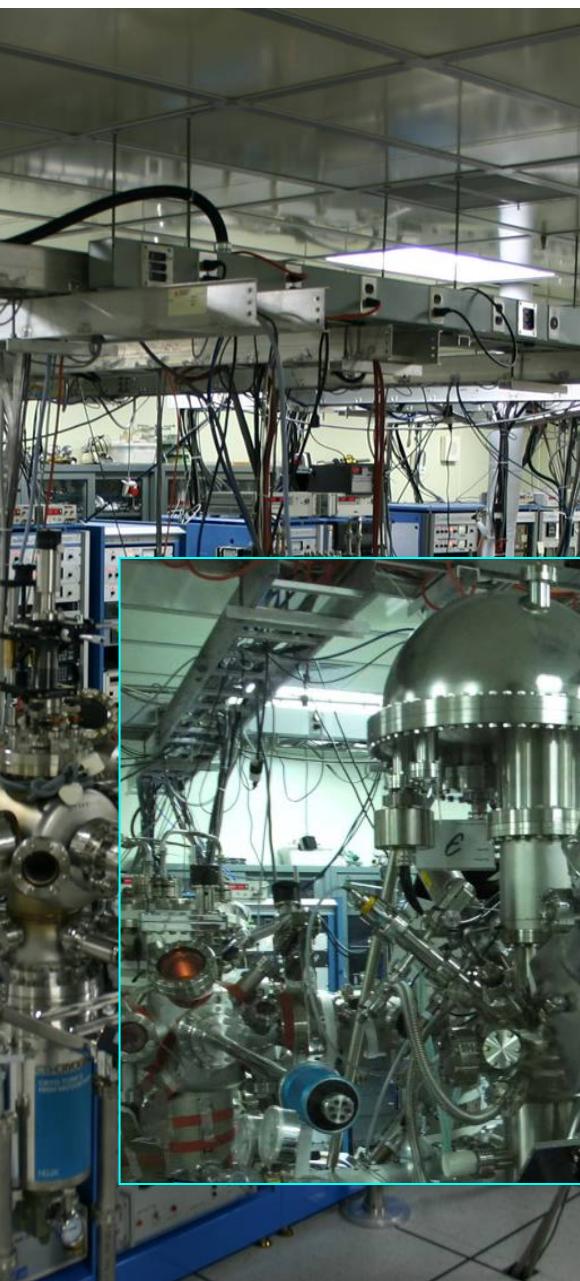


**50 years of development of oxides on III-V.  
Is *in-situ* process the best choice?**

**Minghwei Hong and J. Raynien Kwo**

*National Tsing Hua University, Hsinchu, Taiwan*

*National Taiwan University, Taipei, Taiwan*



- MBE – compound semiconductor growth – A. Y. Cho (National Medal of Science 1993 and National Medal of Technology 2007)
- MBE – metal and oxide growth – J. Kwo (first in discovering anti-ferromagnetic coupling through non-magnetic layer in magnetic superlattices PRL's 1985 – 1986)



Frank Shu, UC University Professor and former President of Tsing Hua Univ.

# Fundamental requirements for high $\kappa$ 's + metal gates on InGaAs (or any channels) for technology beyond Si CMOS

- ✓ EOT < 1 nm
- ✓ Interfacial density of states  $D_{it} \leq 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$
- ✓ Self-aligned process
  - High-temperature thermodynamic stability
- ✓ Low parasitic
  - Ohmic contacts and sheet resistance
- ✓ Integration with Si

# GaAs passivation (efforts since 1960)

**Previous ex-situ Efforts** (see M. Hong, C. T. Liu, H. Reese, and J. Kwo, in *Encyclopedia of Electrical and Electronics Engineering*, edited by J. G. Webster (Wiley, New York, 1999), Vol. 19, pp. 87–100, and *Physics and Chemistry of III–V Compound Semiconductor Interfaces*, edited C. W. Wilmsen (Plenum, New York, 1985)).

Anodic, thermal, and plasma oxidation of GaAs

Wet or dry GaAs surface cleaning followed by deposition of various dielectric materials

## ➤ Previous *in-situ* Efforts

### Growth using single chamber

- AlGaAs doped with O or Cr, Cho and Cassey 1978
- native oxides or  $\text{Al}_2\text{O}_3$  on GaAs during the same growth, i.e. introduction of oxygen in III-V MBE chamber, Ploog et al 1979
- ZnSe ( $a_0$  of 5.67 Å and a direct energy gap of 2.7 eV) on GaAs, Yao et al, 1979
- Si on InGaAs or GaAs, IBM at Zurich 1990 (?) and Morkoc et al, 1996

### **❖ Our Breakthrough Growth using two chambers**

- $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ ,  $\text{Ga}_2\text{O}_{3-x}$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  on GaAs using two growth chambers, Hong et al, 1994
- Have been applied to GaAs, InGaAs, GaN, and Si

# Do we need a new methodology for GaAs passivation?

Green and Spicer, *Stanford Univ.* : JVST A11(4), 1061, 1993

**Sulfur** passivation – Sandroff et al, Bell Labs: APL51, 33, 1987

**Sb** passivation – Cao et al, Stanford: Surf. Sci. 206, 413, 1988

“A new methodology for passivating compound semiconductors is presented in which **two over-layers** are used. In this approach, the first layer defines the surface electronically and the second provides long term protection.”

**Is it possible to have InGaAs MOS and Ge MOS, similar to  $\text{SiO}_2/\text{Si}$ , to achieve a low  $D_{it}$ , a low  $J$ , thermal stability at high temp. ( $>850$  and  $500^\circ\text{C}$ ), without any interfacial passivation layers (IPLs)?**

**YES!!!**

“MBE - enabling technology beyond Si CMOS”, (invited talk) J. Kwo, M. Hong, et al, J. Crystal Growth 323 511 (2011).

“InGaAs and Ge MOSFETs with high k dielectrics” (invited talk), J. Kwo, M. Hong, et al, Microelectronic Engineering 88, 336 (2011)

**S, Sb, Si, Ge as IPLs for InGaAs MOS**

GeON, GeO<sub>2</sub>, Si as IPLs for Ge MOS

# Pioneering work of GaAs and InGaAs MOSFET's using $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ at Bell Labs without 2 overlayers

- 1994
  - novel oxide  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$  to effectively passivate GaAs surfaces
- 1995
  - establishment of accumulation and inversion in p- and n-channels in  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ -GaAs MOS diodes with a low  $D_{it}$  of  $2-3 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$  (IEDM)
- 1996
  - first e-mode GaAs MOSFETs in p- and n-channels with inversion (IEDM)
  - Thermodynamically stable
- 1997
  - e-mode inversion-channel n-InGaAs/InP MOSFET with  $g_m = 190 \text{ mS/mm}$ ,  $I_d = 350 \text{ mA/mm}$ , and mobility of  $470 \text{ cm}^2/\text{Vs}$  (DRC, EDL)
- 1998
  - d-mode GaAs MOSFETs with negligible drain current drift and hysteresis (IEDM)
  - e-mode GaAs MOSFETs with improved drain current (over 100 times)
  - Dense, uniform microstructures; smooth, atomically sharp interface; low leakage currents
- 1999
  - GaAs power MOSFET
  - Single-crystal, single-domain  $\text{Gd}_2\text{O}_3$  epitaxially grown on GaAs
- 2000
  - demonstration of GaAs CMOS inverter



- "Use of Hybrid Reflectors to Achieve Low Thresholds in All MBE Grown Vertical Cavity Surface Emitting Laser Diodes", R. J. Fischer, K. Tai, **M. Hong**, and A. Y. Cho, IEEE IEDM, 861, Washington, D.C., Dec.3-6, 1989; J. Vac. Sci. Technol. B8, p.336, 1990.
- "Array Operation of GaAs/AlGaAs Vertical Cavity Surface Emitting Lasers", K. Tai, Y.H. Wang, J.D. Wynn, **M. Hong**, R. J. Fischer, J.P. Mannaerts, and A.Y. Cho, *CLEO/IQEC'90*, Anaheim, Ca, May 21-25, 1990.
- "MBE Growth and Properties of Fe<sub>3</sub>(Al,Si) on GaAs(100)", M. Hong, H. S. Chen, J. Kwo, A. R. Kortan, J. P. Mannaerts, B. E. Weir, and L. C. Feldman, J. Crystal Growth, V.111, 984, 1991.
- "Vertical Cavity Top-Surface Emitting Lasers with Thin Ag Mirrors and Hybrid Reflectors", M. Hong, L. W. Tu, J. Gamelin, Y. H. Wang, R. J. Fischer, E. F. Schubert, K. Tai, G. Hasnain, J. P. Mannaerts, B. E. Weir, J. D. Wynn, R. F. Kopf, G. J. Zydzik, and A. Y. Cho, J. Crystal Growth 111, 1071, 1991.
- "In-Situ Non-Alloyed Ohmic Contacts to p-GaAs", M. Hong, D. Vakhshoori, J. P. Mannaerts, F. A. Thiel, and J. D. Wynn, J. Vac. Sci. Technol. 12 (2), p.1047, 1994.
- "New Frontiers of Molecular Beam Epitaxy with In-Situ Processing", M. Hong, invited paper for the 1994 International MBE Conference and published in J. Crystal Growth V.150, pp.277-284, 1995.
- "X-Ray Scattering Studies of the Interfacial Structure of Au/GaAs", D. Y. Noh, Y. Hwu, H. K. Kim, and M. Hong, Phys. Rev. B51 (7), p.4441, 1995.

# Background leading to unpin surface Fermi level in III-V compound semiconductors

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- Late 1980s to early 1990s, problems in then AT&T's pump lasers (980 nm) for undersea optical fiber cable (trans-Atlantic)
- Semiconductor facet (HR, AR) coating
  - Reducing defects between InGaAs (GaAs) and coating dielectrics
- Passivation of the facets
- Electronic passivation much more stringent than optical passivation
  - (110) vs (100) of InGaAs (GaAs)

# ULTRAHIGH VACUUM DEPOSITION OF OXIDES

M. Hong et al, JVST B14 2297 (1996); J. Kwo et al, APL 75 1116 (1999); M. Hong et al, APL 76 312 (2000)

Initial thinking: to attain  $\text{Ga}_2\text{O}_3$  film for passivation

High-purity single crystal  $\text{Ga}_5\text{Gd}_3\text{O}_{12}$  (GGG) source

Evaporation (sublime) by e-beam

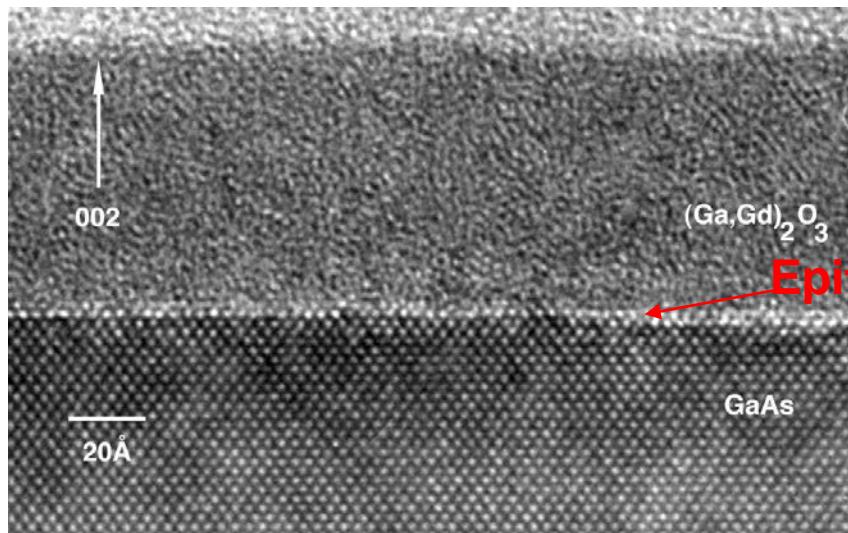
$\text{Gd}_2\text{O}_3$  ionic oxide  
 $T_m > 4000\text{K}$

$\text{Ga}_2\text{O}_3$  more covalent oxide  
 $T_m \sim 2000\text{K}$

$\text{Ga}_2\text{O}_3$  evaporated mostly, and formed amorphous  $\text{Ga}_2\text{O}_3$  film

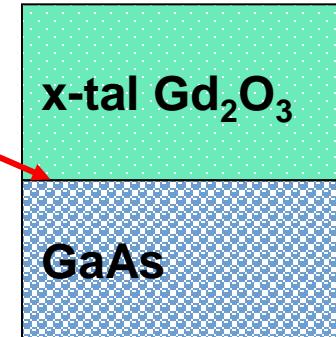
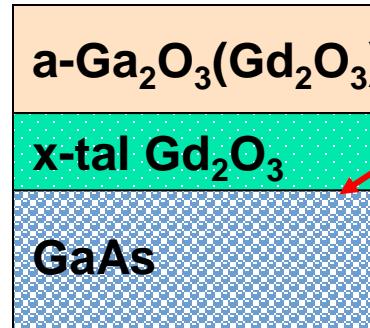
High Resolution TEM of  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$  on GaAs

Mixed Oxide  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$       Pure  $\text{Gd}_2\text{O}_3$  Film



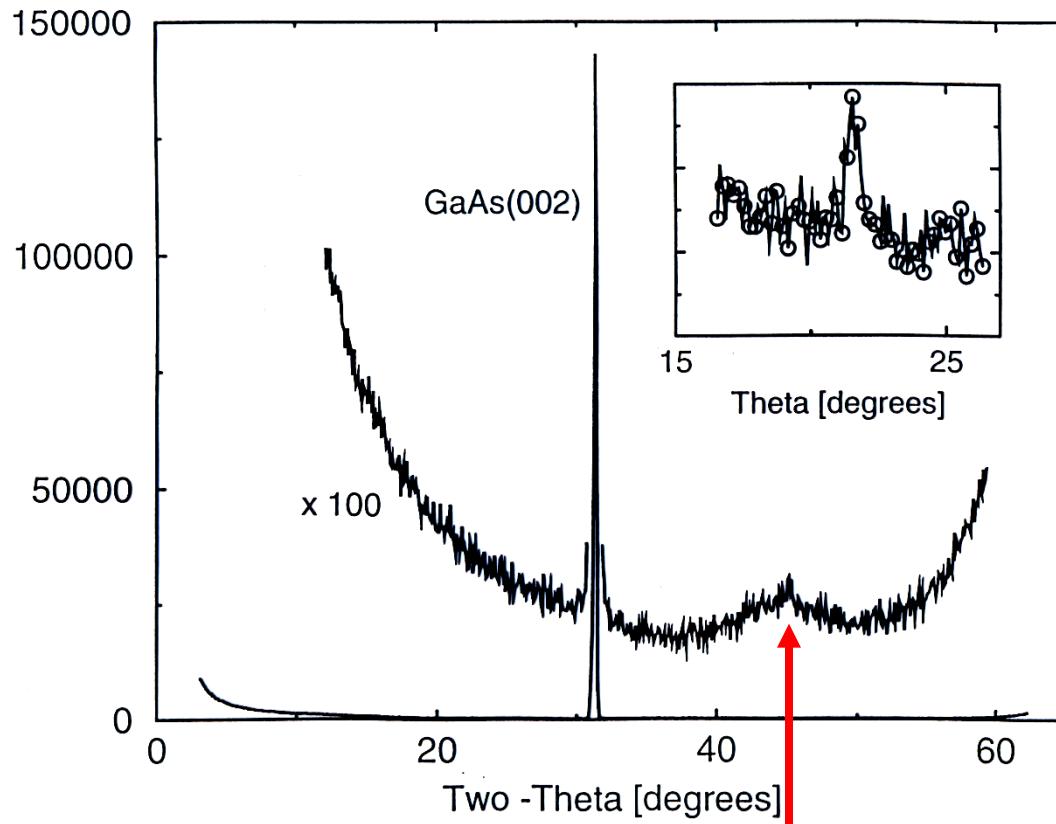
$\text{Gd}/(\text{Ga}+\text{Gd}) > 20\%$   
 $\text{Gd}^{+3}$  stabilize  $\text{Ga}^{+3}$

Single domain, epitaxial film  
in (110)  $\text{Mn}_2\text{O}_3$  structure



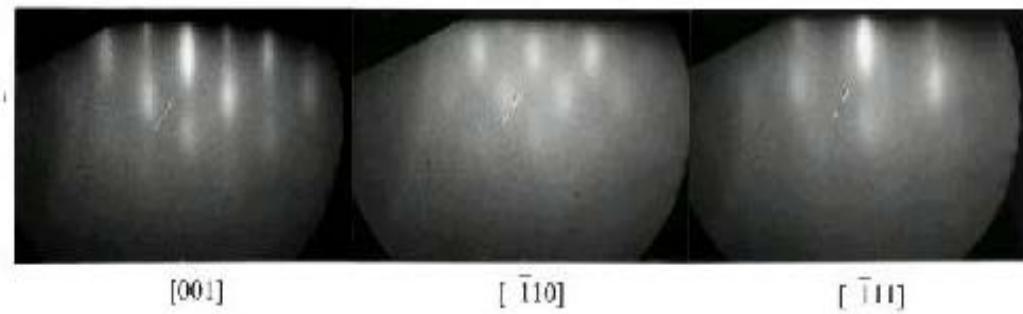
# Initial growth of $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ 1.1 nm thick

Intensity [arbitr.units]

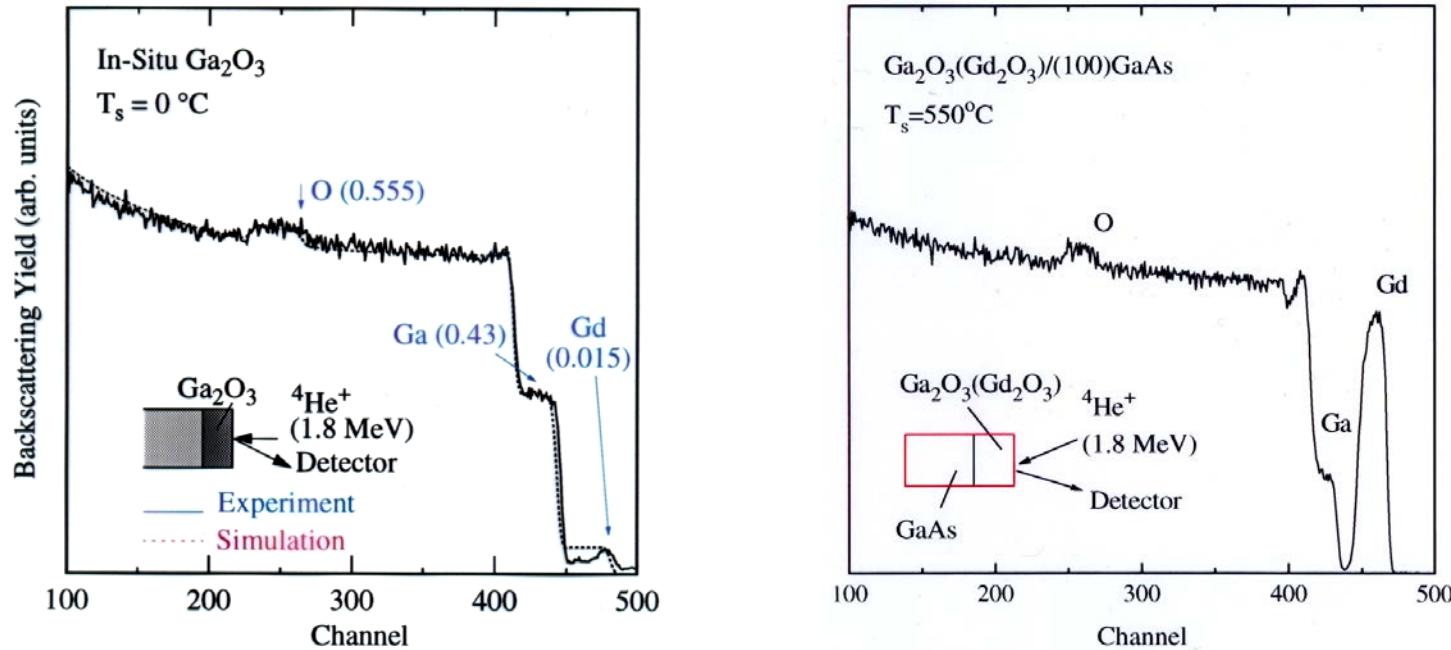


X-ray diffraction of normal  
scan and rocking curve

In-situ RHEED  
pattern showing a  
single crystal  
growth



# Growth of $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ films using e-beam evaporation from $\text{Ga}_5\text{Gd}_3\text{O}_{12}$ target – RBS studies



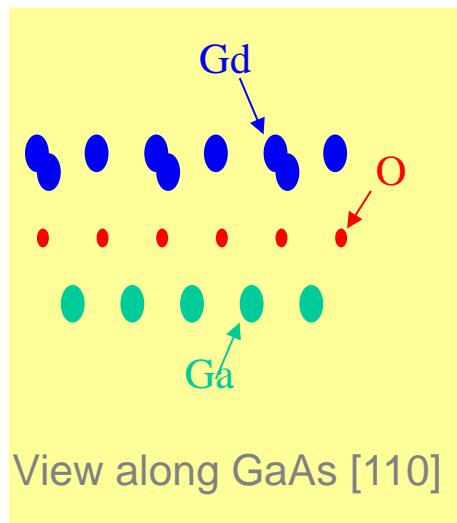
**Identified the essential role of  $\text{Gd}_2\text{O}_3$     Kwo et al, APL 75 1116 (1999)**  
**The  $\text{Gd}/(\text{Ga}+\text{Gd})$  ratio needs to be greater than 20%**  
**The electropositive  $\text{Gd}^{+3}$  may stabilize  $\text{Ga}^{+3}$  in the film**

"Low  $D_{it}$  thermodynamically stable  $\text{Ga}_2\text{O}_3$ -GaAs interfaces: fabrication, characterization, and modeling", M. Passlack, M. Hong, J. P. Mannaerts, J. Kwo, R. L. Opila, S. N. G. Chu, N. Moriya, and F. Ren, IEEE TED, 44 No. 2, 214-225, 1997.

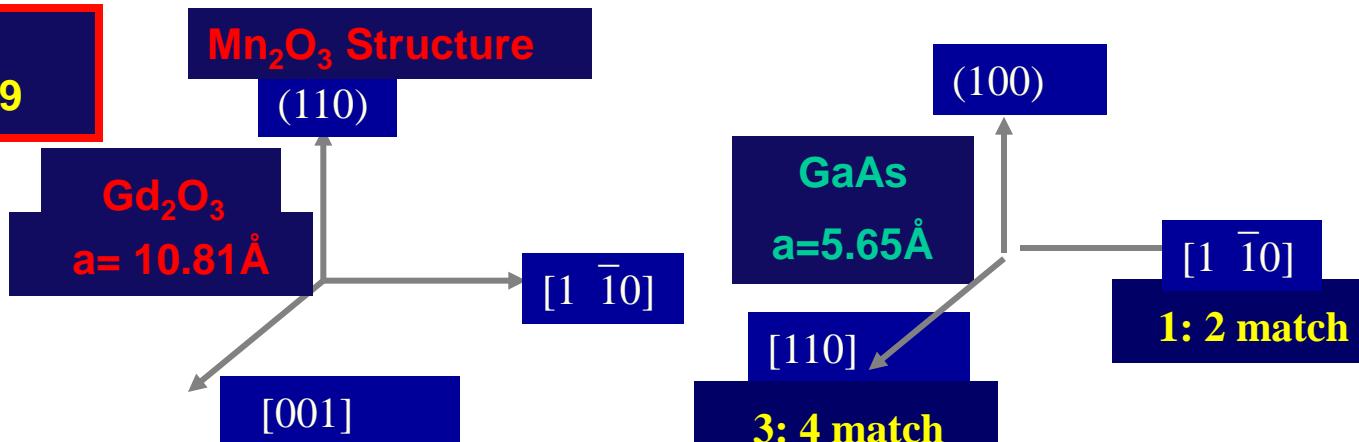
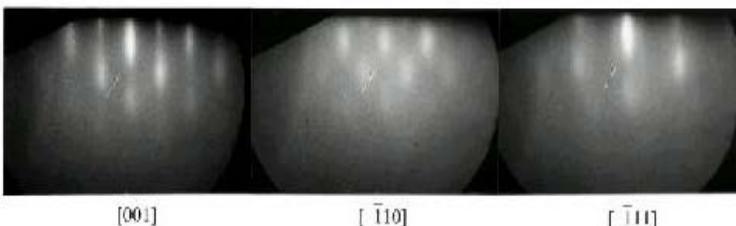
"Novel  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$  passivation techniques to produce low  $D_{it}$  oxide-GaAs interfaces", M. Hong, J. P. Mannaerts, J. E. Bowers, J. Kwo, M. Passlack, W-Y. Hwang, and L. W. Tu, J. Crystal Growth, 175/176, pp.422-427, 1997.

# Pioneer Work : Single Crystal Gd<sub>2</sub>O<sub>3</sub> Films on GaAs

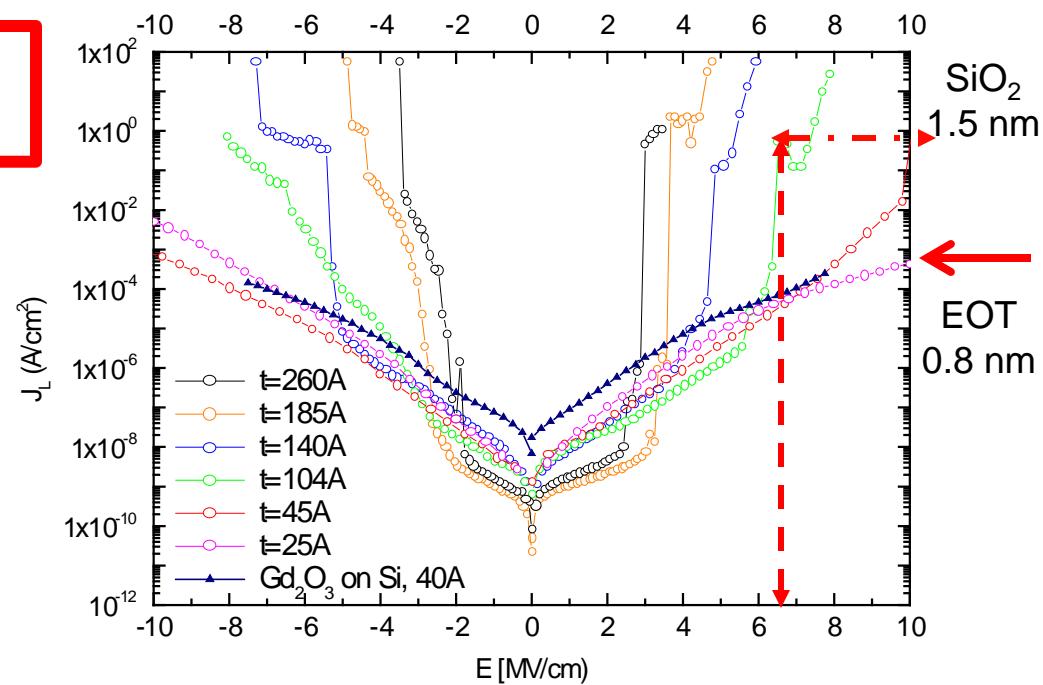
M. Hong, J. Kwo et al,  
Science 283, p.1897, 1999



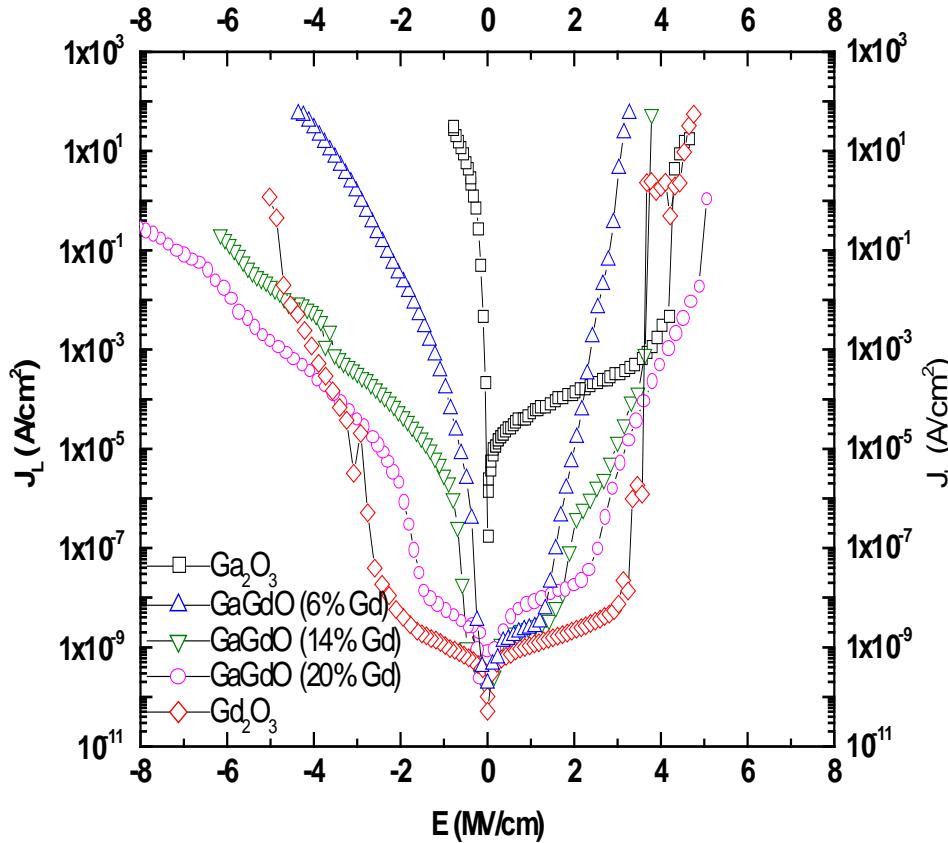
Gd<sub>2</sub>O<sub>3</sub> (110) 25Å



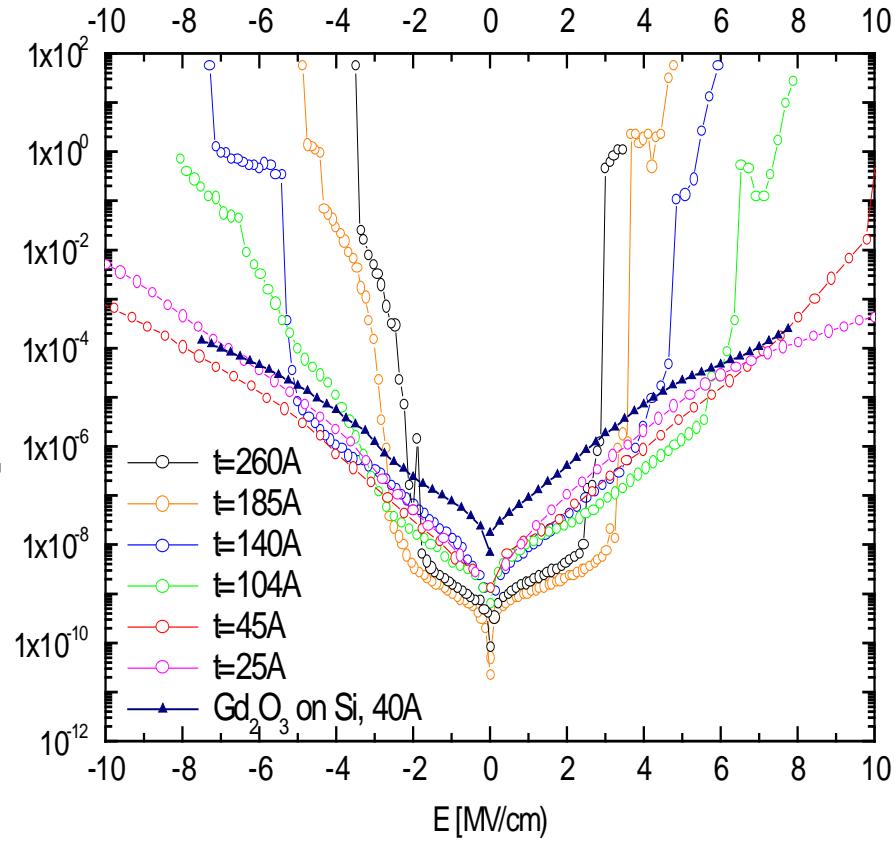
Low D<sub>it</sub>'s  
and low J<sub>L</sub>



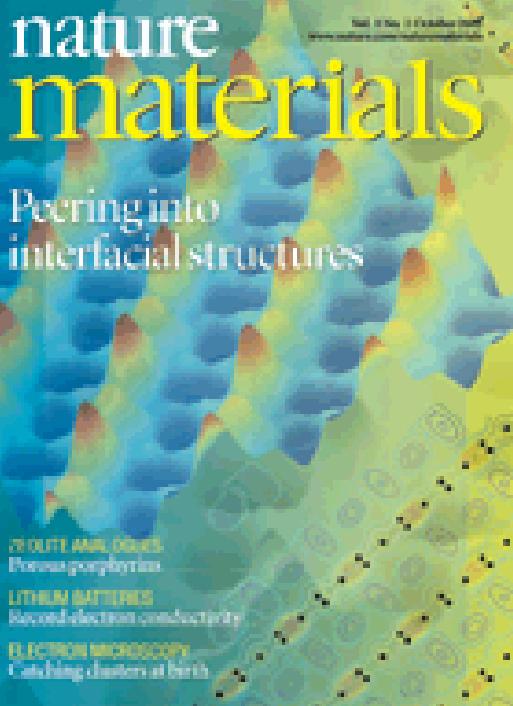
## Gd Composition Dependence of Electrical leakage of GGG on GaAs



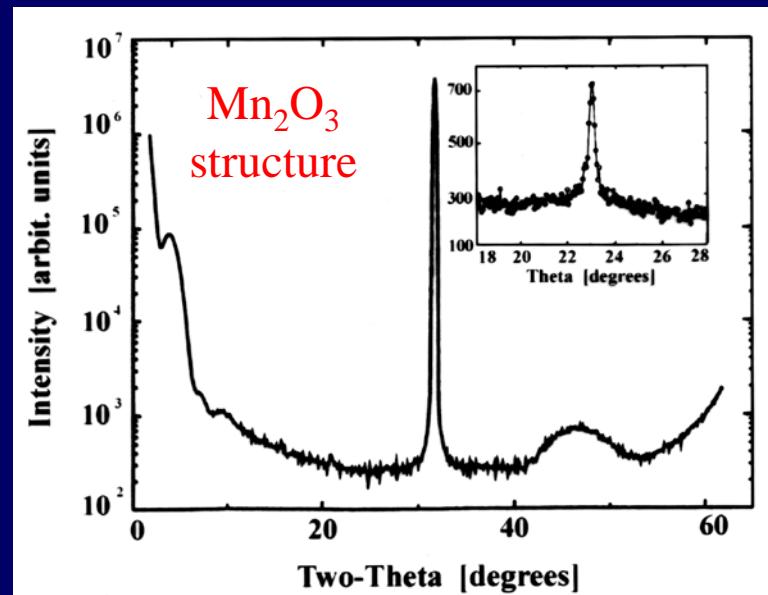
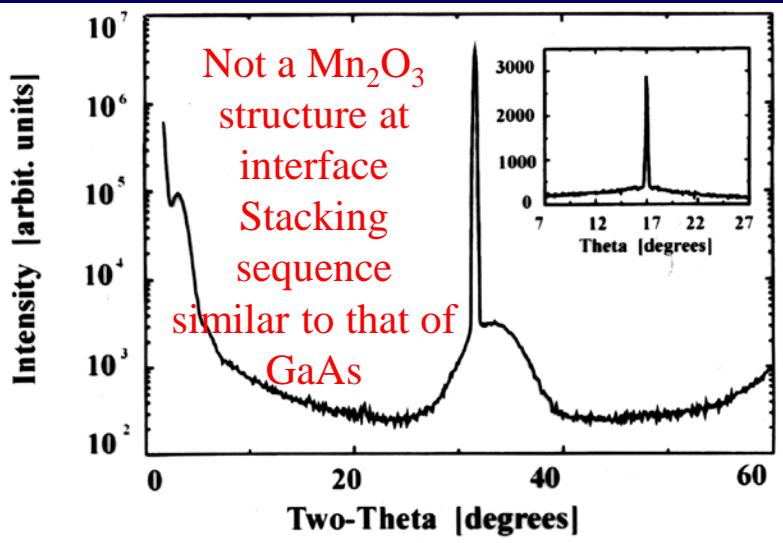
## Thickness Dependence of Electrical Leakage of $\text{Gd}_2\text{O}_3$ on GaAs



# Single crystal $\text{Gd}_2\text{O}_3$ on GaAs - Epitaxial interfacial structure



- “New Phase Formation of  $\text{Gd}_2\text{O}_3$  films on GaAs (100)”, J. Vac. Sci. Technol. B 19(4), p. 1434, 2001.
- “ Direct atomic structure determination of epitaxially grown films:  $\text{Gd}_2\text{O}_3$  on GaAs(100) ” PRB 66, 205311, 2002
- A new X-ray method for the direct determination of epitaxial structures, coherent Bragg rod analysis (COBRA)
  - Nature – Materials 2002 Oct issue cover paper



## **CET (EOT), $D_{it}$ and *thermal stability at high Temp* in high $\kappa$ 's on **InGaAs, Ge, and GaN****

High  $\kappa$ 's: single crystals, amorphous

MBE- $\text{Ga}_2\text{O}_3$ ( $\text{Gd}_2\text{O}_3$ )

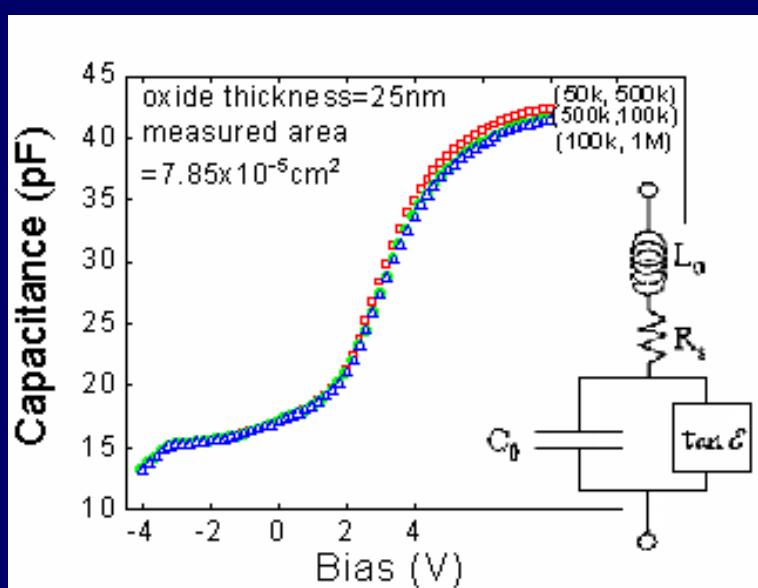
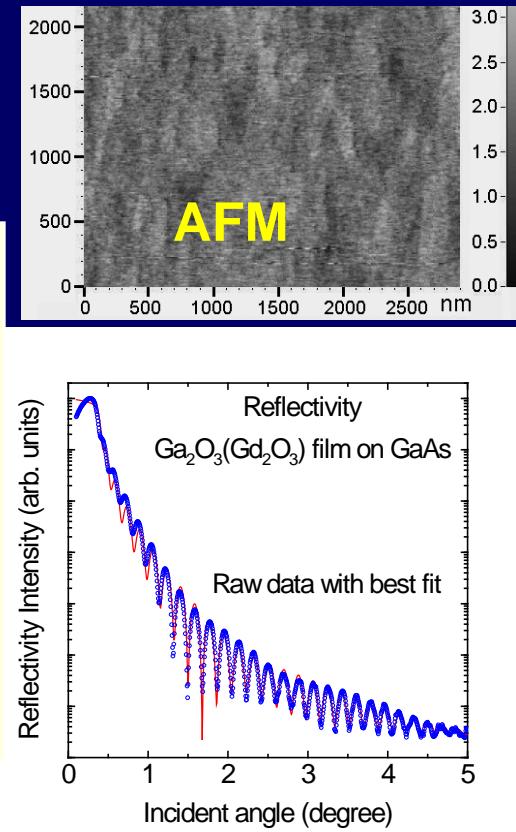
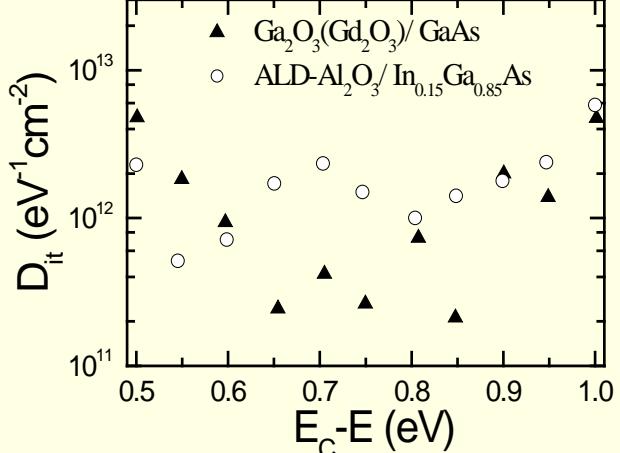
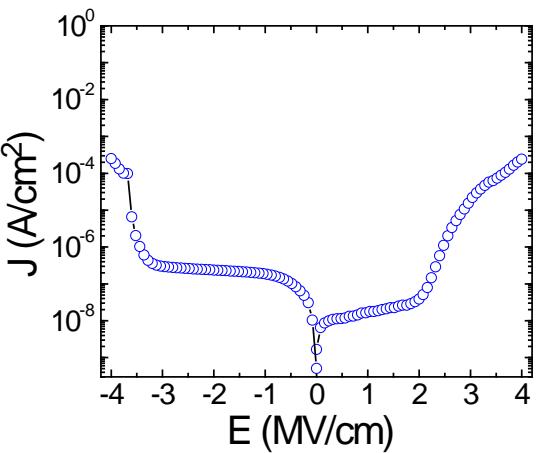
MBE- $\text{HfAlO}/\text{HfO}_2$

MBE- $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$

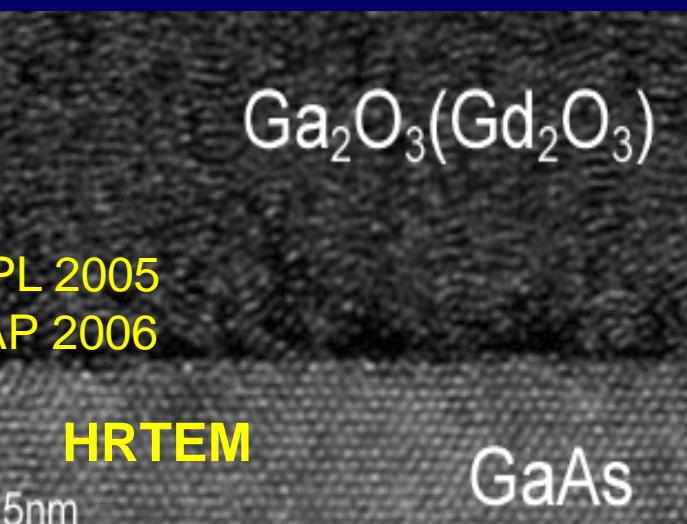
ALD- $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$

ALD+MBE

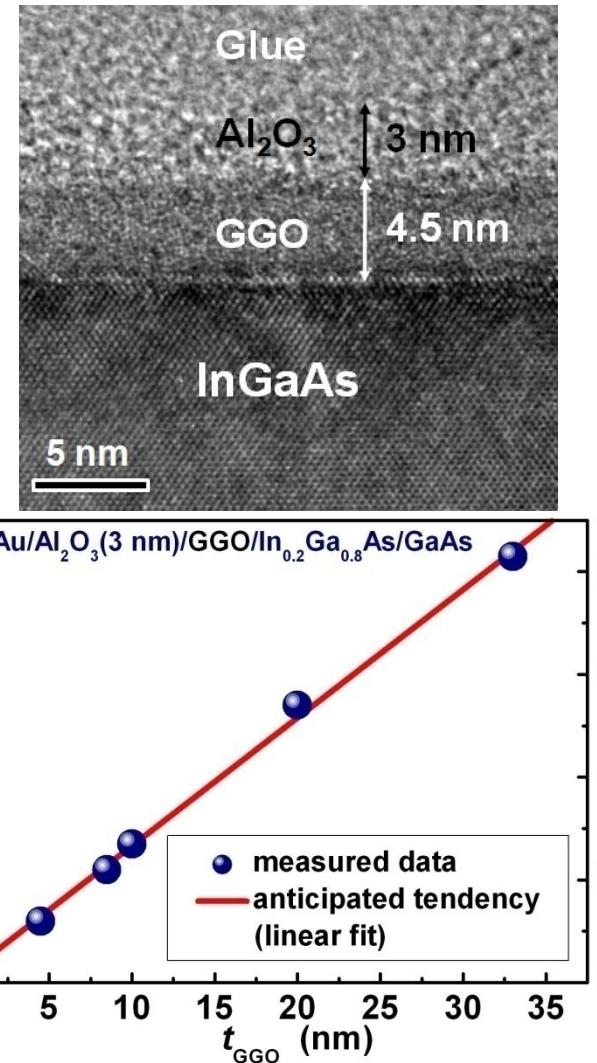
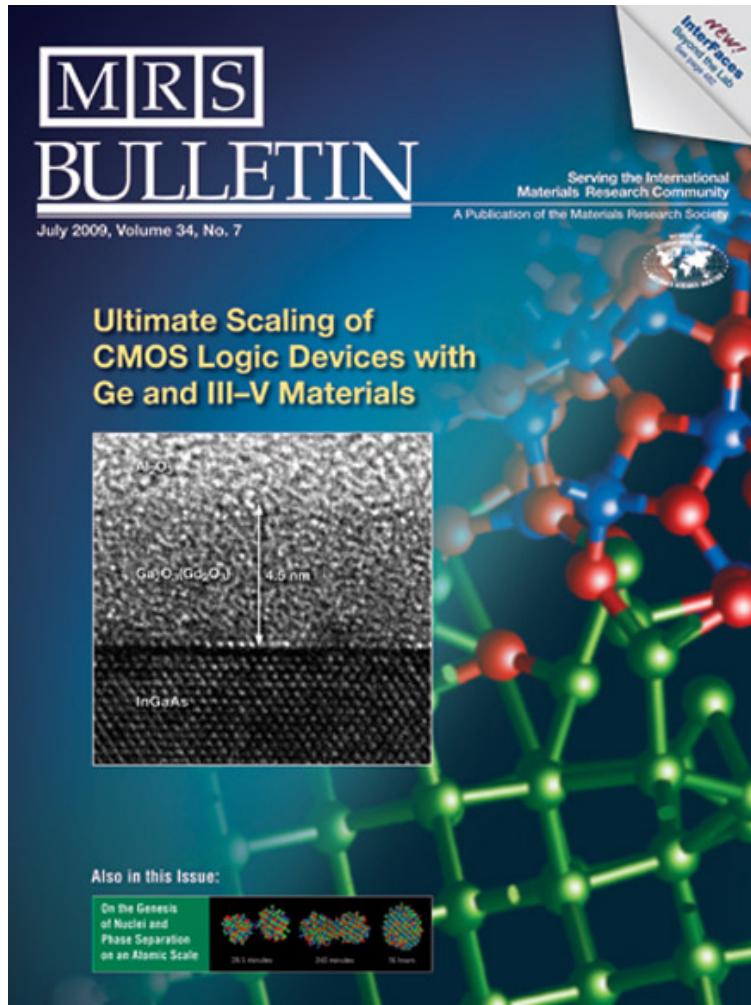
# $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)/\text{GaAs}$ under high temperature annealing in UHV and non-UHV



Y. L. Huang et al, APL 2005  
C. P. Chen et al, JAP 2006

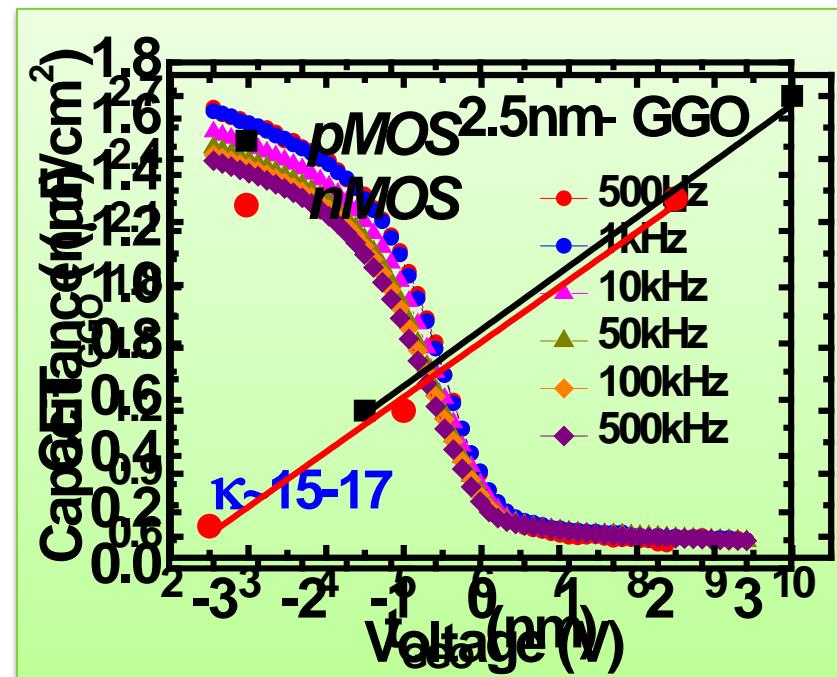
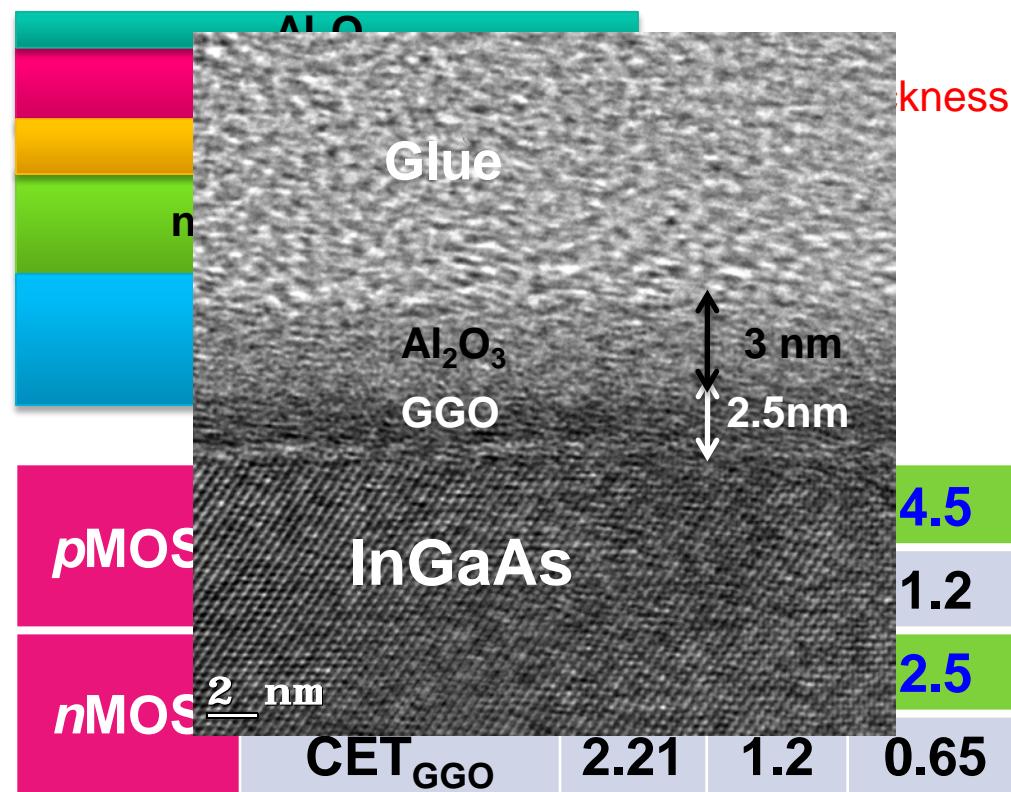


# MRS Bulletin, July 2009



**Cover Image & Theme Article – “*InGaAs Metal Oxide Semiconductor Devices with  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$  High- $\kappa$  Dielectrics for Science and Technology beyond Si CMOS*”, M. Hong, J. Kwo, T. D. Lin, and M. L. Huang, MRS Bulletin 34, 514 July 2009.**

# GGO Scalability and Thermal Stability



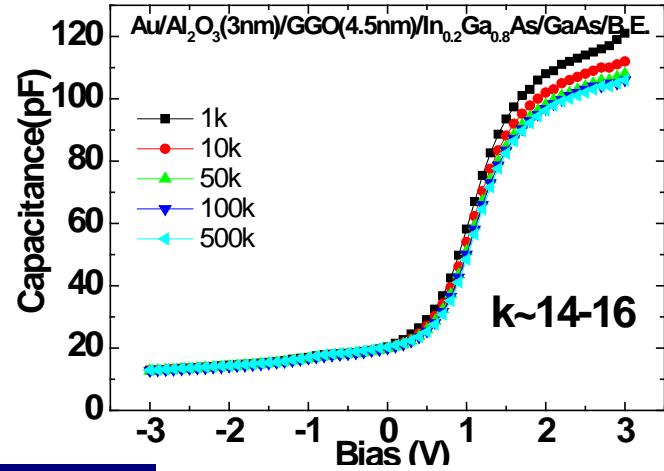
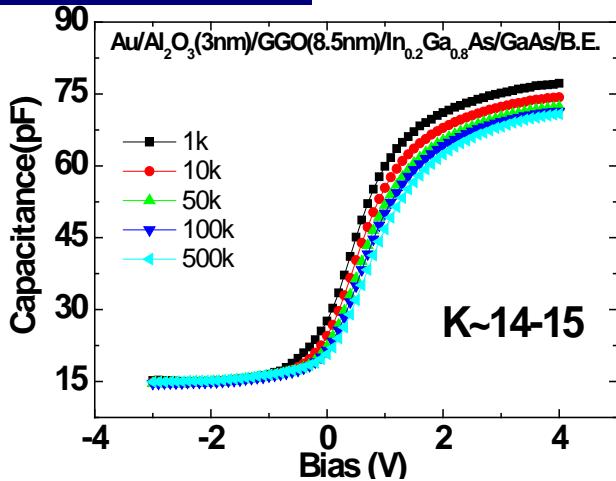
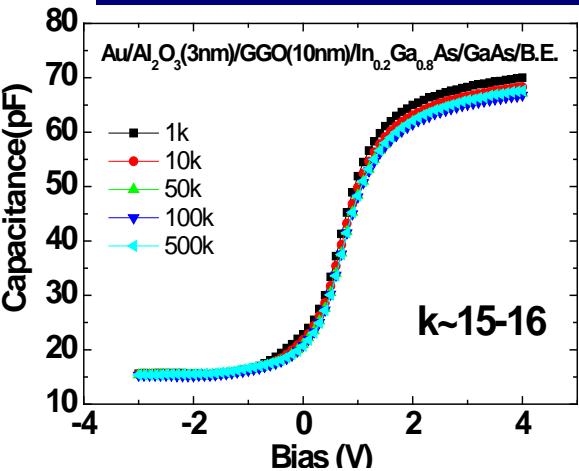
K. H. Shiu *et al.*, APL 92, 172904 (2008)

T. H. Chiang *et al.*, unpublished

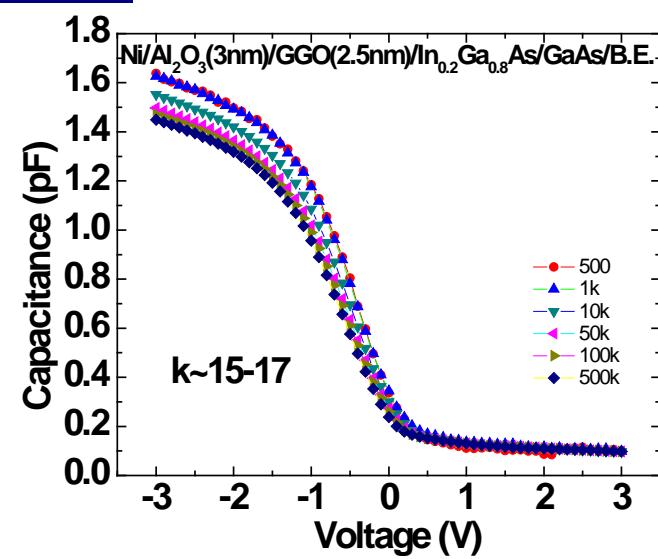
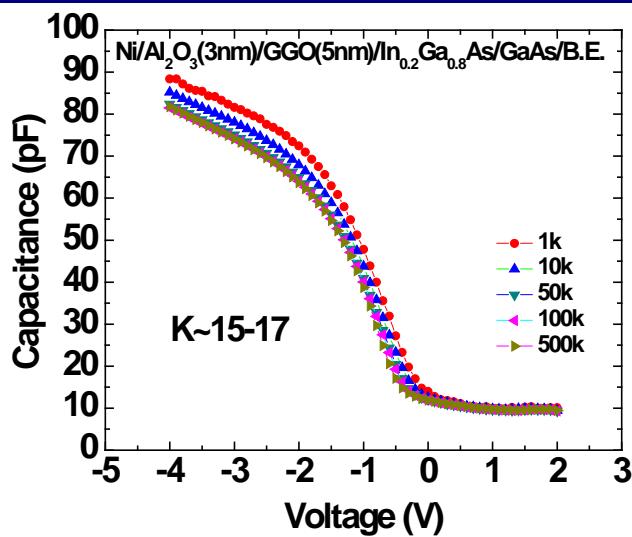
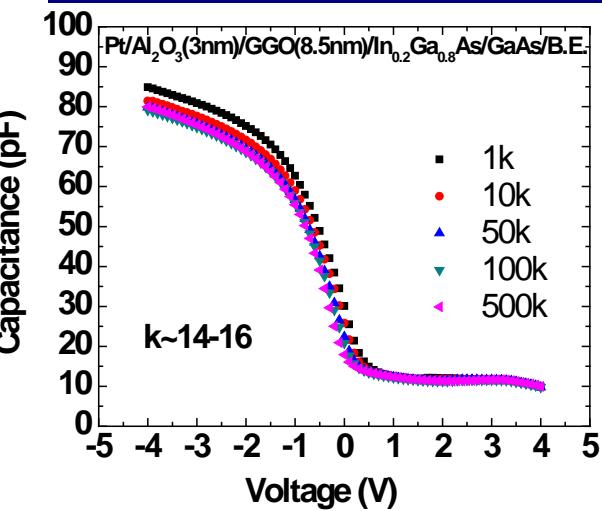
- Al<sub>2</sub>O<sub>3</sub> capping effectively minimized absorption of moisture in GGO
- GGO (2.5nm) dielectric constant maintains ~15 (CET~7Å)
- D<sub>it</sub>'s ~ low  $10^{11}(\text{cm}^{-2}\text{eV}^{-1})$  range even subjected to 850°C annealing (Conductance Method)

# C-V Characteristics – GGO/ $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$

K. H. Shiu et al, APL 92, 172904 (2008)



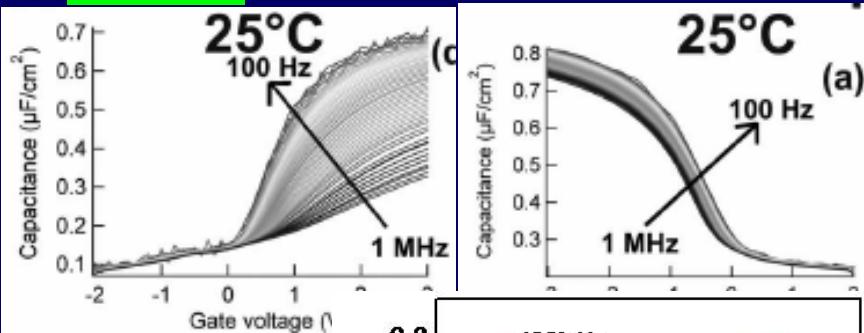
T. H. Chiang et al, National Tsing Hua University (unpublished)



# State-of-the-art work of ALD $\text{Al}_2\text{O}_3/\text{GaAs}$

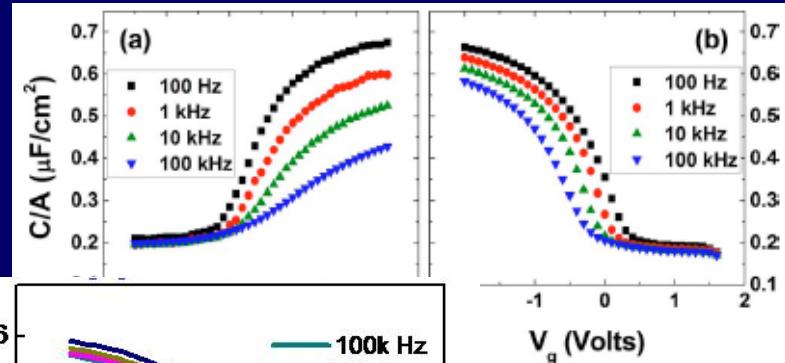
**IMEC**

$(\text{NH}_4)_2\text{S}$  treated GaAs



**U.T.Dallas**

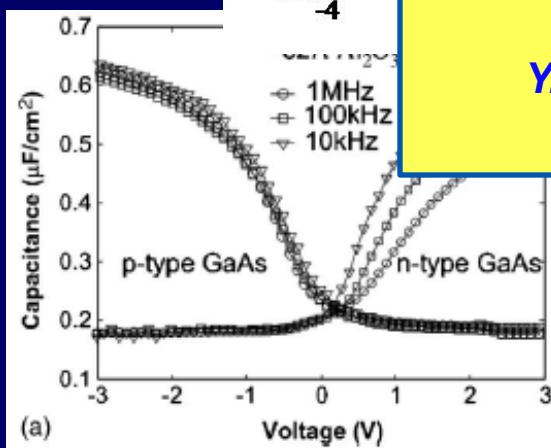
$\text{NH}_4\text{OH}$  treated GaAs



G. Brammertz, et al. A

ys. Lett. **93**, 113506 (2008)

**U.T. Austin**

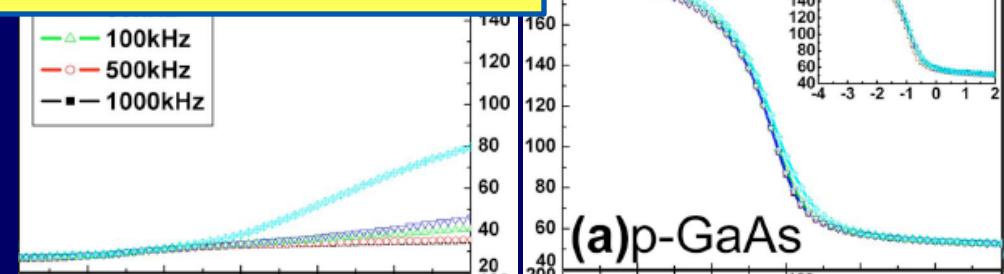


**Our work of In-situ ALD + MBE  $\text{Al}_2\text{O}_3/\text{GaAs}$   
No pre-treatments and no interfacial  
passivation layers**

**Y. H. Chang, et al, Microelectronic  
Engineering **88**, 440–443 (2011)**

**MIT**

$\text{NH}_3$  treated,  
growth with TMA/IPA



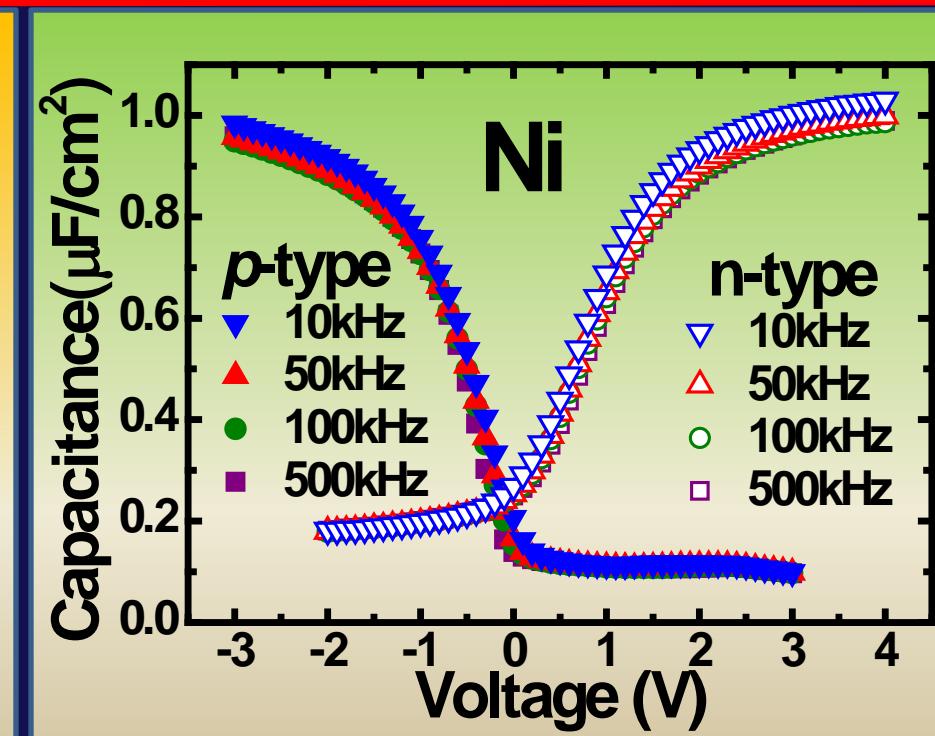
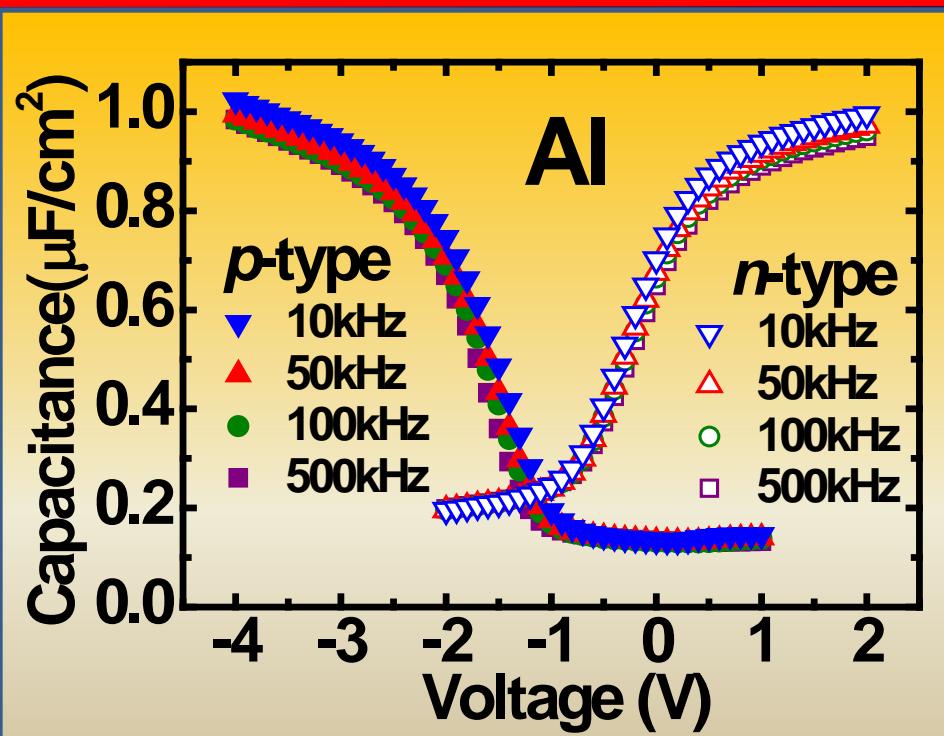
D. Shahrjerdi, et al. Appl. Phys. Lett. **92**, 203505 (2008)

C.-W. Cheng, et al. Appl. Phys. Lett. **95**, 082106 (2009)



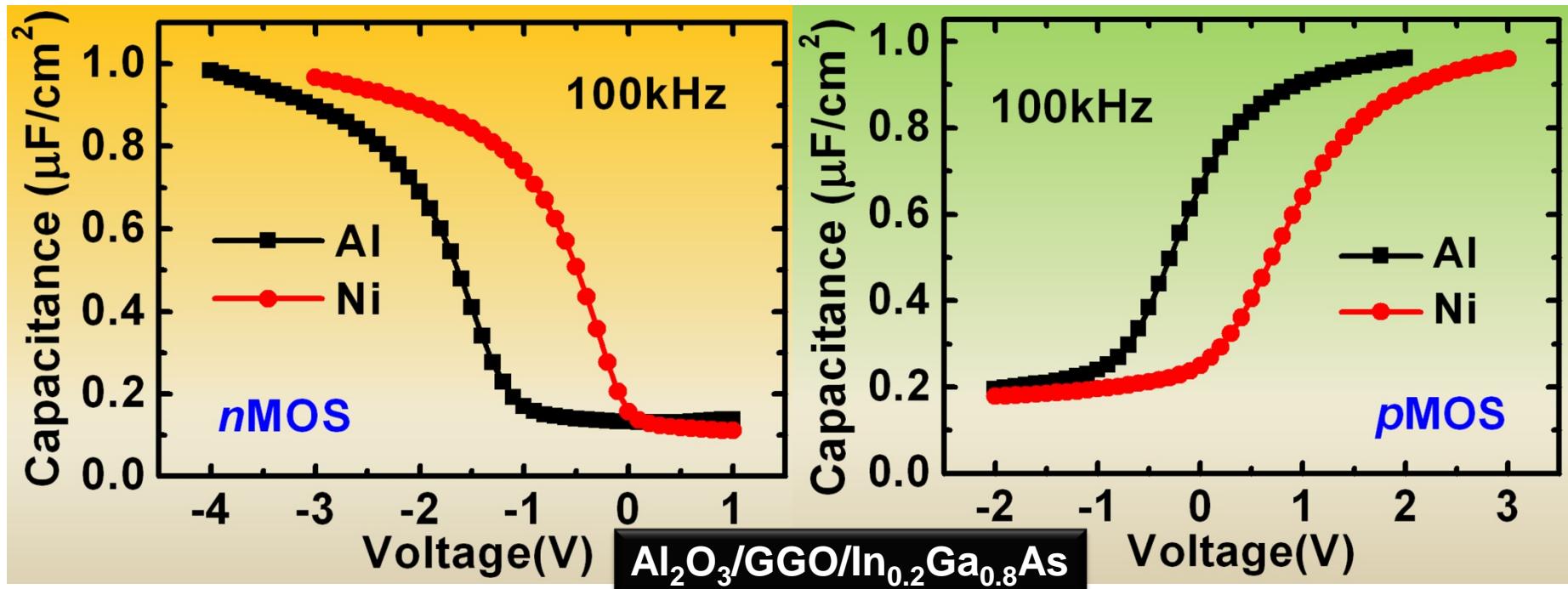
# CV Characteristics of $\text{Al}_2\text{O}_3/\text{GGO}/\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$

Y. D. Wu et al., JVST B 28(3), C3H10 (2010)



Gate	Substrate	$\kappa$ value	$C_{FB}(\text{F}/\text{cm}^2)$	Dispersion (10k-500k)
Al	p-type	15-17	0.38	2.6%
Al	n-type	14-16	0.69	4.4%
Ni	p-type	14-16	0.37	3.5%
Ni	n-type	14-17	0.69	4.2%

# Metal-work-function dependent flat-band voltages

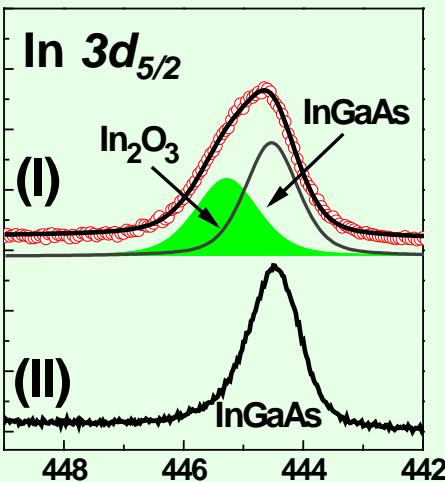


nMOS						
Gate metal	$\phi_m$ (volt)	$C_{fb}$ ( $\mu\text{F}/\text{cm}^2$ )	$V_{fb}$ (volt)	$\Delta V_{fb}$ (volt)	Dispersion (10-500kHz)	$V_{th}$ (volt)
Al	$4.16 \pm 0.1$	0.38	-1.42	$-0.29 \pm 0.1$	2.6%	0.04
Ni	$5.19 \pm 0.15$	0.37	-0.32	$-0.22 \pm 0.15$	3.5%	1.15
pMOS						
Gate metal	$\phi_m$ (volt)	$C_{fb}$ ( $\mu\text{F}/\text{cm}^2$ )	$V_{fb}$ (volt)	$\Delta V_{fb}$ (volt)	Dispersion (10-500kHz)	$V_{th}$ (volt)
Al	$4.16 \pm 0.1$	0.69	0.05	$0.17 \pm 0.1$	4.4%	-1.94
Ni	$5.19 \pm 0.15$	0.69	1.12	$0.21 \pm 0.15$	4.2%	-0.88

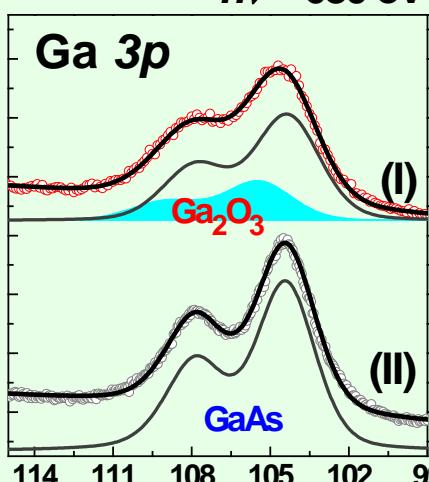
# Depth profile of ALD-HfO<sub>2</sub>/In<sub>0.15</sub>Ga<sub>0.85</sub>As: SR-XPS

## Native oxide/In<sub>0.15</sub>Ga<sub>0.85</sub>As

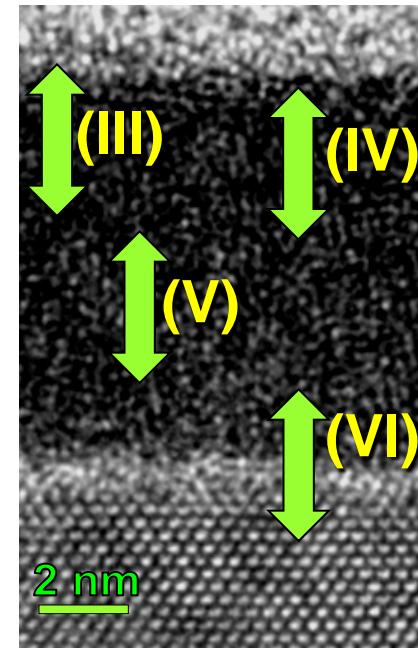
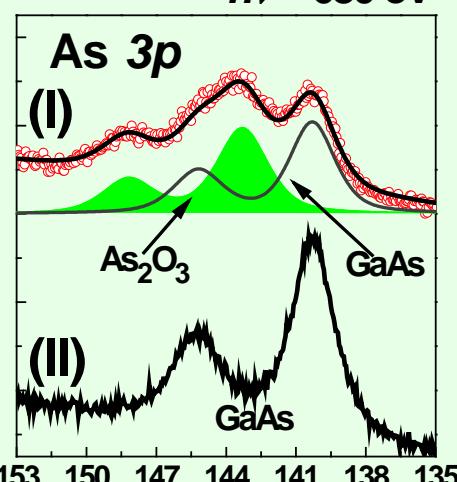
$h\nu = 680 \text{ eV}$



$h\nu = 680 \text{ eV}$

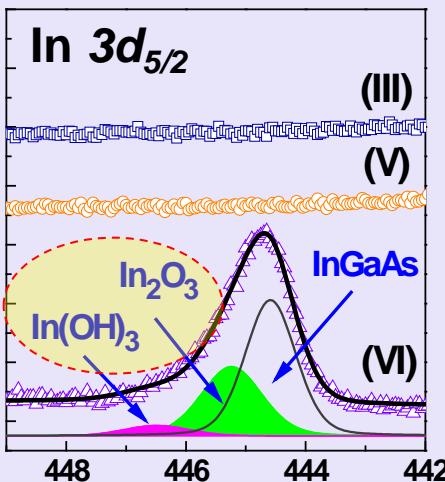


$h\nu = 680 \text{ eV}$

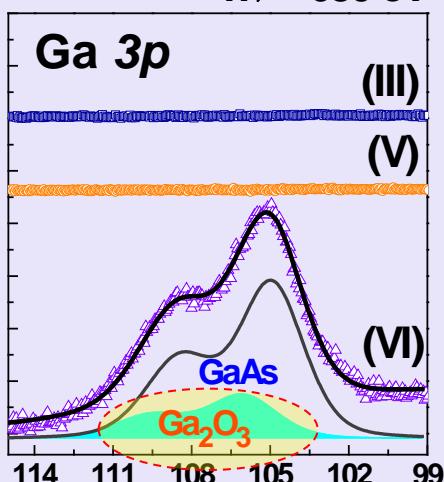


## 8nm-HfO<sub>2</sub>/In<sub>0.15</sub>Ga<sub>0.85</sub>As

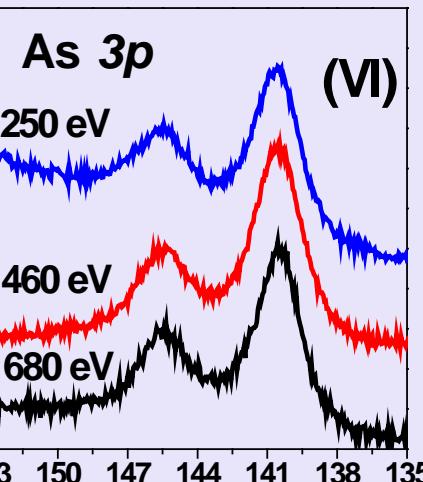
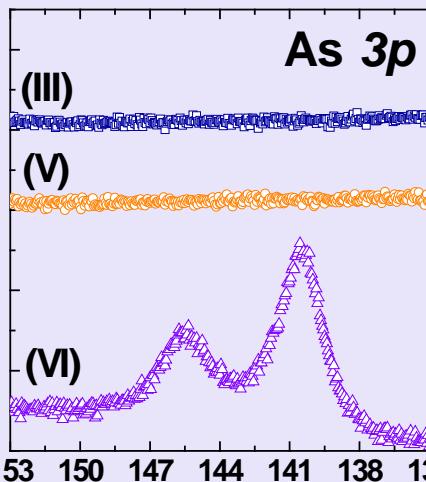
$h\nu = 680 \text{ eV}$



$h\nu = 680 \text{ eV}$



$h\nu = 680 \text{ eV}$

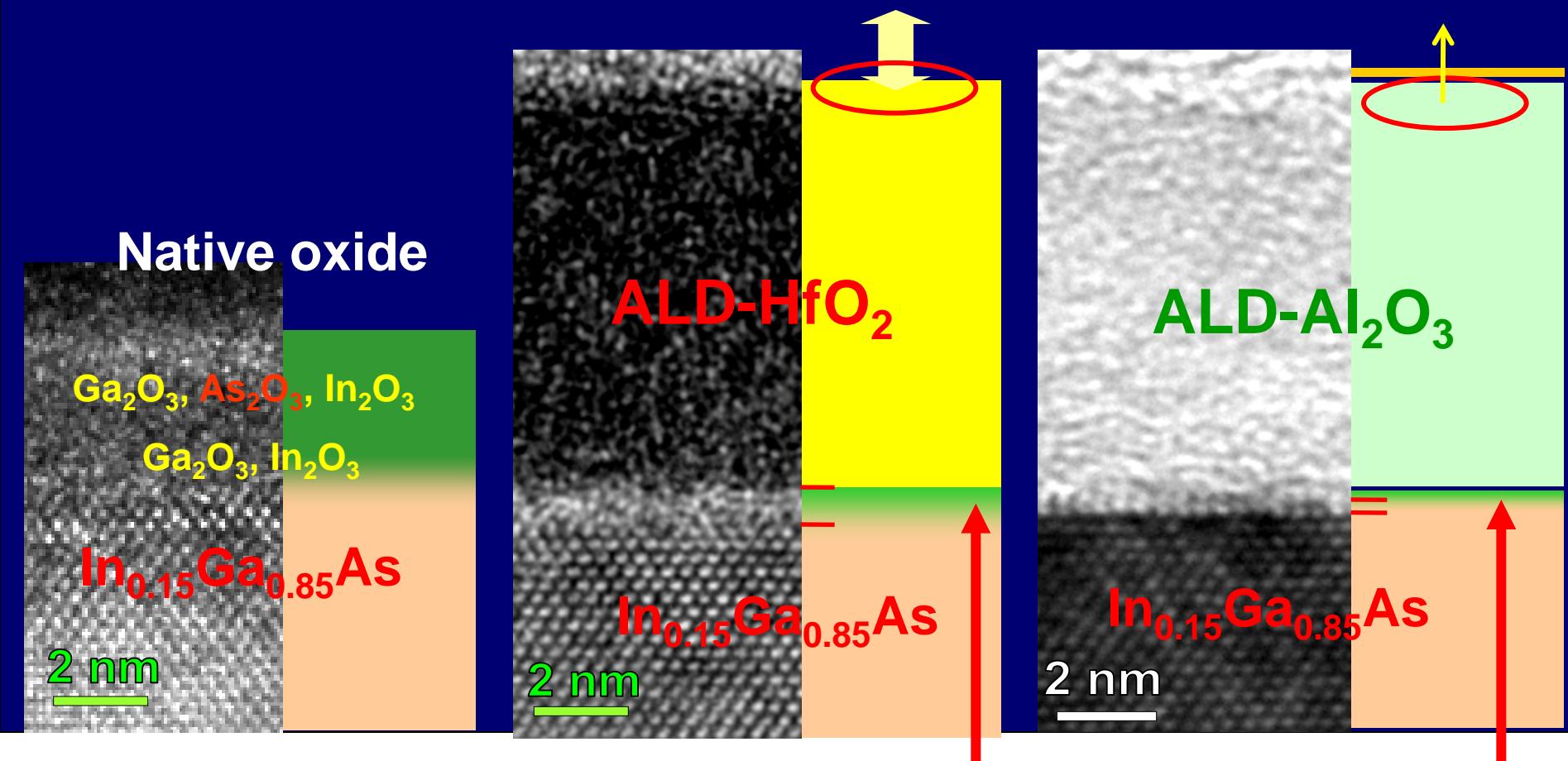


# Fermi level unpinning at ALD-oxide/InGaAs

M.L.Huang, et al, APL 87, 252104 (2005); citations:115

Different chemical reaction for TEMAH/H<sub>2</sub>O and TMA/H<sub>2</sub>O on air-exposed InGaAs surface

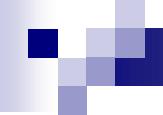
Fraction of a mono-layer As<sub>2</sub>O<sub>5</sub>



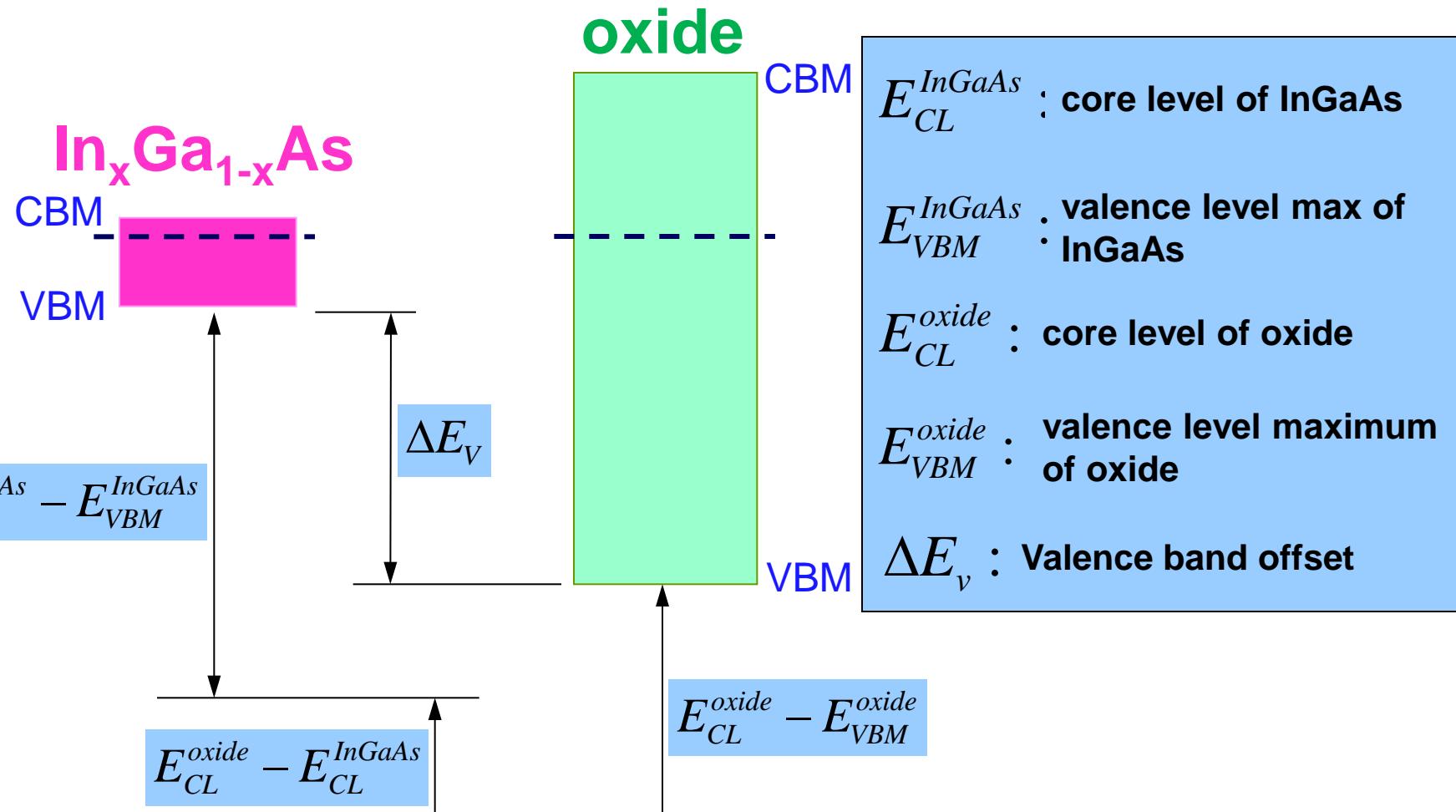
Fermi Level  
unpinning

arsenic oxide  
was removed

Interfacial layer:  
Ga<sub>2</sub>O<sub>3</sub>; In<sub>2</sub>O<sub>3</sub>; In(OH)<sub>3</sub>



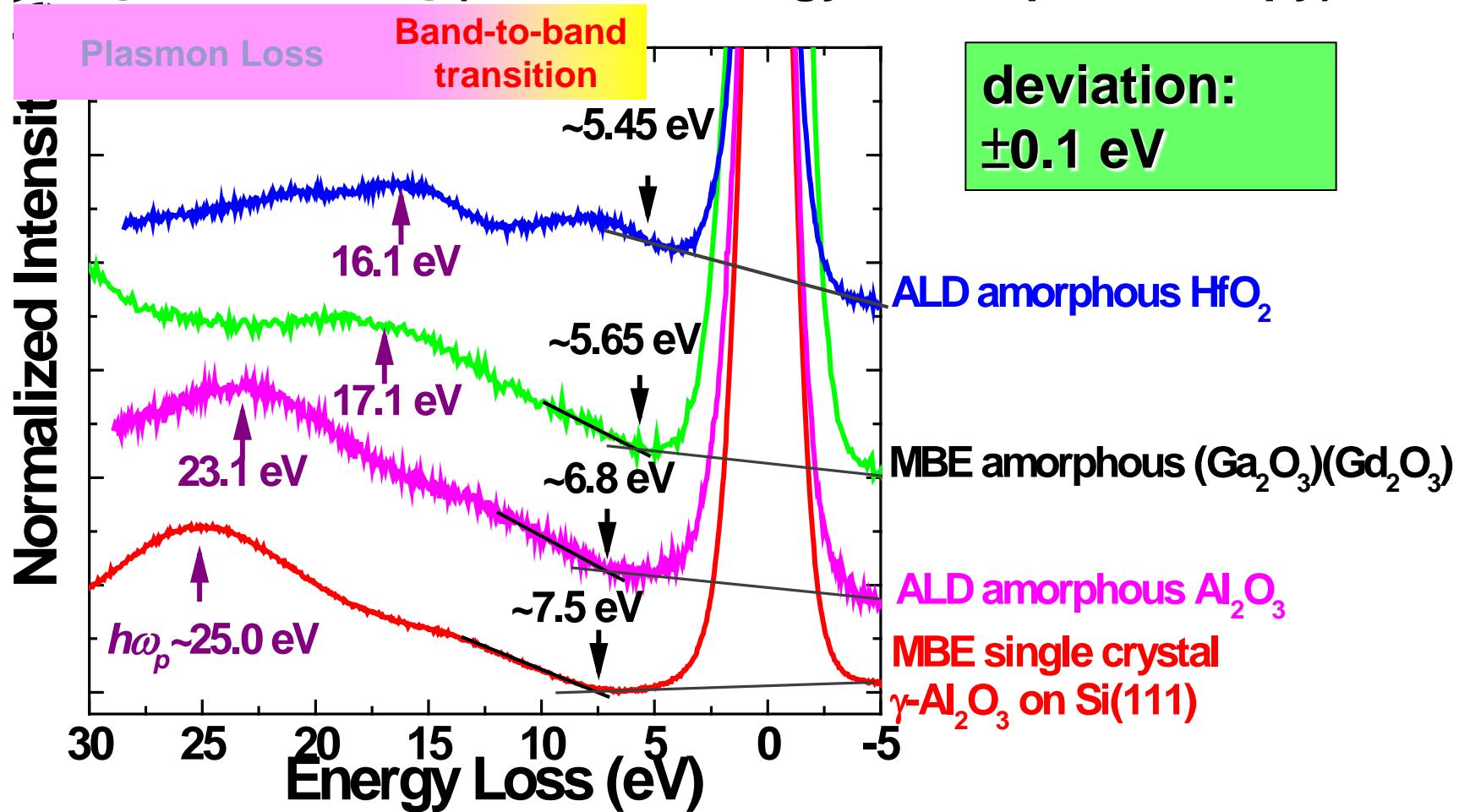
# Valence band offsets: determined by XPS



$$\Delta E_v = (E_{CL}^{\text{InGaAs}} - E_{VBM}^{\text{InGaAs}}) + (E_{CL}^{\text{oxide}} - E_{CL}^{\text{InGaAs}}) - (E_{CL}^{\text{oxide}} - E_{VBM}^{\text{oxide}})$$

# Bandgap of oxide : determined by photoemission-EELS

## O 1s EELS(Electron Energy Loss Spectroscopy)



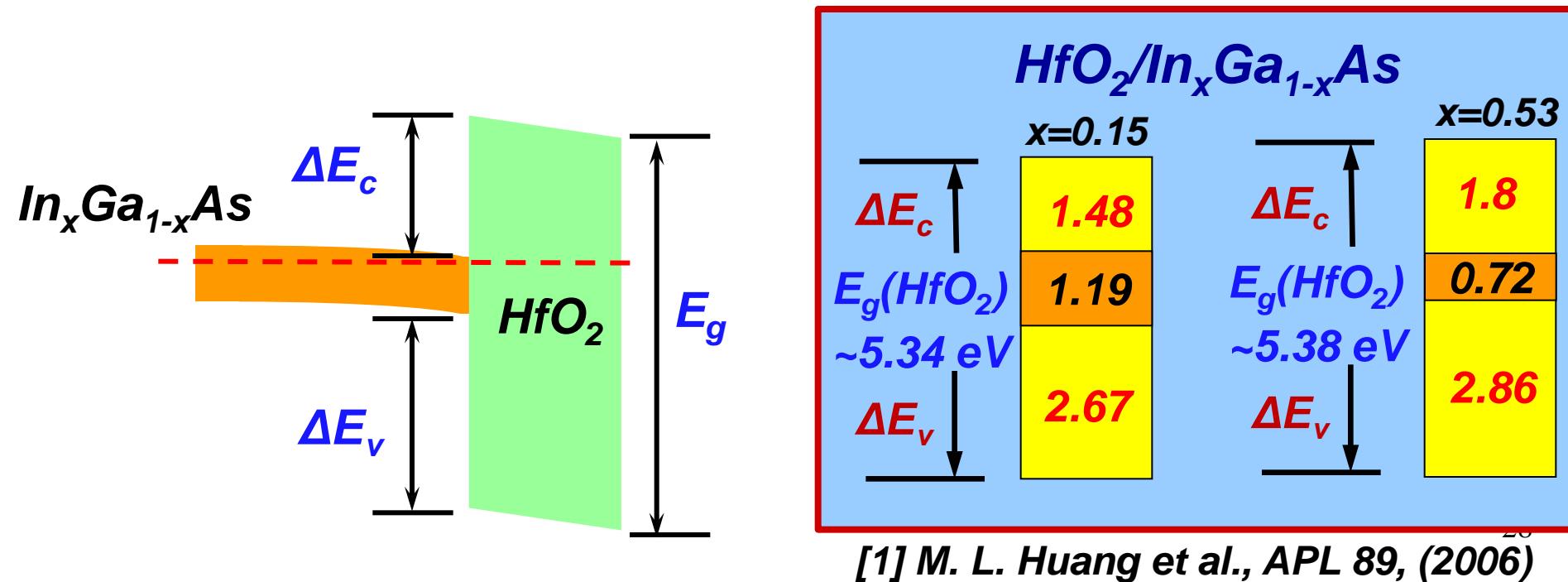
The minimum energy of band-to-band transition => Bandgap ( $E_g$ )



# Energy-Band Parameters at $HfO_2/InGaAs$

$$\Delta E_v = (E_{CL}^{InGaAs} - E_{VBM}^{InGaAs}) + (E_{CL}^{oxide} - E_{CL}^{InGaAs}) - (E_{CL}^{oxide} - E_{VBM}^{oxide})$$

	$E_{As3d_{5/2}}^{InGaAs} - E_{VBM}^{InGaAs}$	$E_{Hf4f_{7/2}}^{oxide} - E_{As3d_{5/2}}^{InGaAs}$	$E_{Hf4f_{7/2}}^{oxide} - E_{VBM}^{oxide}$	$\Delta E_V$
$HfO_2/GaAs$	40.36 eV	-23.58 eV	14.19 eV	2.62 eV
$HfO_2/In_{0.15}Ga_{0.85}As$	40.42 eV	-23.56 eV	14.19 eV	2.67 eV
$HfO_2/In_{0.53}Ga_{0.47}As$	40.57 eV	-23.52 eV	14.19 eV	2.86 eV



# Conduction band offsets: F-N tunneling

$$\ln(J_{FN}/E_{ox}^2) = S/E_{ox} + \ln(C)$$

$$S = -8\pi(2m^*)^{1/2}(\varphi)^{3/2}/3qh$$

$$C = q^3/8\pi\hbar\varphi m^*$$

$\Phi_m$ : metal work function

$X_s$ : electron affinity of InGaAs

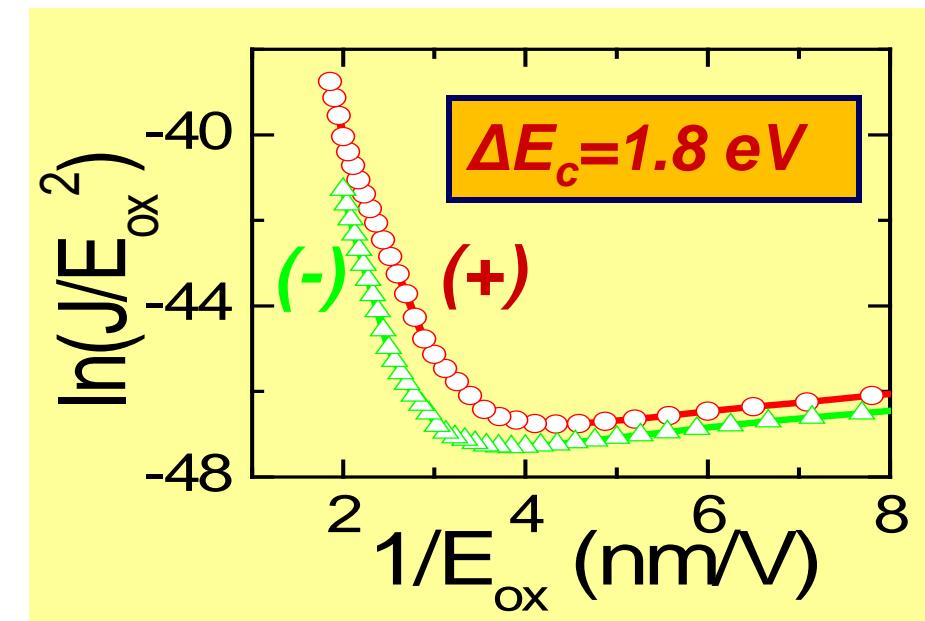
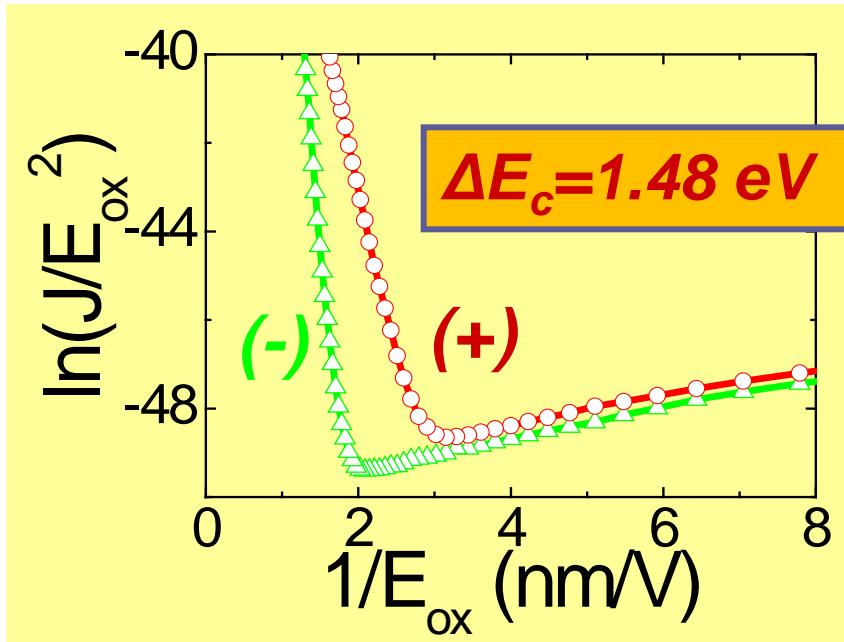
$$(\varphi^- - \varphi^+) = (\Phi_m - X_s) \quad \dots (1)$$

$$S^+ = -8\pi(2m^*)^{1/2}(\varphi^+)^{3/2}/3qh \quad \dots (2)$$

$$S^- = -8\pi(2m^*)^{1/2}(\varphi^-)^{3/2}/3qh \quad \dots (3)$$

**8.3nm-HfO<sub>2</sub> / In<sub>0.15</sub>Ga<sub>0.85</sub>As**

**7.8nm-HfO<sub>2</sub> / In<sub>0.53</sub>Ga<sub>0.47</sub>As**



[1] T.S. Lay et al, Solid State Electron. 45, (2001)

[2] Y. C. Chang, et. al. Appl. Phys. Lett, 92, 072901 (2008).

deviation :  $\pm 0.08 \text{ eV}$  29

# Discussion: Energy band parameters

**ALD-Al<sub>2</sub>O<sub>3</sub>/In<sub>x</sub>Ga<sub>1-x</sub>As**

	x=0	x=0.15	x=0.25	x=0.5
$\Delta E_c$	1.71	1.83	1.89	2.09
E <sub>g</sub> (Al <sub>2</sub> O <sub>3</sub> ) ~6.8 eV	1.42	1.19	1.05	0.75
$\Delta E_v$	3.67	3.78	3.86	3.96

**ALD-Al<sub>2</sub>O<sub>3</sub>/In<sub>0.15</sub>Ga<sub>0.85</sub>As**

$\Delta E_c$	1.83 ± 0.1 eV	$\Delta E_c$	1.6 ± 0.1 eV
E <sub>g</sub> (Al <sub>2</sub> O <sub>3</sub> ) ~6.8 eV	1.19 eV		
$\Delta E_v$	3.78 eV	$\Delta E_v$	

XPS method      FN tunneling

**ALD-HfO<sub>2</sub>/In<sub>x</sub>Ga<sub>1-x</sub>As**

	x=0	x=0.15	x=0.25	x=0.5
$\Delta E_c$	1.41	1.59	1.66	1.84
E <sub>g</sub> (HfO <sub>2</sub> ) ~5.45 eV	1.42	1.19	1.05	0.75
$\Delta E_v$	2.62	2.67	2.74	2.86

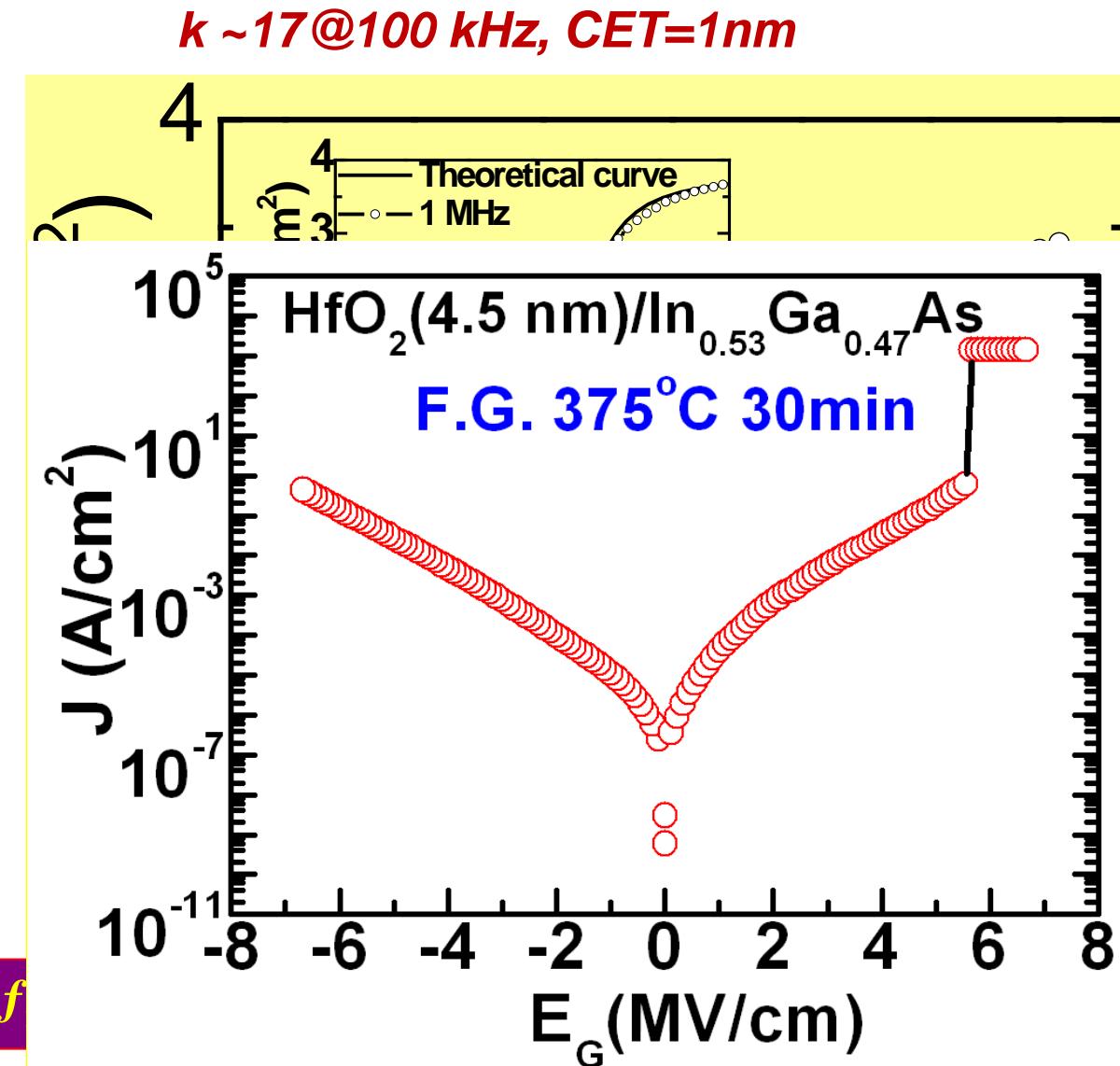
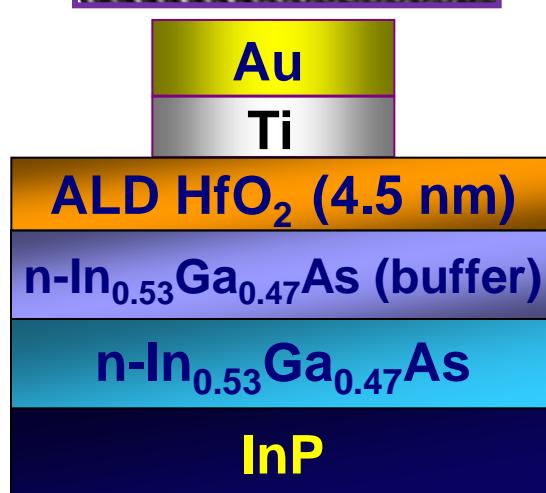
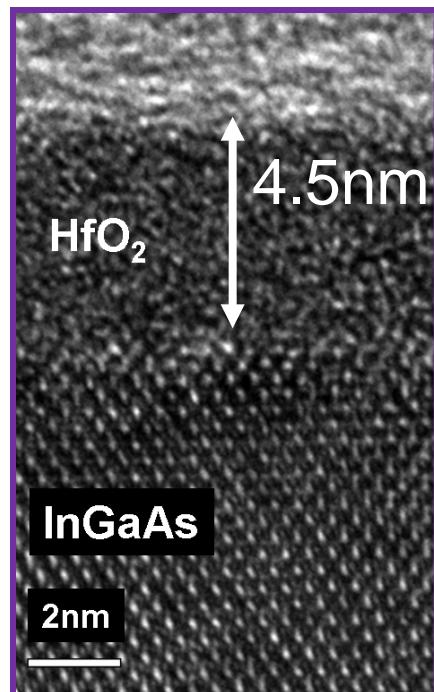
deviation : ±0.1 eV

**ALD-HfO<sub>2</sub>/In<sub>0.5</sub>Ga<sub>0.5</sub>As**

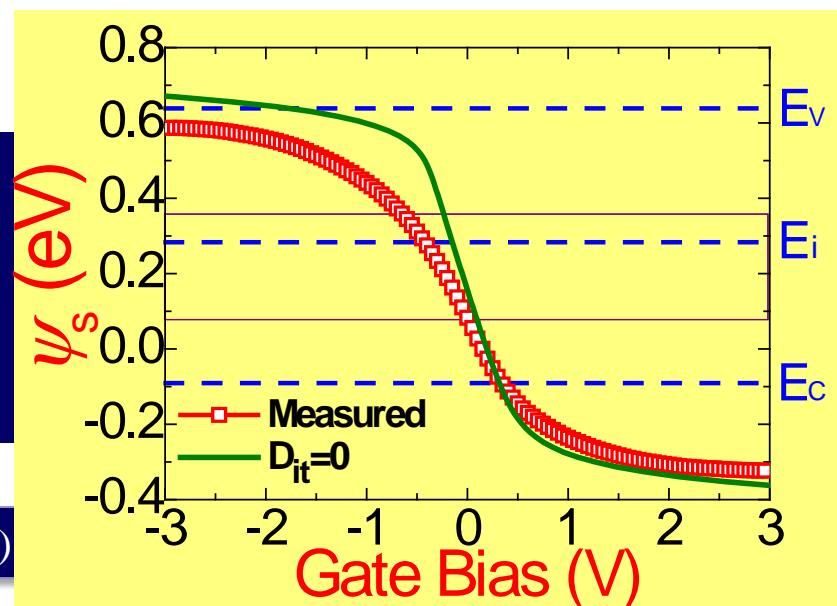
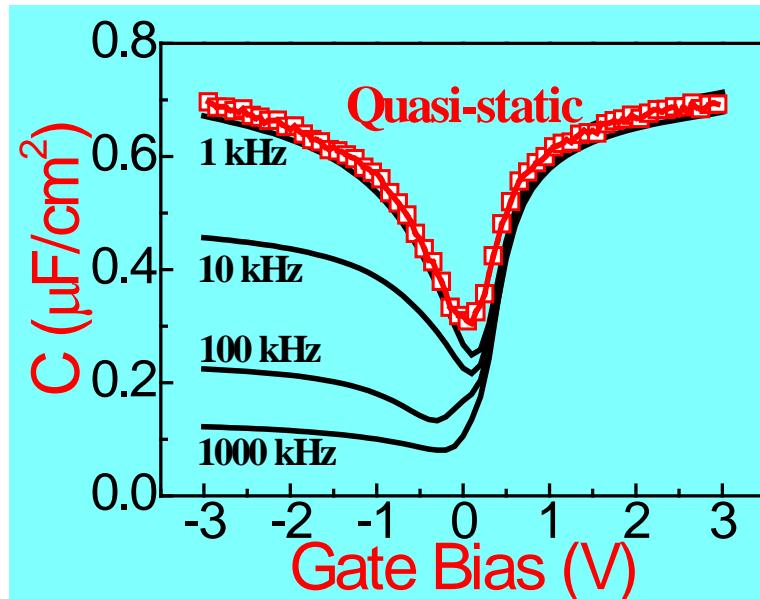
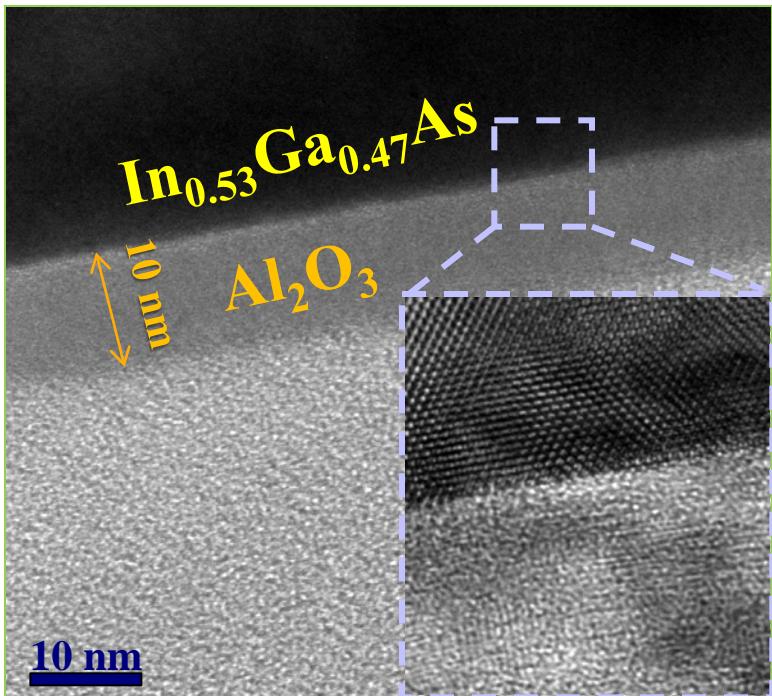
$\Delta E_c$	1.84 ± 0.1 eV	$\Delta E_c$	1.8 ± 0.1 eV
E <sub>g</sub> (HfO <sub>2</sub> ) ~5.45 eV	0.75 eV		
$\Delta E_v$	2.86 eV	$\Delta E_v$	

XPS method      FN tunneling

# *ALD-HfO<sub>2</sub> on In<sub>0.53</sub>Ga<sub>0.47</sub>As with short air exposure ~10 min*



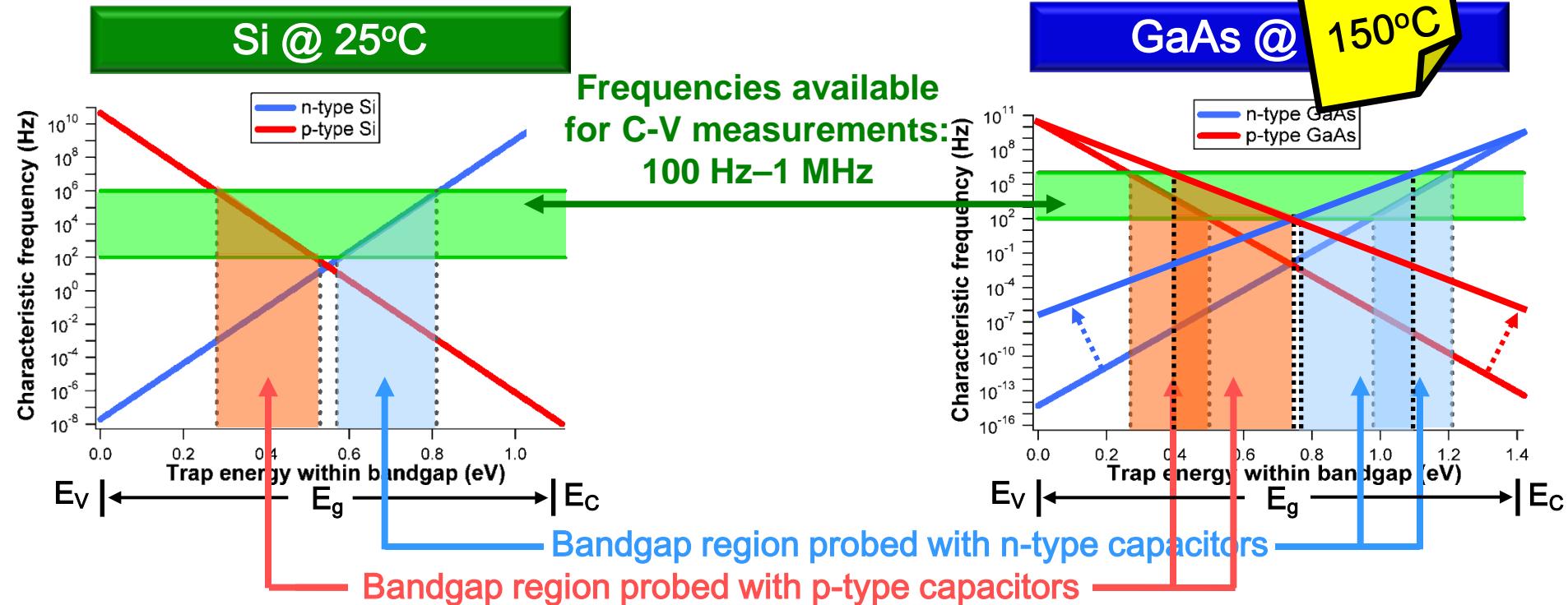
# Achieving a low $D_{it}$ in ALD- $\text{Al}_2\text{O}_3$ on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ with short air exposure



- very sharp  $\text{Al}_2\text{O}_3/\text{InGaAs}$  interface
- Fermi-level moves across the nearly entire bandgap
- high FLME of **63%** near midgap

# $D_{it}$ Extraction for Wide Bandgap Semiconductors

Characteristic trapping frequency as a function of trap depth:

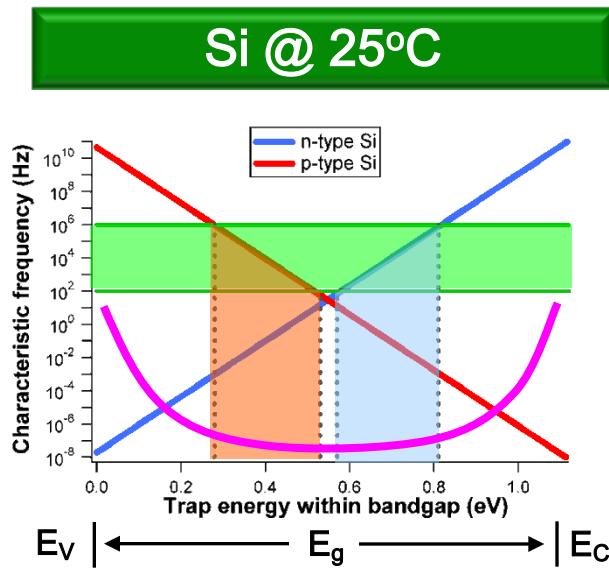


For GaAs MOS devices:

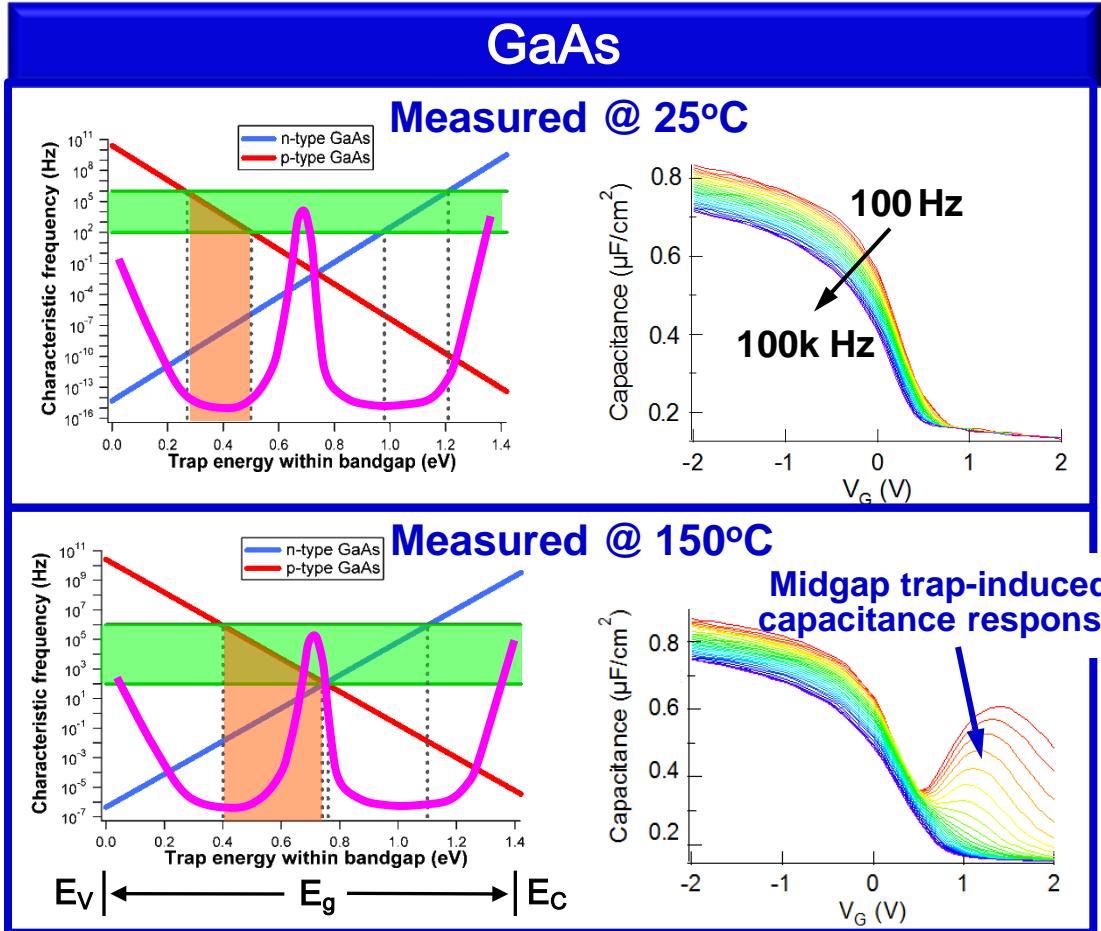
- Only very small portions of bandgap can be probed at 25°C.
  - The midgap region is not accessible at all with these frequency range.
- Measurements at 150°C giving a better coverage of the midgap region

# Why $D_{it}$ Extraction at Midgap is Important for GaAs?

$D_{it}$  distribution (—) as a function of the energy above  $E_v$ :



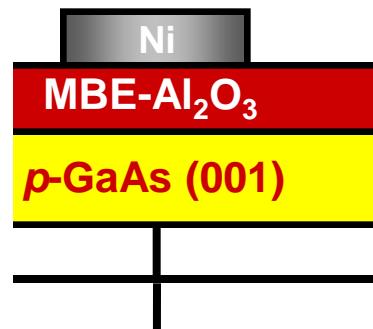
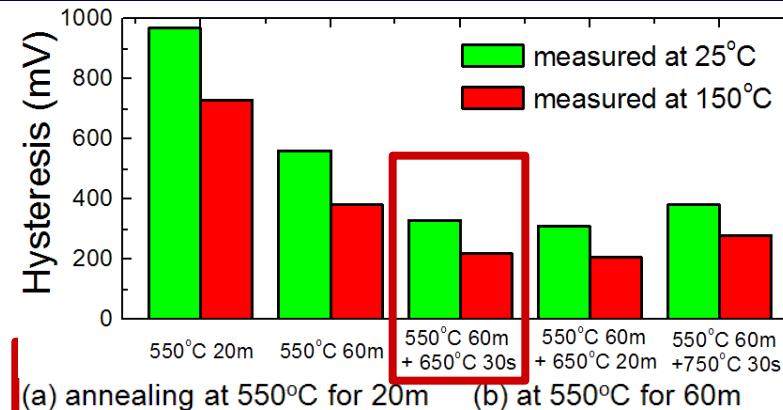
- Unlike  $\text{SiO}_2/\text{Si}$  showing a flat  $D_{it}$  distribution at midgap, oxide/GaAs interfaces have high  $D_{it}$  at midgap → serious Fermi level pinning near midgap



W.E. Spicer *et al.*, JVST 91, 1422 (1979)  
Y.C. Chang *et al.*, 68<sup>th</sup> DRC (2010)

G. Brammertz *et al.*, APL 91, 133510 (2007)  
K. Martens *et al.*, IEEE TED 55, 547 (2008)

# Impact of Post-Deposition-Annealing



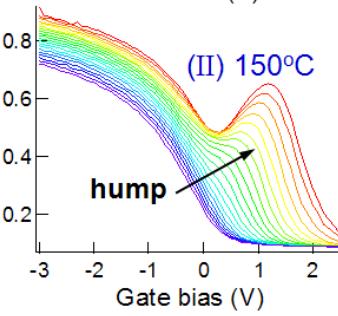
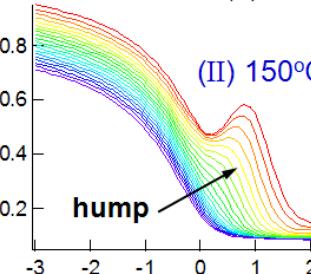
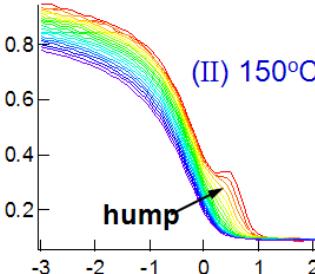
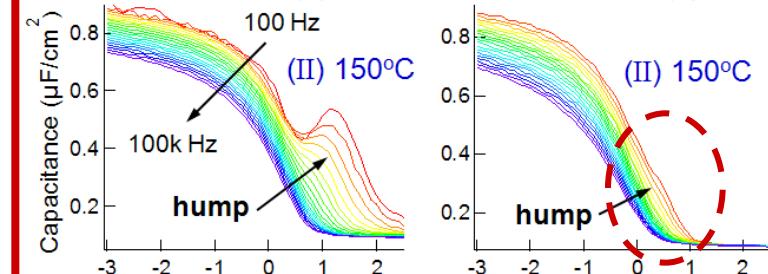
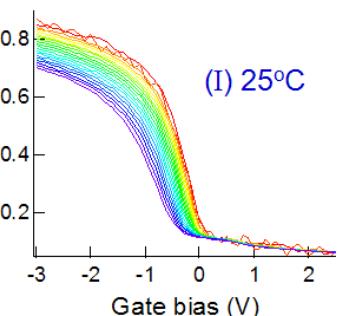
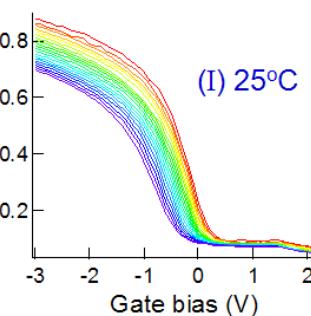
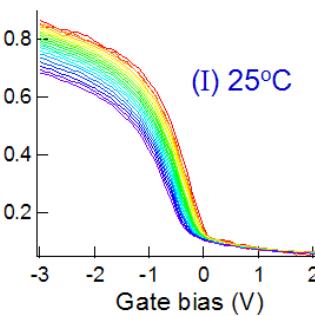
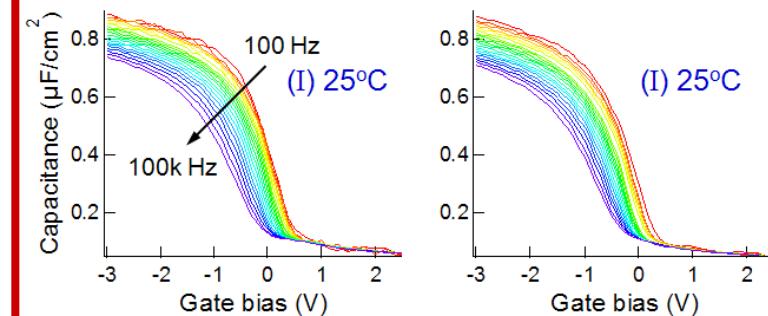
**Ga-rich reconstructed surface**

(a) annealing at 550°C for 20m    (b) at 550°C for 60m

(c) at 550°C for 60m and 650°C for 30s

(d) at 550°C for 60m and 650°C for 20m

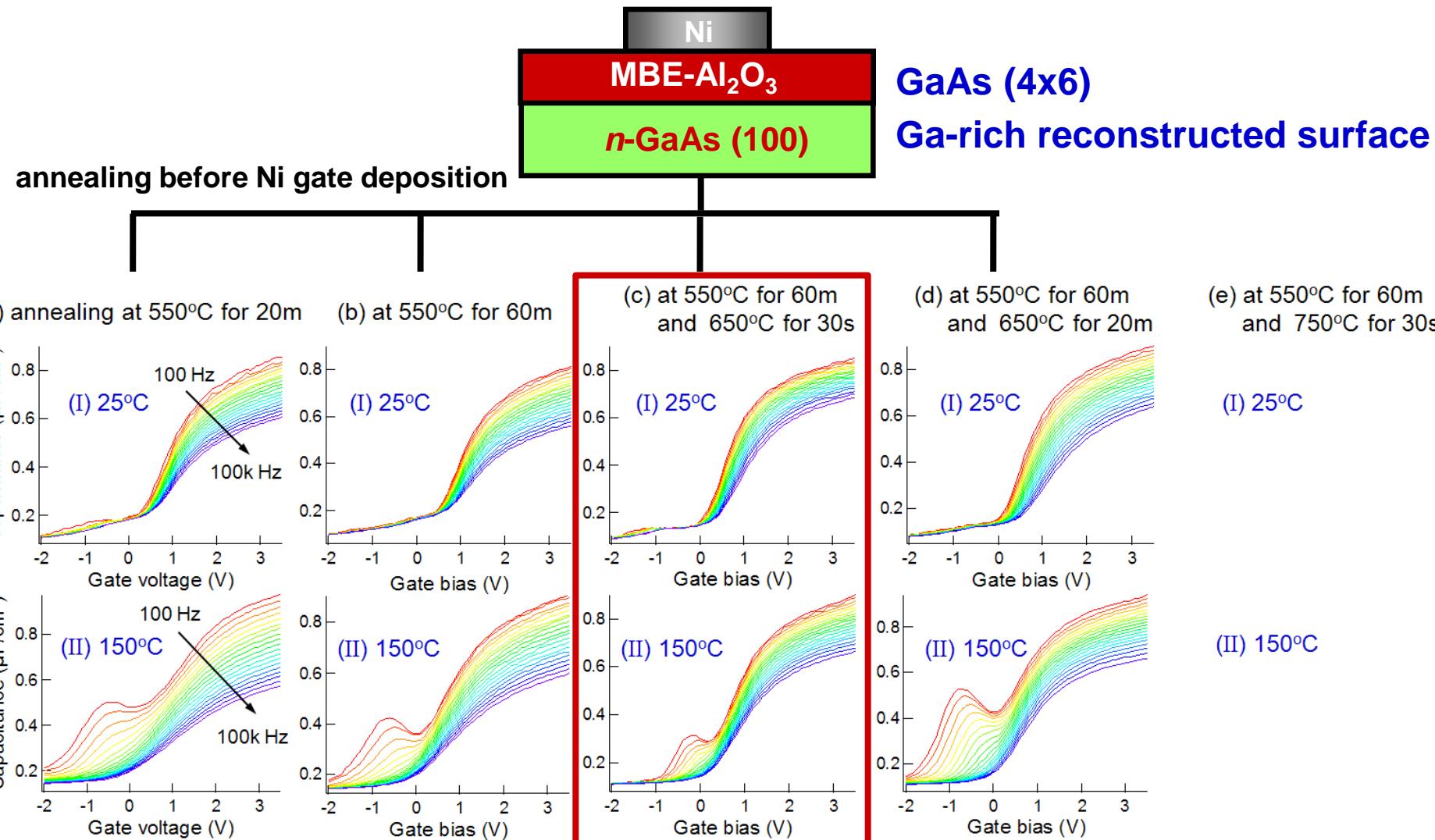
(e) at 550°C for 60m and 750°C for 30s



**Long time annealing at 550°C is necessary for reducing the hump**

Additional **RTP 650°C** is useful for optimizing the frequency dispersion and hysteresis

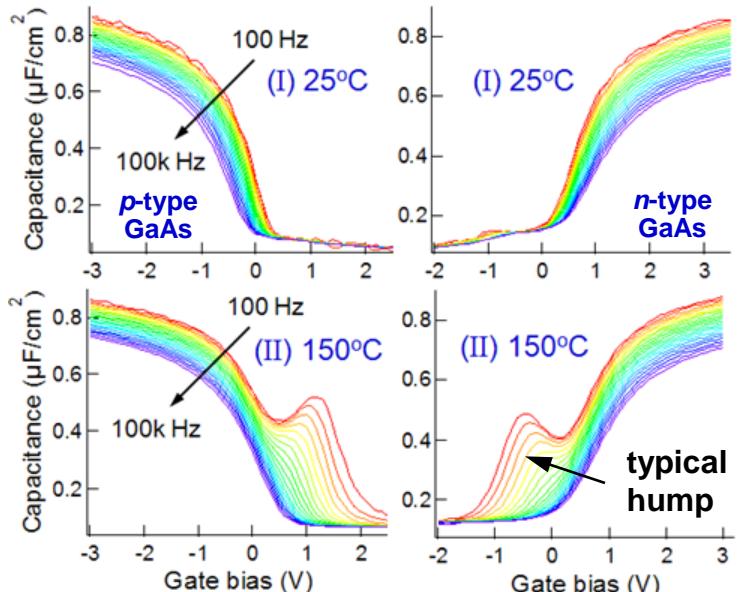
# Impact of *Post-Deposition-Annealing*



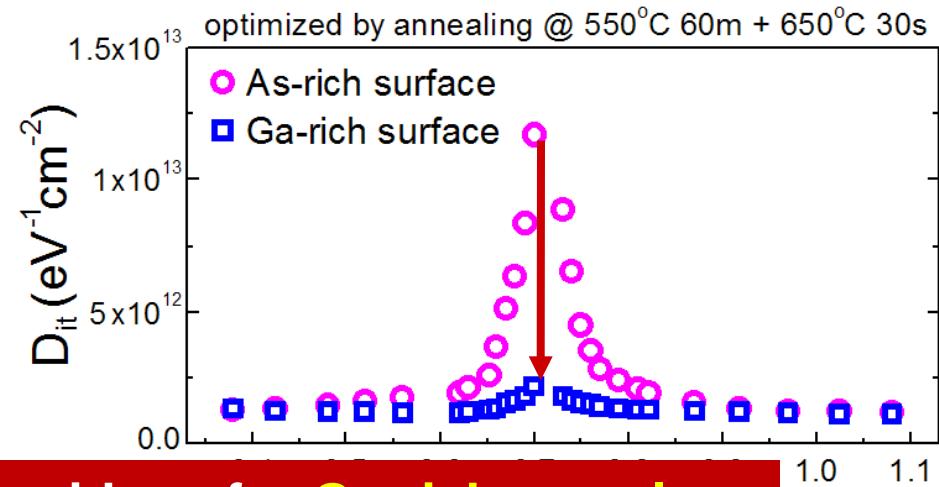
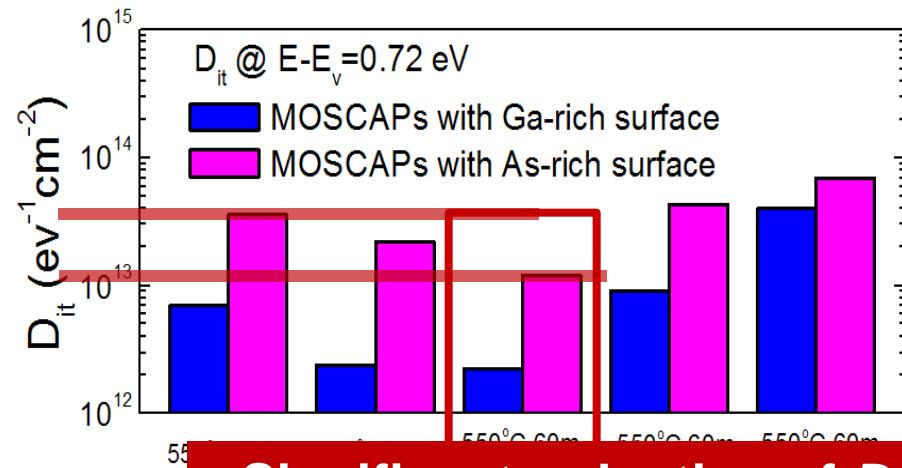
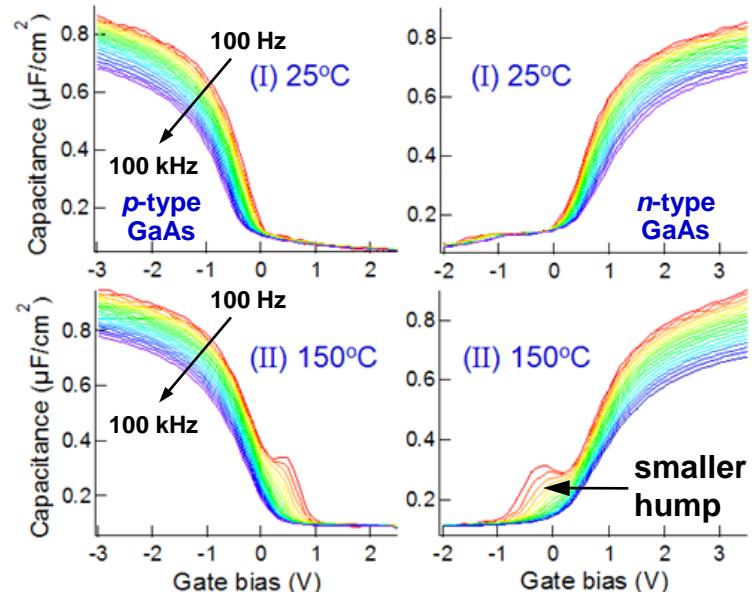
**Same trend of annealing effect on *n*-type GaAs substrates**

# Impact of Initial Surface Reconstruction

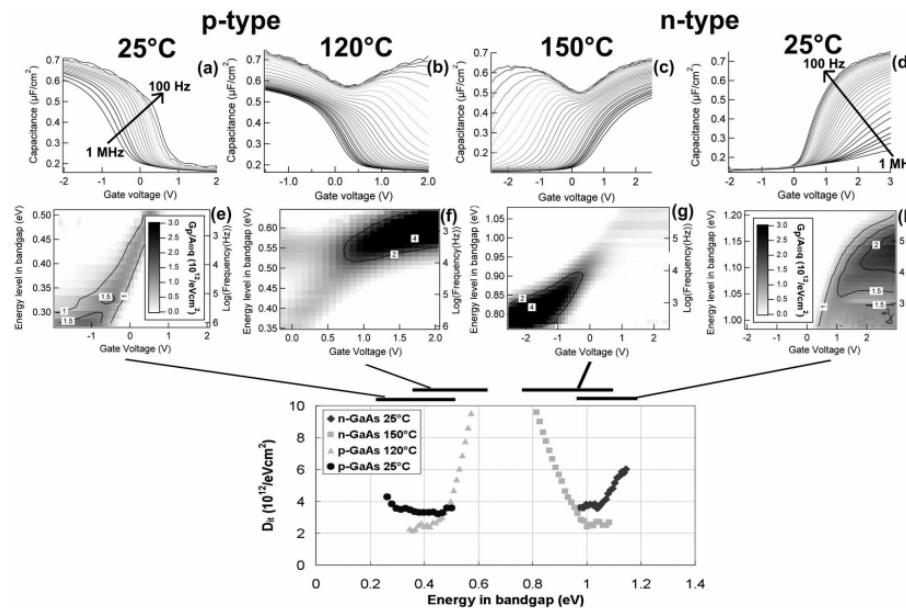
## As-rich reconstruction: c(4x4)



## Ga-rich reconstruction: 4x6

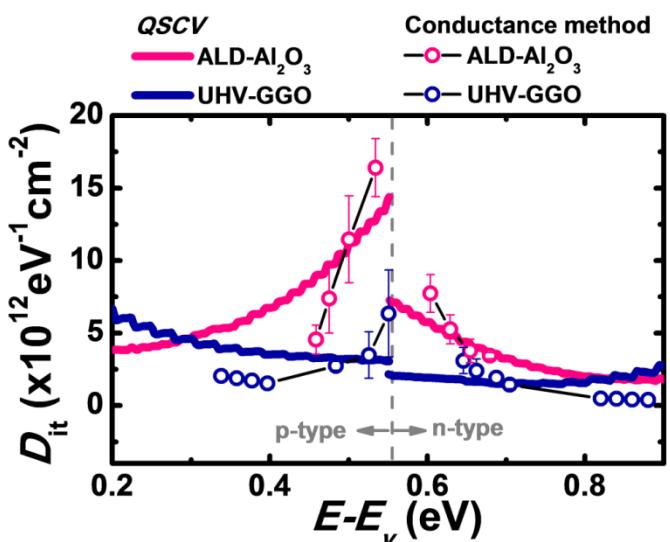
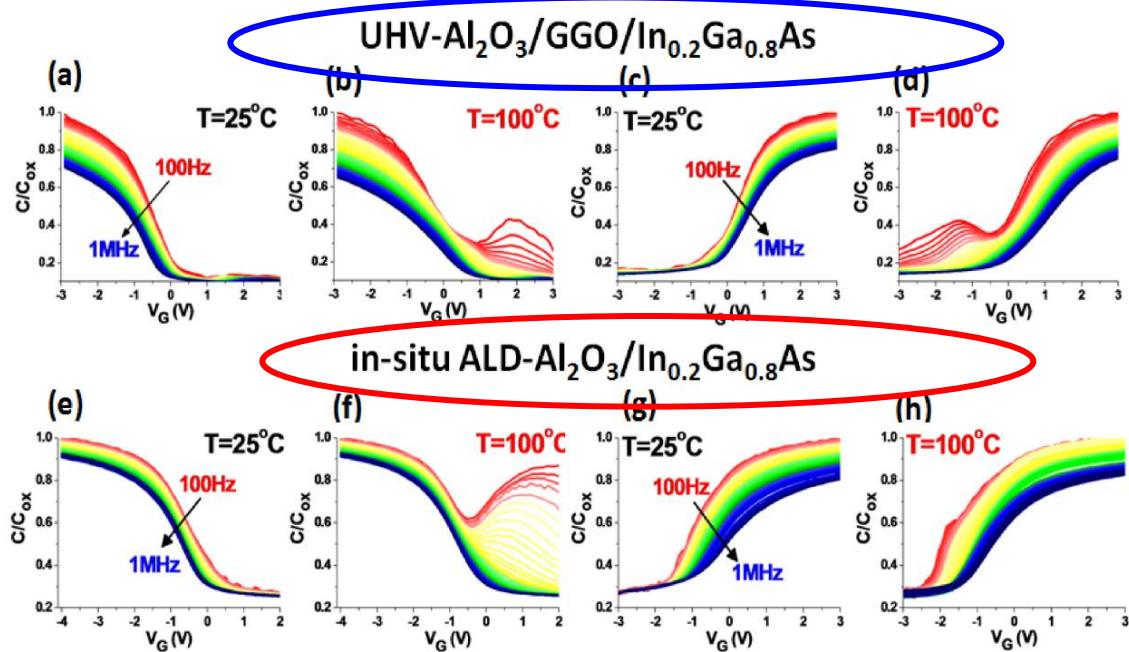


Significant reduction of  $D_{it}$  at midgap for **Ga-rich samples**

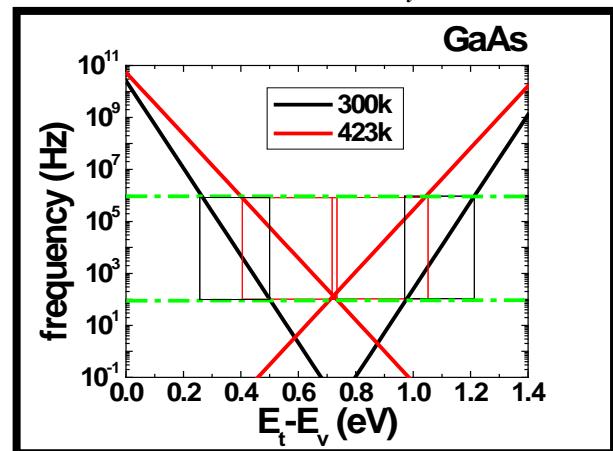


$D_{it}$  spectrum for ALD-Al<sub>2</sub>O<sub>3</sub>/GaAs with HCl clean  
 (G. Brammertz *et al*, Appl. Phys. Lett. **93**, 183504 (2008))

# $D_{it}$ distribution – Conductance method



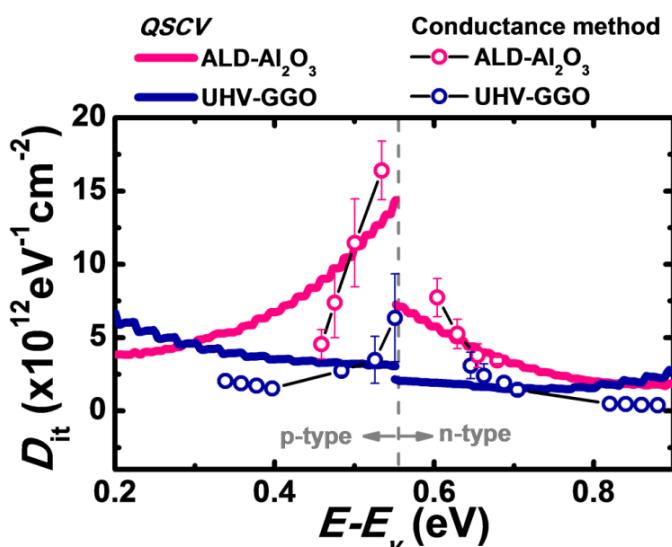
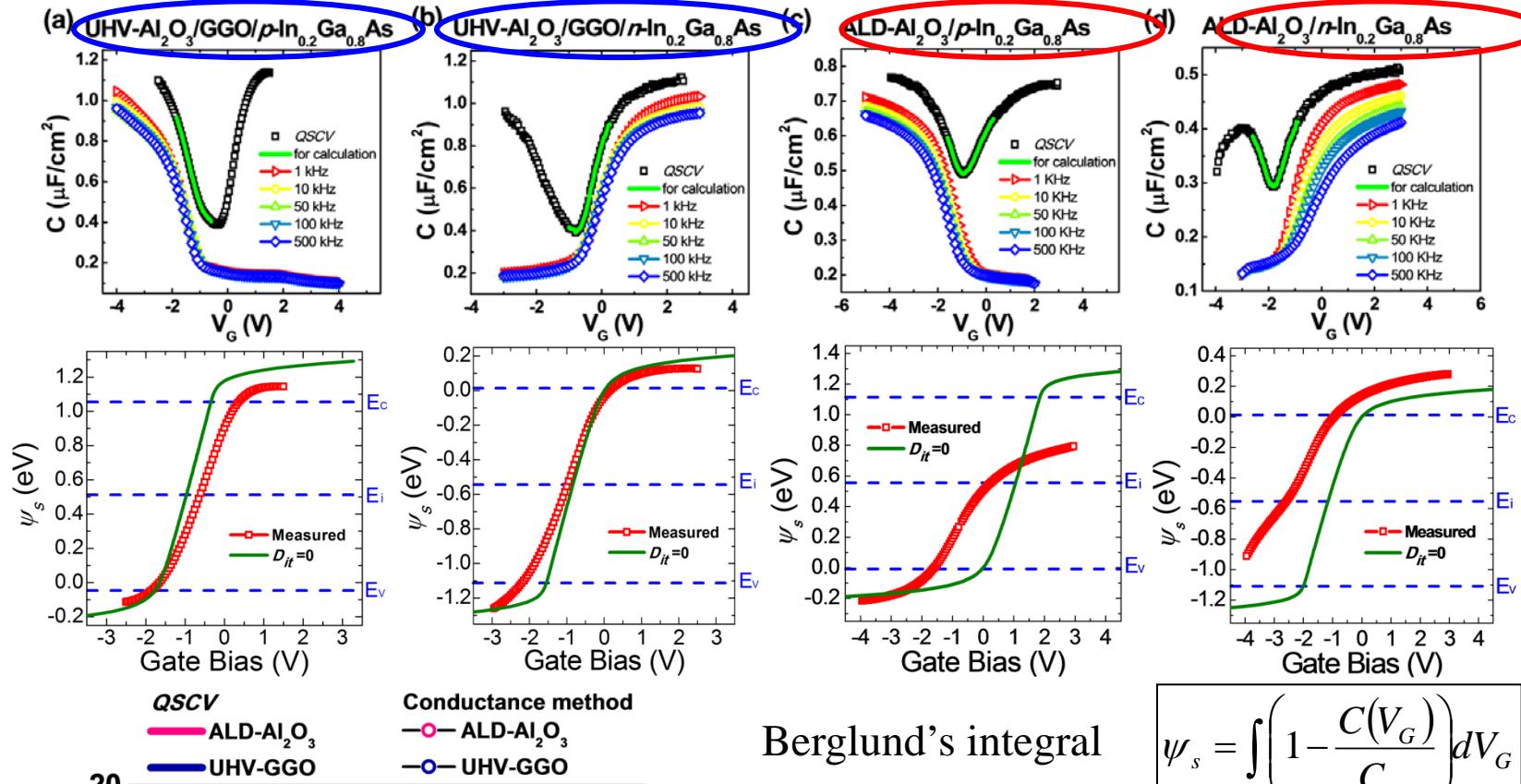
$$\tau = \frac{1}{2\pi f} = \frac{\exp(\Delta E / kT)}{\sigma v_t N}$$



Mid-gap  $D_{it}$ 's from conductance measured at high temperatures (G. Brammertz et al, IMEC)

1.  $D_{it}$  spectra derived using both QSCV and temperature-dependent conductance method;
2. both UHV- $\text{Al}_2\text{O}_3/\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)/$  and ALD- $\text{Al}_2\text{O}_3/n-$  and  $p-\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  MOSCAPs were investigated;
3. ALD- $\text{Al}_2\text{O}_3/\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  interface shows a high mid-gap  $D_{it}$  peak spectrum;
4. no discernible  $D_{it}$  peak for UHV- $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)/\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  interface

# $D_{it}$ distribution – calculation from QS-CV method



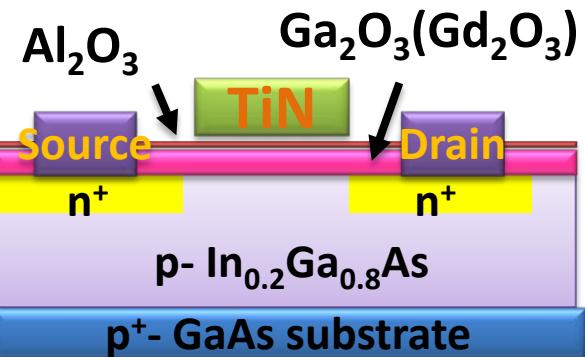
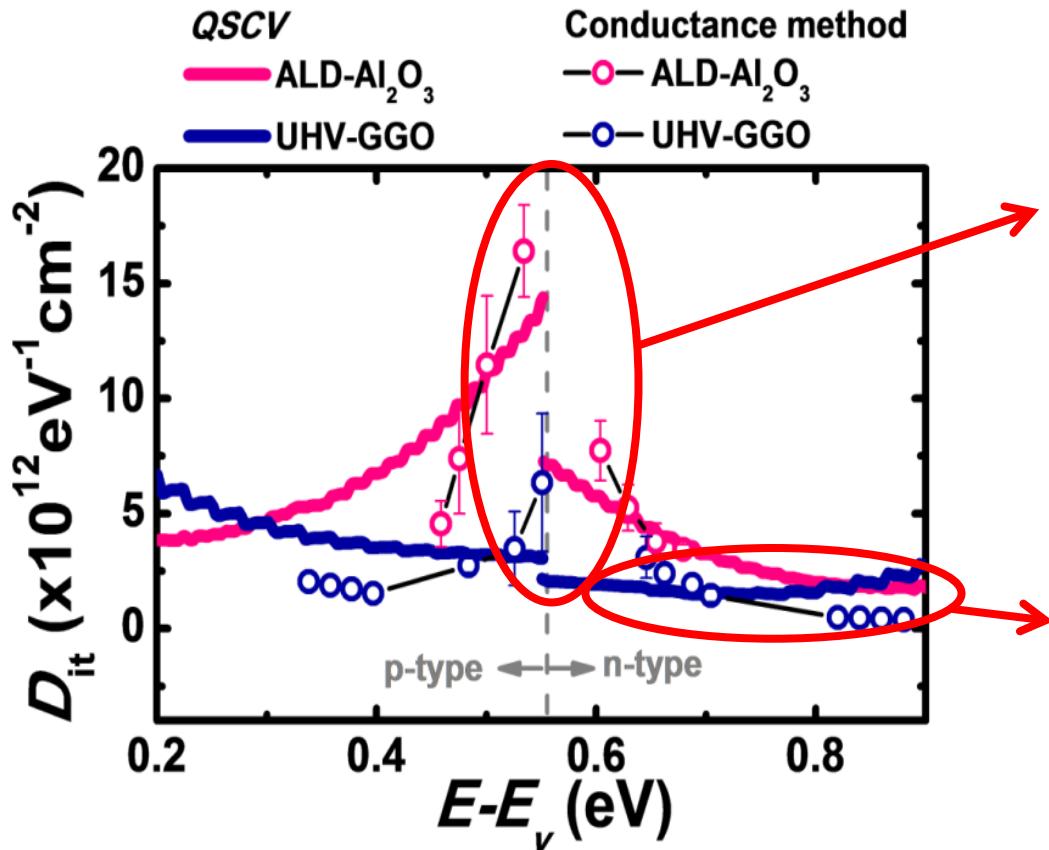
Berglund's integral

$$\psi_s = \int \left( 1 - \frac{C(V_G)}{C_{ox}} \right) dV_G$$

$$D_{it} = \frac{C_{ox}}{q^2} \left[ \left( \frac{d\psi}{dV_G} \right)^{-1} - 1 \right] - \frac{C_D}{q^2} = \frac{C_{ox}}{q^2} \frac{d(V_G(\psi) - V_G^0(\psi))}{d\psi}$$

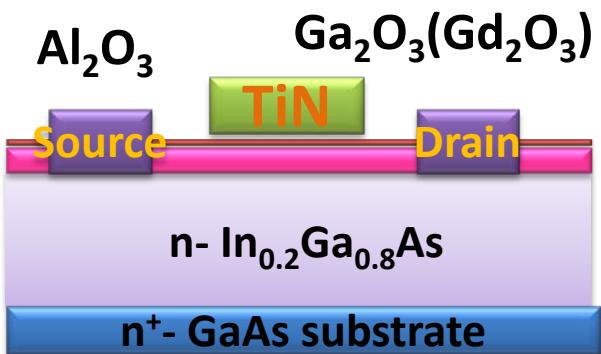
1. a gradual trending down of  $D_{it}$  from  $E_v$  to  $E_c$ ;
2. a mean  $D_{it} \sim 10^{12} \text{ eV}^{-1} \text{cm}^{-2}$  near the mid-gap of  $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  with no discernible peak

# Impact of $D_{it}$ on Device Performance



## Inversion channel MOSFET

Fermi level near  $E_v$  should be driven across mid-gap to generate minority carriers



## Depletion-mode MOSFET

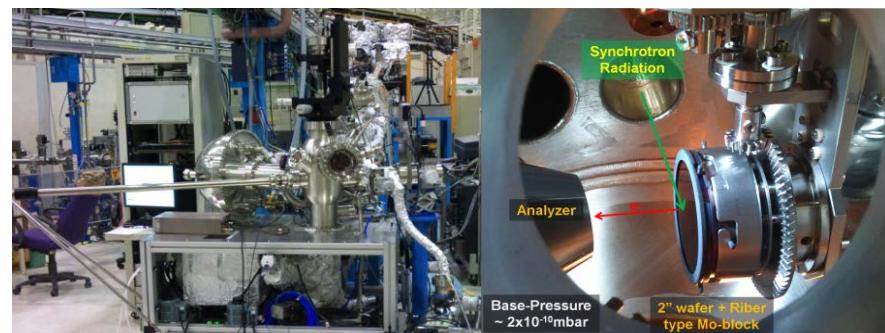
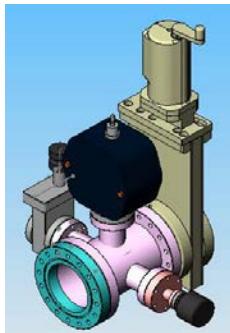
Fermi level near  $E_c$  should be driven back to mid-gap to deplete channel

# *In situ* growth and analysis of oxide/III-V interfaces

- ✓ *In-situ* ALD- & MBE-oxides on freshly MBE grown InGaAs surfaces
- ✓ Portable UHV chamber for 2"wafer (Pressure  $< 3 \times 10^{-10}$  torr)
- ✓ *In-situ* high resolution synchrotron radiation photoemission analysis

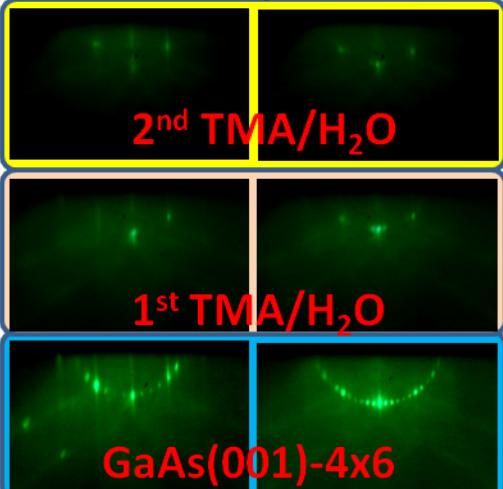


*In-situ* MBE/ALD/XPS/STM Portable UHV chamber

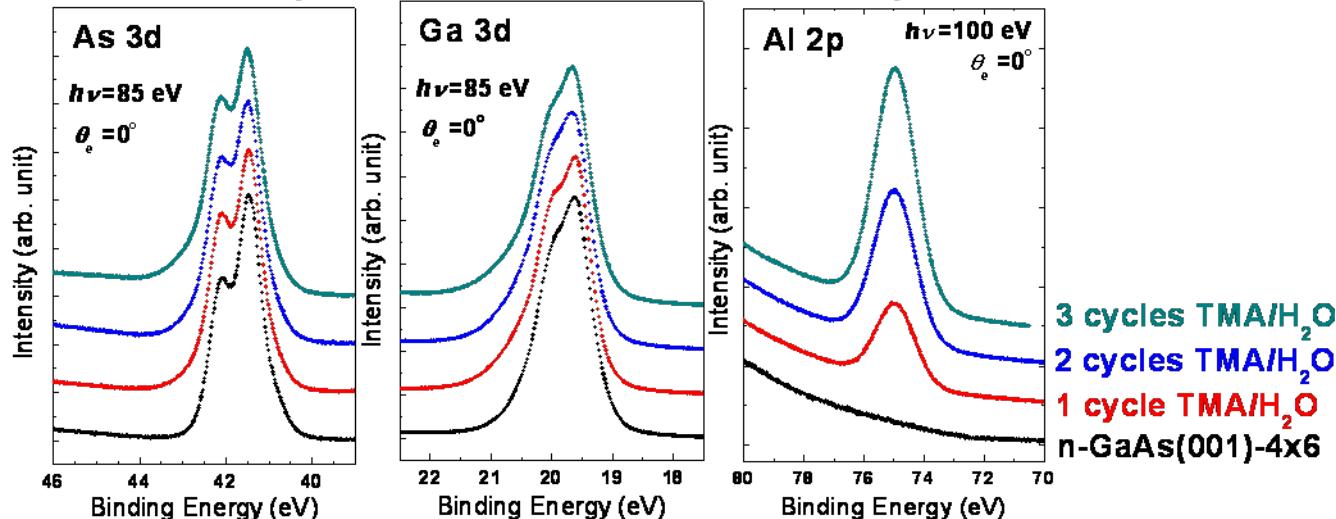


*In-situ* synchrotron radiation XPS analysis

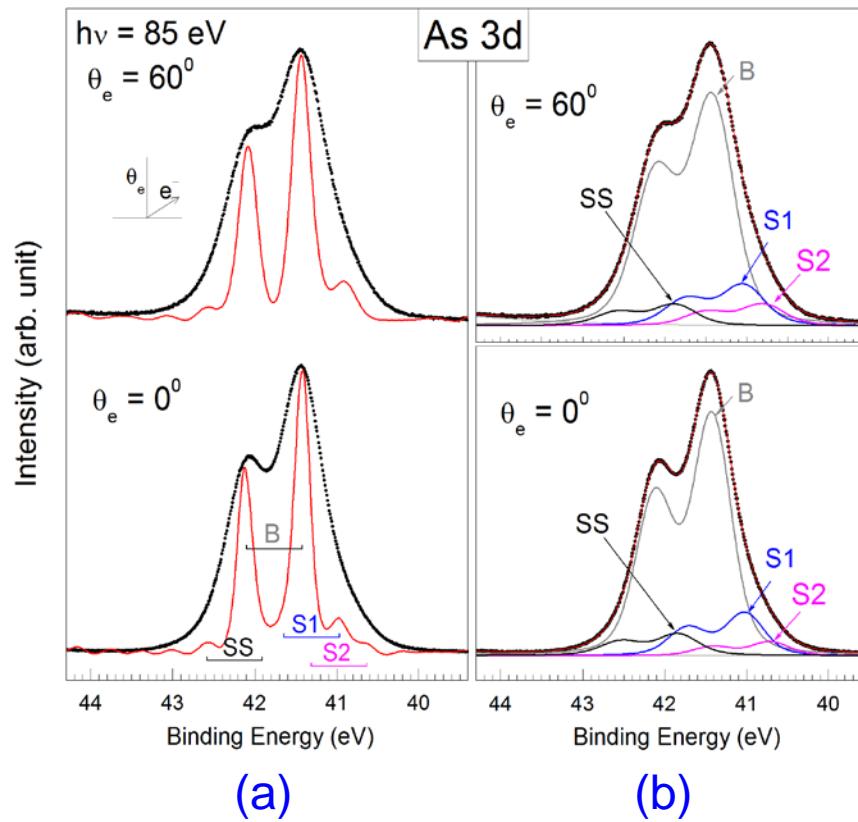
RHEED pattern



*In situ* synchrotron radiation-XPS analyses



# In-situ ALD-Al<sub>2</sub>O<sub>3</sub> on Ga-rich n-GaAs(001)-4x6 surface: A synchrotron-radiation photoemission study

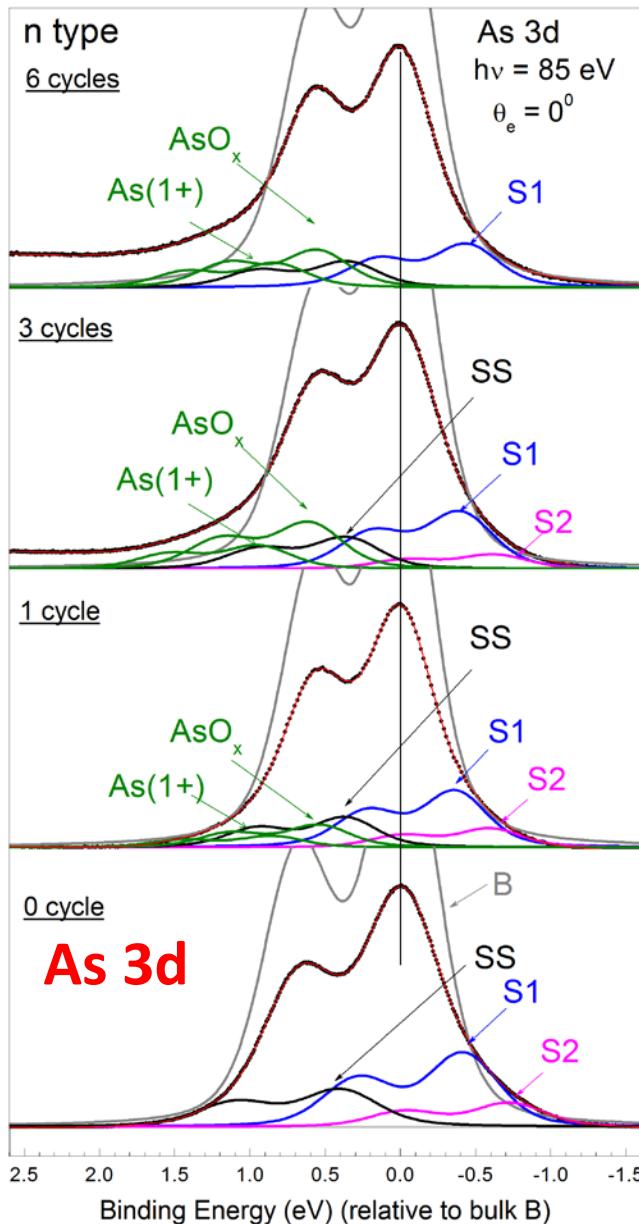


(a) As 3d core level spectra of the clean GaAs(001)-4x6 surface taken with  $h\nu = 85$  eV in normal and  $60^\circ$  off-normal emission. The line represents a de-convolution of the curve. (b) An analytical fit to the spectra plotted in (a).

Symbols B, SS, S1, and S2 stand for the doublets of bulk, the subsurface, the surface As atoms at the faulted position, and the As in the surface As-Ga dimer.

# *In situ* ALD-Al<sub>2</sub>O<sub>3</sub>/GaAs(001) interfaces: cycle by cycle analyses

Y. H. Chang et al, Microelectronic Engineering 88, 1101 (2011)



**TMA/H<sub>2</sub>O: 6 cycles**

S1 : can not be passivated completely

S2: peak disappeared

As(1+), AsOx: exist at interface

**TMA/H<sub>2</sub>O: 3 cycles**

S1, S2 peak ↓

As(1+), AsOx ↑

**\*No As-As at the ALD-Al<sub>2</sub>O<sub>3</sub>/GaAs interface**

**TMA/H<sub>2</sub>O: 1 cycles**

S1, S2 peak ↓

As(1+): S1 As bond to O-Al (As-O-Al)

AsOx: S2 As bond to Al-O(As-Al-O)

**Clean GaAs(001)-4x6**

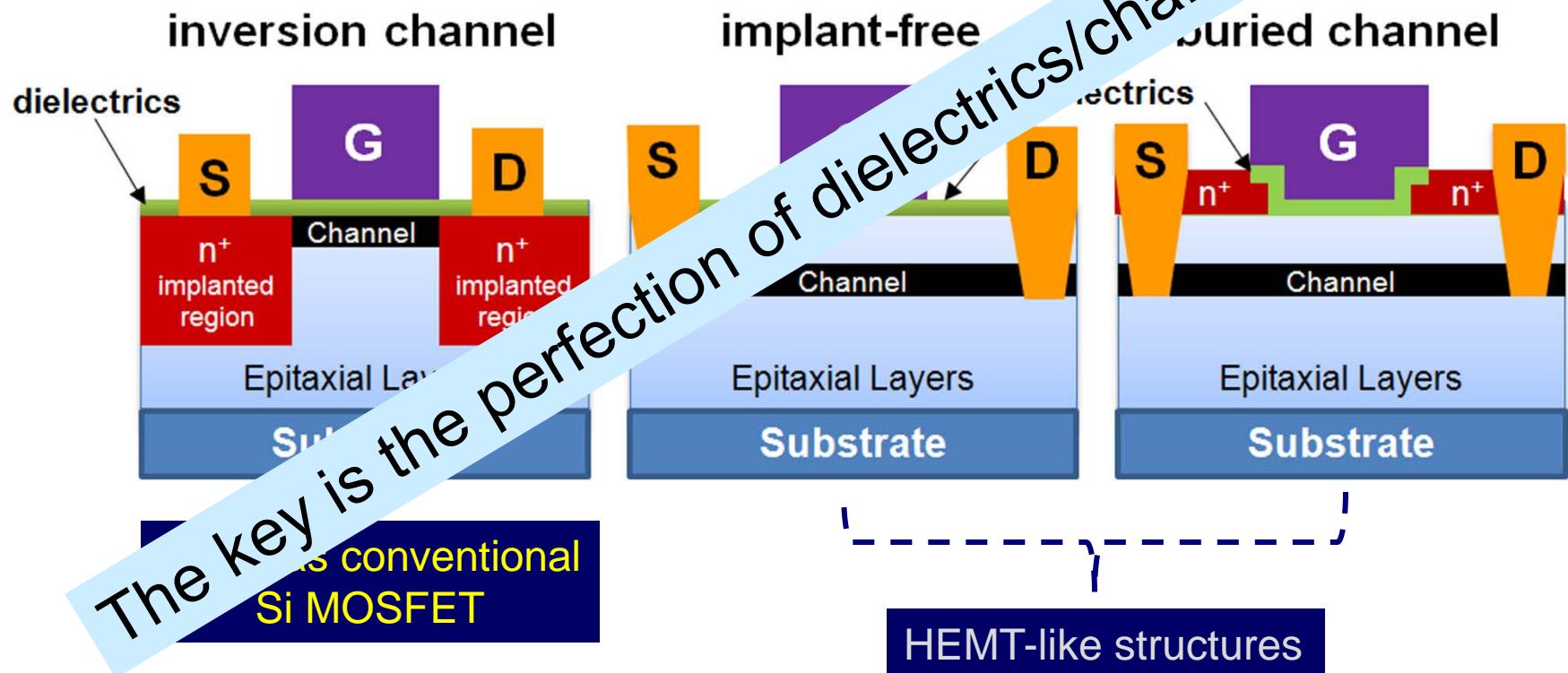
Surface-related doublet peak

**S1: As in the faulted position (-380meV), excess charge**

**S2: As in As-Ga dimer (-652meV), excess charge**

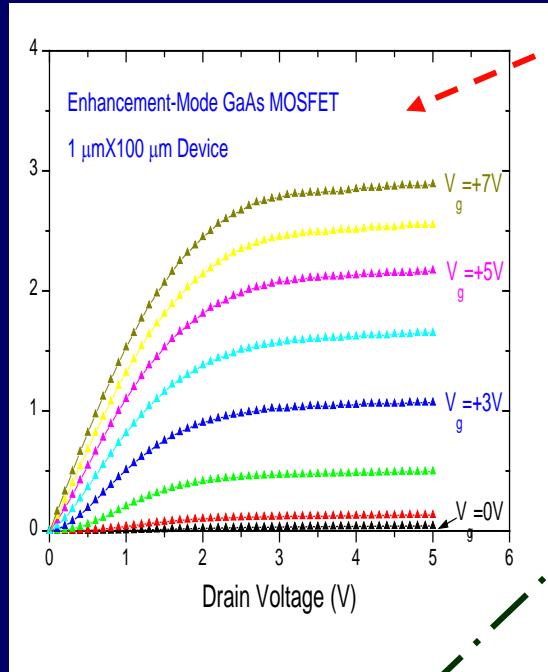
**SS: As-As dimer in the subsurface layer (+338meV)**

# Enhancement-mode devices

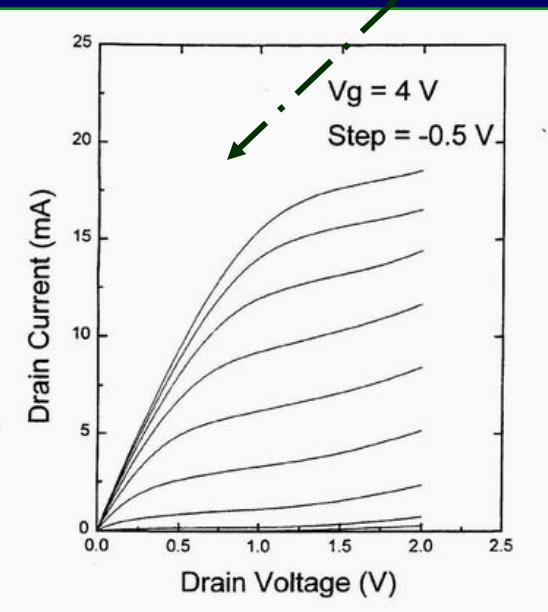
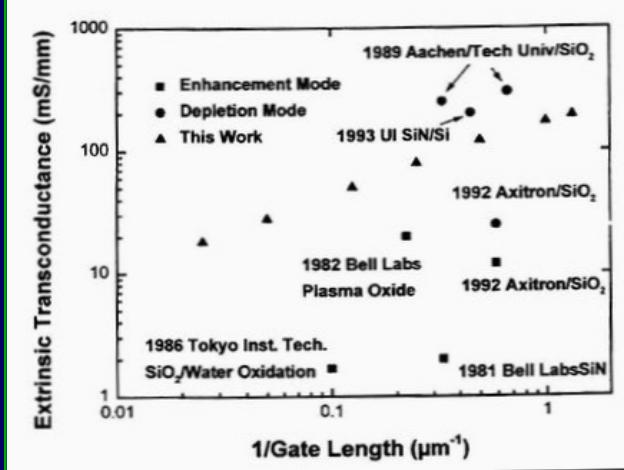
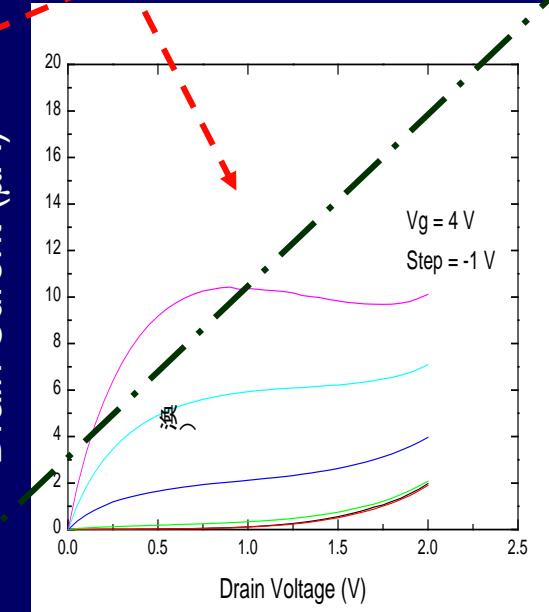


# Inversion channel n-GaAs and n-InGaAs/InP MOSFET

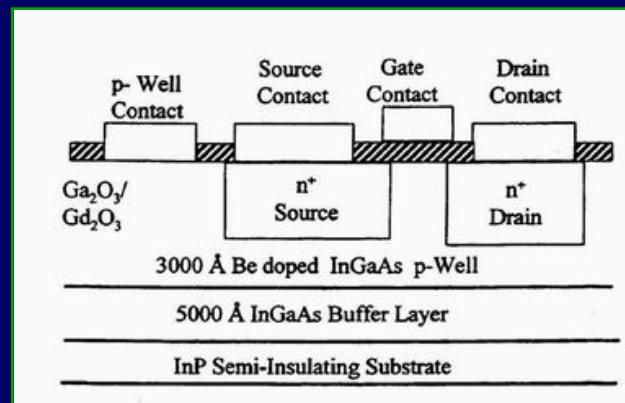
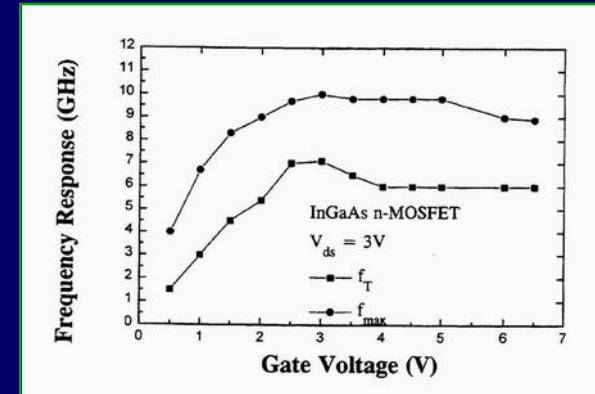
Drain Current (mA)



Drain Current ( $\mu\text{A}$ )



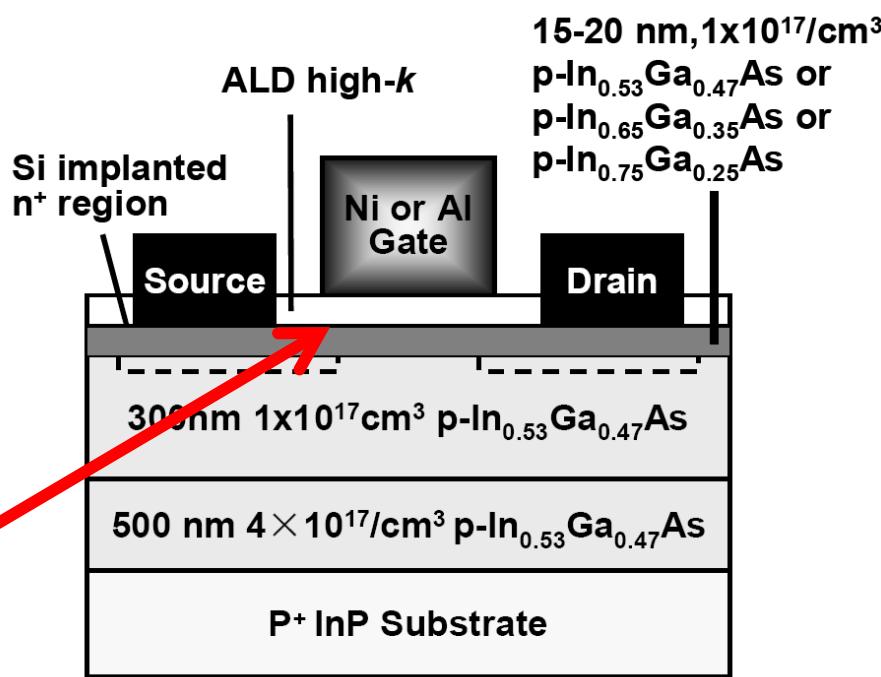
Drain current drive capability improved over 100 times  
Due to the improved oxide quality and device fabrication



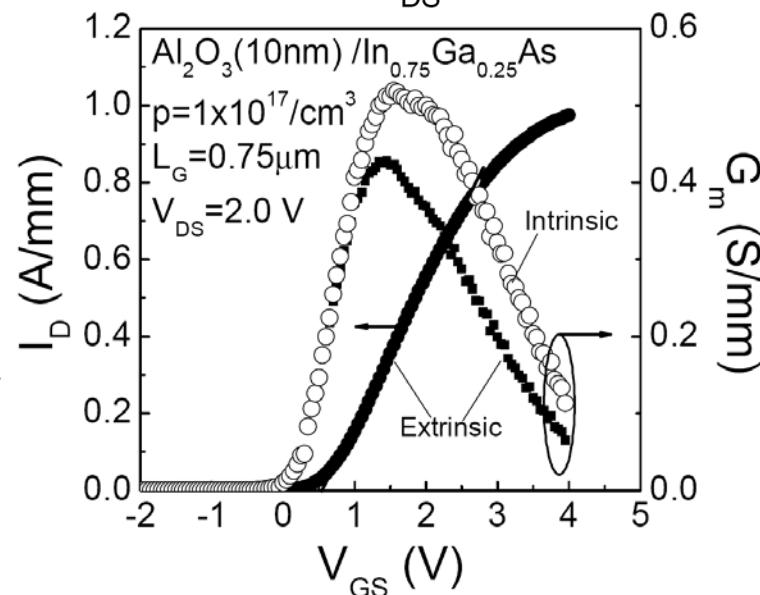
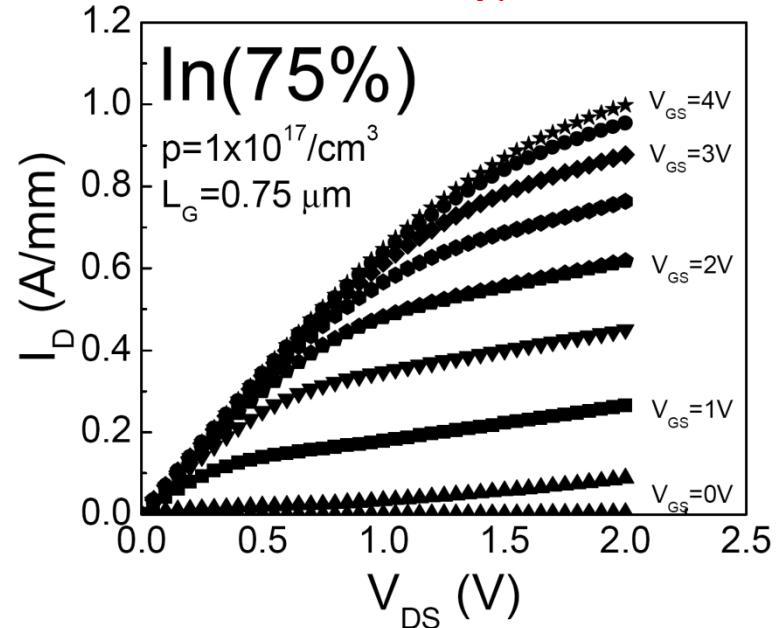
- $0.75 \times 50 \mu\text{m}^2$
- $g_m = 190 \text{ mS/mm}$
- $f_T = 7 \text{ GHz}$
- $f_{max} = 10 \text{ GHz}$
- $\mu = 470 \text{ cm}^2/\text{Vs}$

Ren et al, IEDM 1996, SSE  
1997, EDL 1997  
Wang et al, 1999

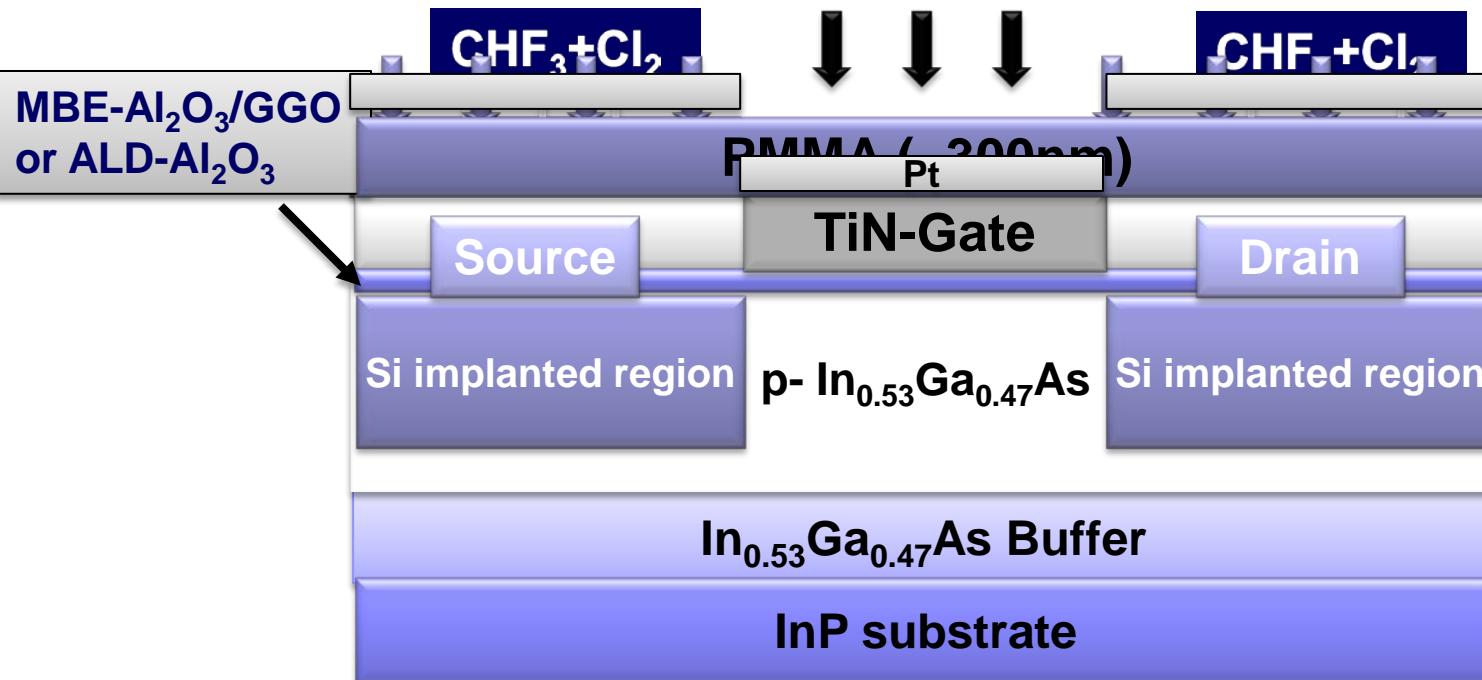
# Surface channel InGaAs MOSFET with non-self-aligned Process



- 1) NH<sub>4</sub>OH surface pretreatment
- 2) ALD Al<sub>2</sub>O<sub>3</sub> 30nm as an encapsulation layer
- 2) S/D patterning and Si implantation (30KeV/1E14 & 80KeV/1E14)
- 3) S/D activation using RTA (700-800 °C 10s in N<sub>2</sub>)
- 4) ALD re-growth: Al<sub>2</sub>O<sub>3</sub>
- 5) PDA: 400-600 °C 30s in N<sub>2</sub>
- 6) S/D contact patterning and Au/Ge/Ni ohmic metal evaporation and 400 °C metallization
- 7) Gate patterning and Ni/Au or Al/Au evaporation



# Self-aligned inversion-channel InGaAs MOSFET

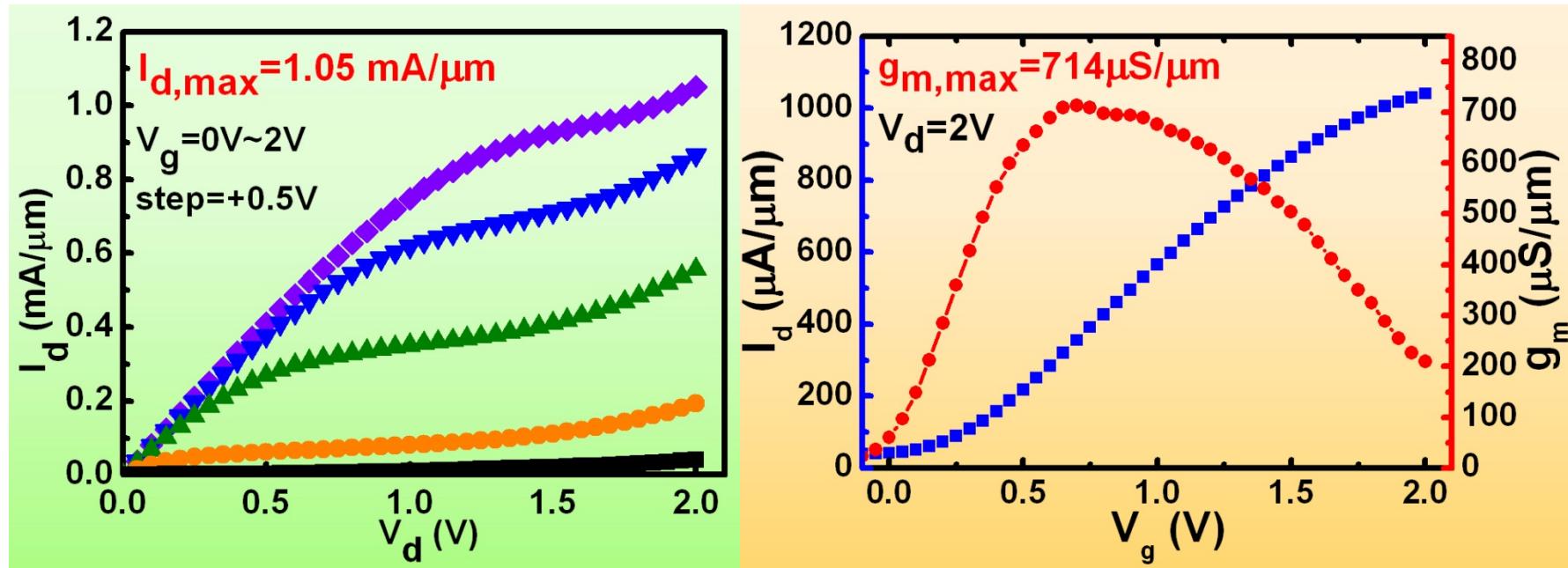


1. TiN sputtering
2. PMMA coating, E-beam writing, and hard mask deposition
3. Dry-etching
4. S/D patterning, implantation & activation
5. S/D contact region patterning, wet-etching of oxide, contact metal deposition, lift-off & ohmic alloying

# Output & Sub-threshold Characteristics

T. D. Lin et al, APL 93 033516 (2008)

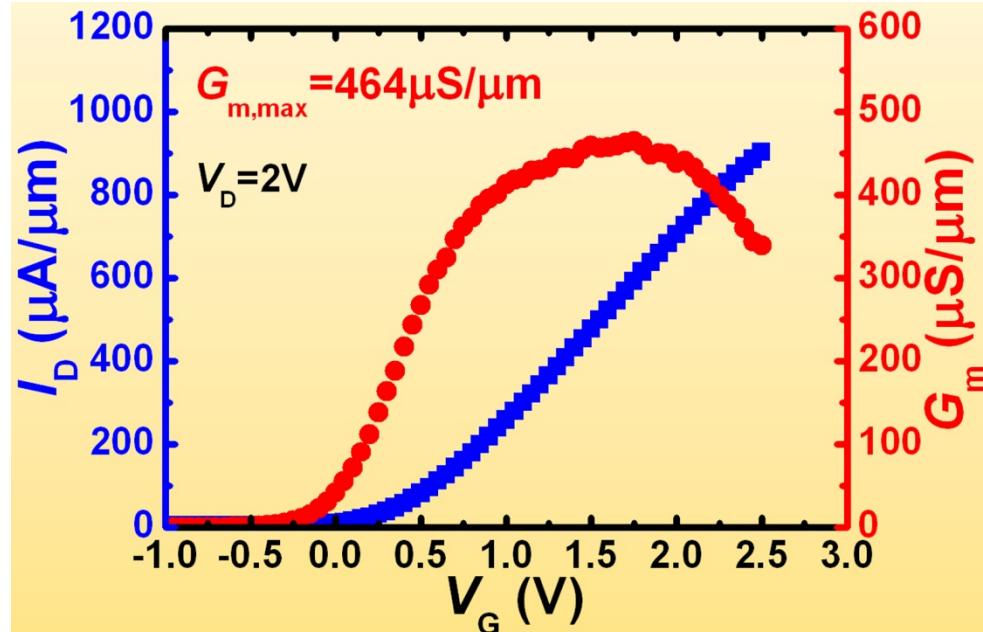
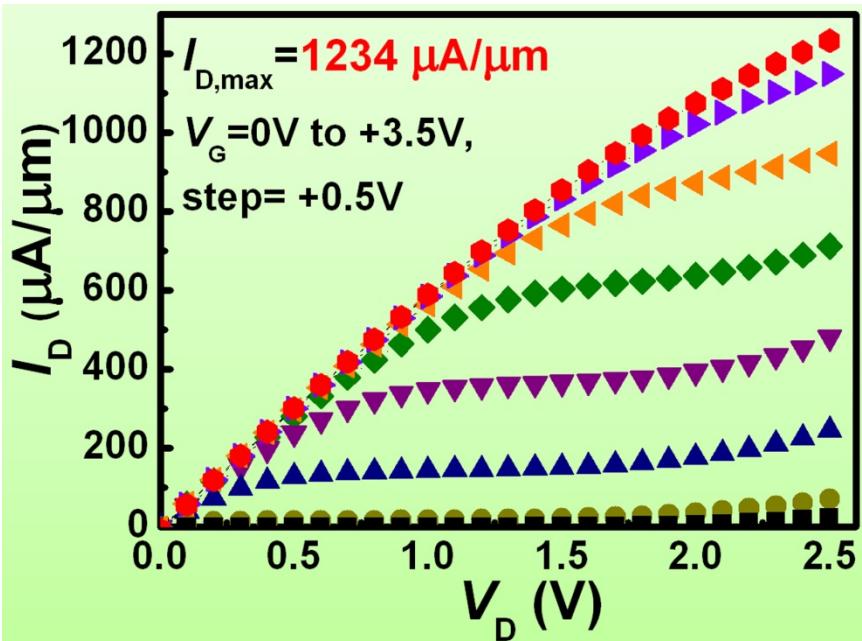
## Self-aligned inversion-channel TiN/Al<sub>2</sub>O<sub>3</sub>/GGO/In<sub>0.53</sub>Ga<sub>0.47</sub>As/InP MOSFET



1.  $t_{\text{TiN}} = 160\text{nm}$ ,  $t_{\text{Al}_2\text{O}_3} = 2\text{nm}$ ,  $t_{\text{GGO}} = 5\text{nm}$ ,  $W/L = 10/1\mu\text{m}$
2.  $I_{d,\max} = 1.05 \text{ mA}/\mu\text{m}$  @  $V_g = 2\text{V}$ ,  $V_d = 2\text{V}$
3.  $g_{m,\max} = 714 \mu\text{S}/\mu\text{m}$  @  $V_g = 0.7\text{V}$ ,  $V_d = 2\text{V}$
4.  $V_{\text{th}} \sim 0.2\text{V}$ ,  $\mu_{\text{FE}} = 1300 \text{ cm}^2/\text{V}\cdot\text{s}$  (from transconductance analysis)

Si NMOSFET  
90nm node  
 $L_g \sim 45\text{nm}$   
 $I_{d,\text{sat}} \sim 1 \text{ mA}/\mu\text{m}$

# UHV- $\text{Al}_2\text{O}_3/\text{GGO}/\text{In}_{0.75}\text{Ga}_{0.25}\text{As}/\text{InP}$ MOSFET



- $t_{\text{TiN}} = 200\text{nm}$ ,  $t_{\text{Al}_2\text{O}_3} = 3\text{nm}$ ,  $t_{\text{GGO}} = 6\text{nm}$ ,  $\text{W/L} = 10/1\mu\text{m}$
- $I_{D,\text{max}} = 1.23 \text{ mA}/\mu\text{m}$  @  $V_G = 3.5\text{V}$ ,  $V_D = 2.5\text{V}$
- $G_{m,\text{max}} = 464 \mu\text{S}/\mu\text{m}$  @  $V_G = 1.75\text{V}$ ,  $V_D = 2\text{V}$
- $V_{\text{th}} \sim 0.25\text{V}$ ,  $\mu_{\text{FE}} = 1600 \text{ cm}^2/\text{V}\cdot\text{s}$  (from transconductance analysis)

# E-mode III-V MOSFETs

## Benchmark



MBE-Al<sub>2</sub>O<sub>3</sub>/GGO/In<sub>0.75</sub>Ga<sub>0.25</sub>As  
 $L_g=1\mu\text{m}$

$I_D=1.23\text{ mA}/\mu\text{m}$ ,  
 $G_m=464\text{ }\mu\text{S}/\mu\text{m}$

T. D. Lin *et al.*, SSE, (2010)

MBE-Al<sub>2</sub>O<sub>3</sub>/GGO/In<sub>0.53</sub>Ga<sub>0.47</sub>As

$L_g=1\mu\text{m}$

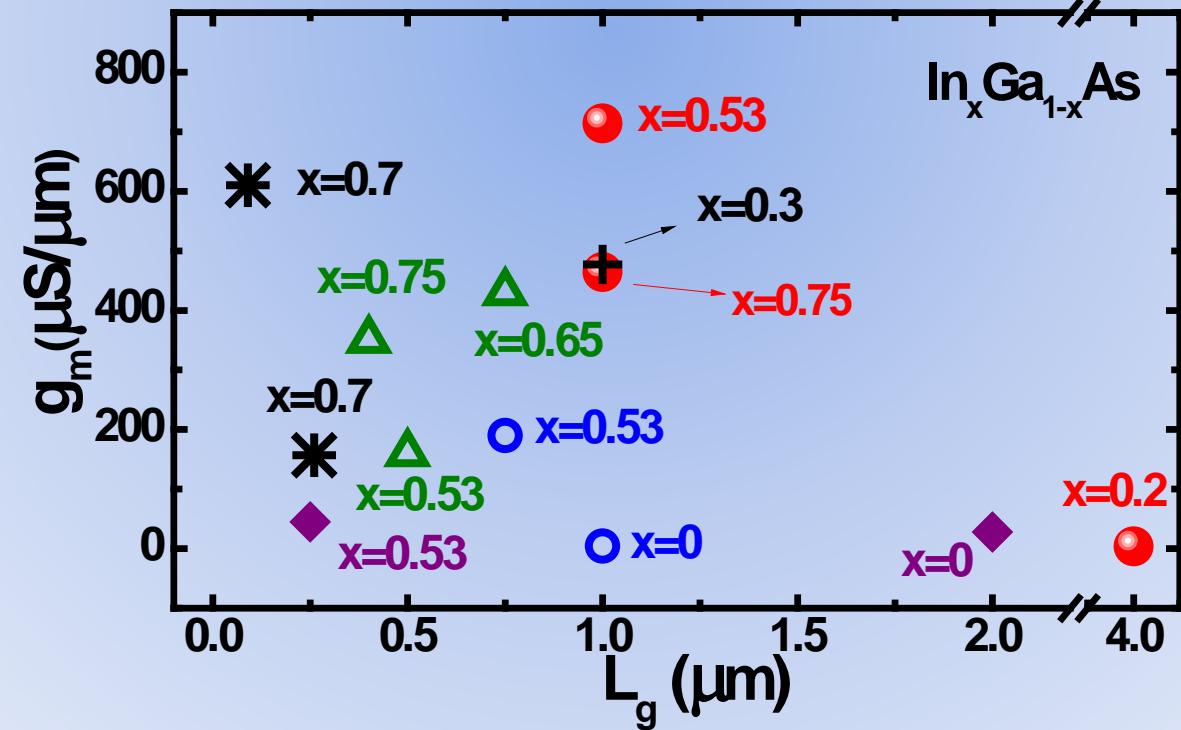
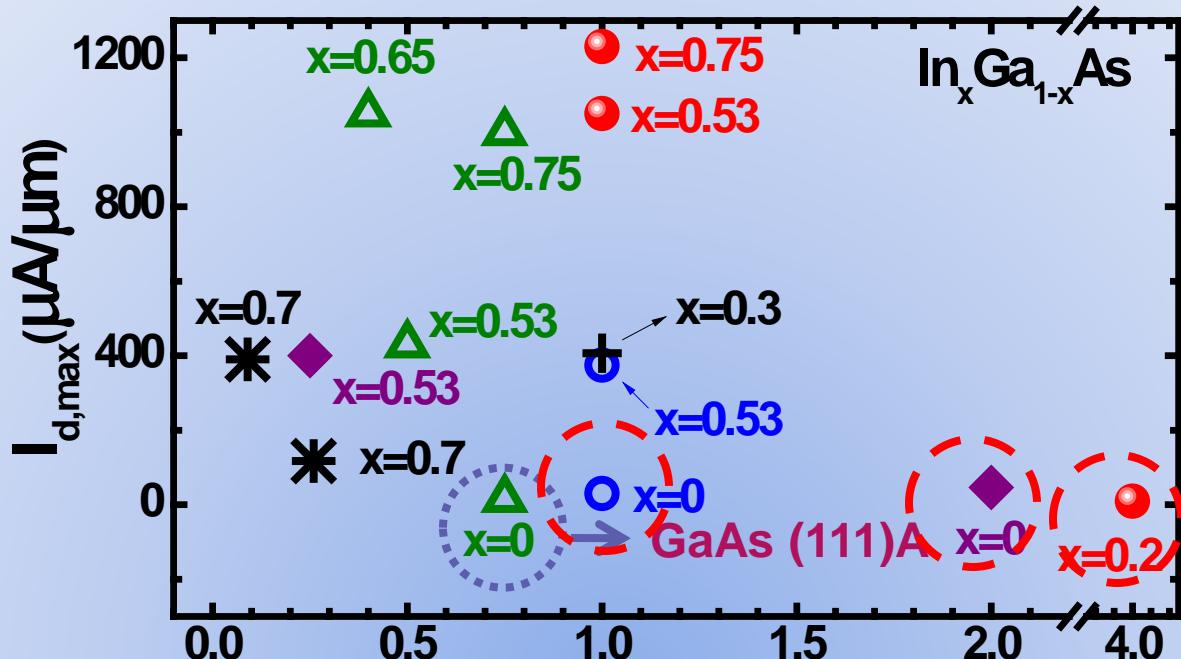
$I_D=1.05\text{ mA}/\mu\text{m}$ ,  
 $G_m=714\text{ }\mu\text{S}/\mu\text{m}$

T. D. Lin *et al.*, APL 93, 033516  
 (2008)

MBE-Al<sub>2</sub>O<sub>3</sub>/GGO/In<sub>0.2</sub>Ga<sub>0.8</sub>As

$L_g=4\mu\text{m}$

$I_D=9.5\text{ }\mu\text{A}/\mu\text{m}$ ,  
 $G_m=3.9\text{ }\mu\text{S}/\mu\text{m}$



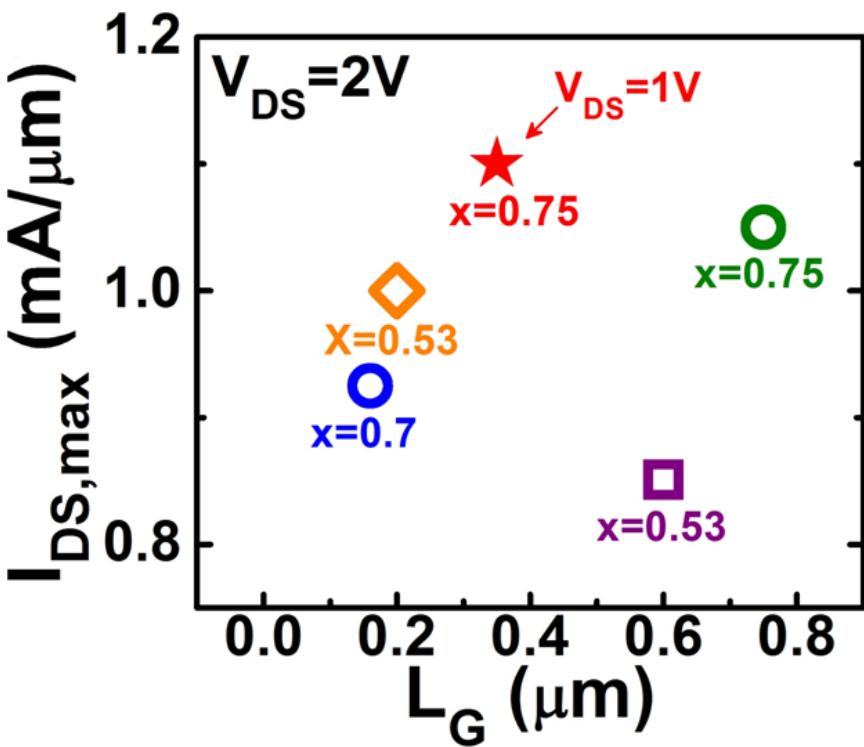
# Conclusion

- Perfecting the best atomic-scale hetero-structures and their interfaces in **high  $\kappa$**  and high carrier mobility semiconductors
- Probing them with the most powerful analytical tools (XPS and x-ray diffraction using synchrotron radiation, *in-situ* XPS, and HR-TEM)
- Producing novel, high-performance electronic devices ready for **beyond Si CMOS**

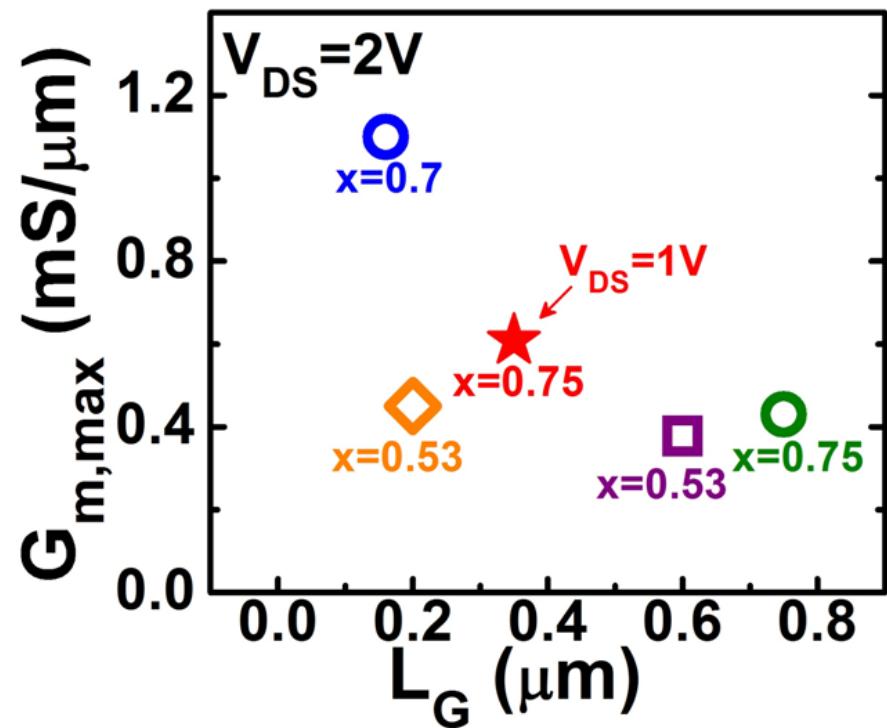
# Benchmark

## E-mode inversion-channel nMOSFETs with ALD or MOCVD oxide as gate dielectric

- Purdue Univ.
- Purdue Univ.
- ★ This work
- Singapore Univ.
- ◇ UCSB

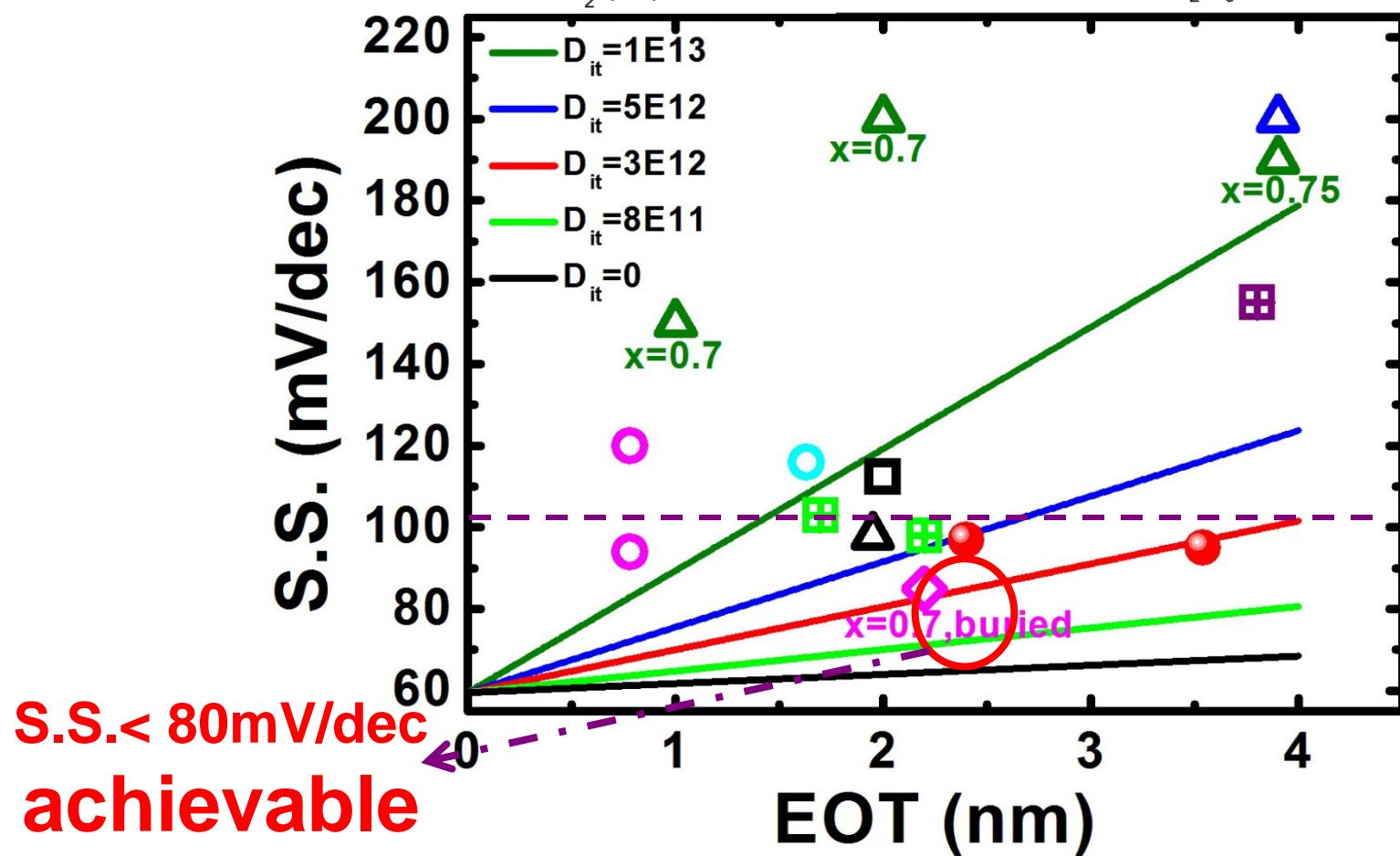


\*Devices with gate-length < 1 $\mu\text{m}$  are included. The number near each data point indicates the In content (x) of the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  channel.



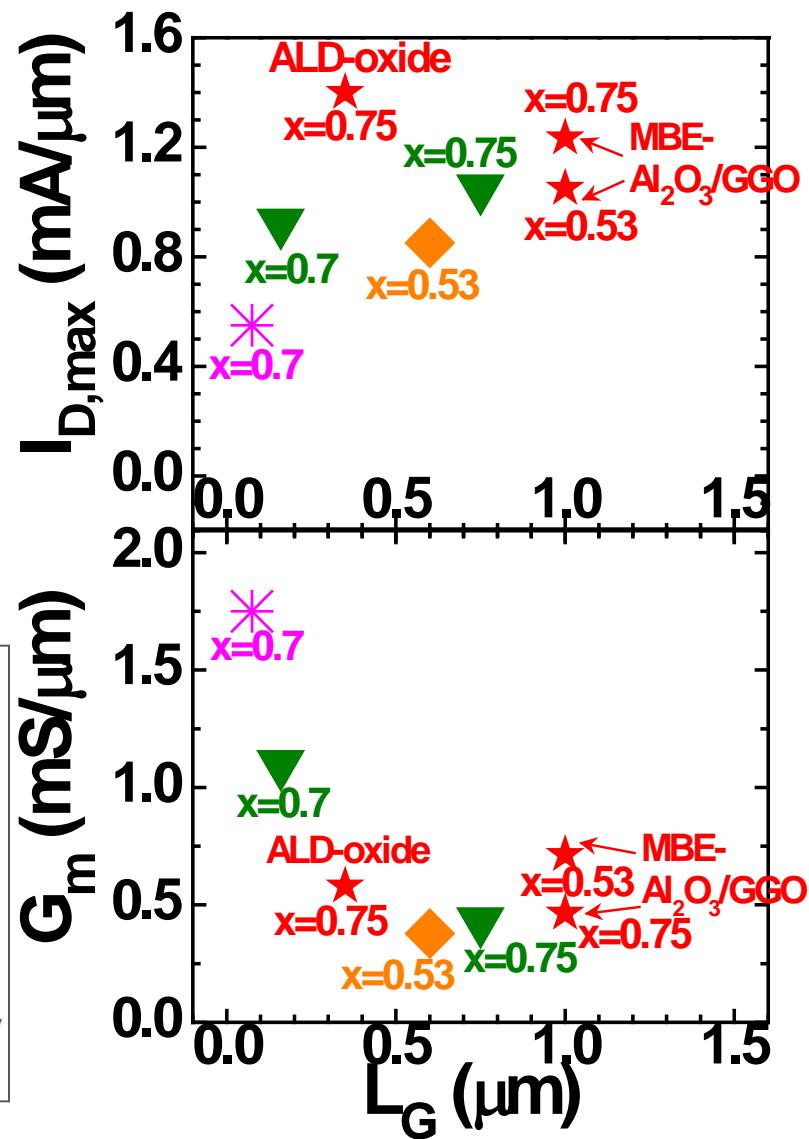
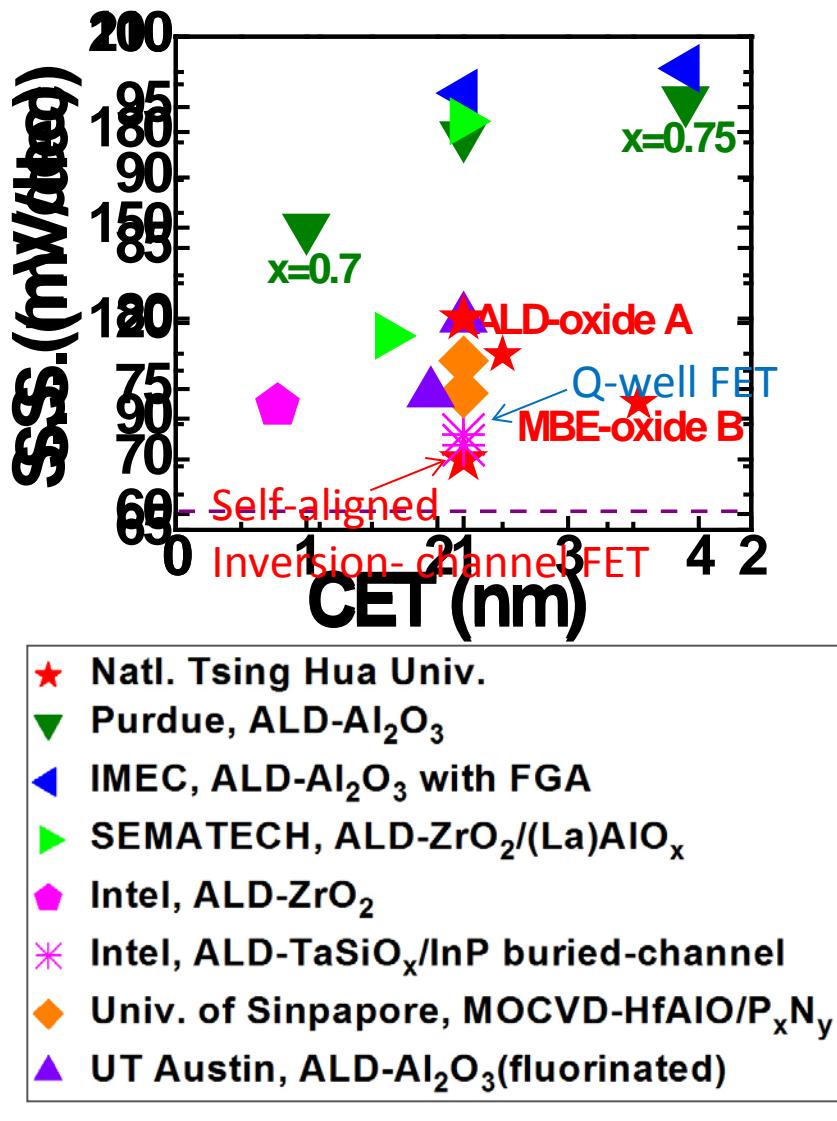
# Benchmark

- This Work
- ▲ Purdue, ALD- $\text{Al}_2\text{O}_3$
- △ IMEC, ALD- $\text{Al}_2\text{O}_3$  with FGA
- △ Purdue, ALD- $\text{Al}_2\text{O}_3$  with HBr treatment
- Intel, ALD-ZrO<sub>2</sub>
- SEMATECH, ALD-ZrO<sub>2</sub>/(La)AlOx
- ◊ Intel, ALD-TaSiOx/InP Buried-channel
- Singapore, MOCVD-HfO<sub>2</sub> with PH<sub>3</sub>-passivated
- Singapore, MOCVD-HfAlO/P<sub>x</sub>N<sub>y</sub>
- Singapore, MOCVD-HfAlO/SiO<sub>x</sub>N<sub>y</sub>(SiH<sub>4</sub>+NH<sub>3</sub>)
- UT Austin, ALD-HfO<sub>2</sub>(Fluorinated)
- △ UT Austin, ALD- $\text{Al}_2\text{O}_3$ (Fluorinated)

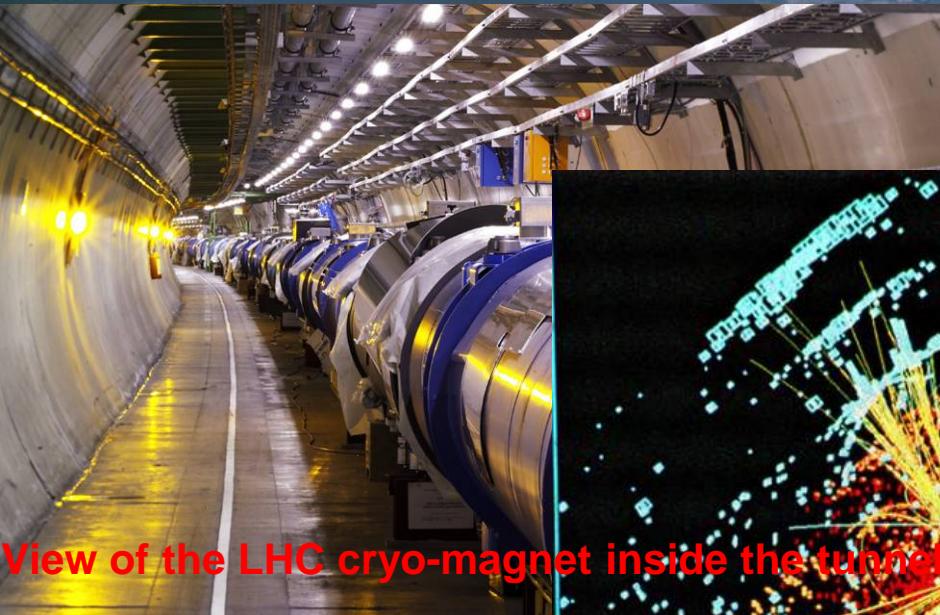


# Benchmark

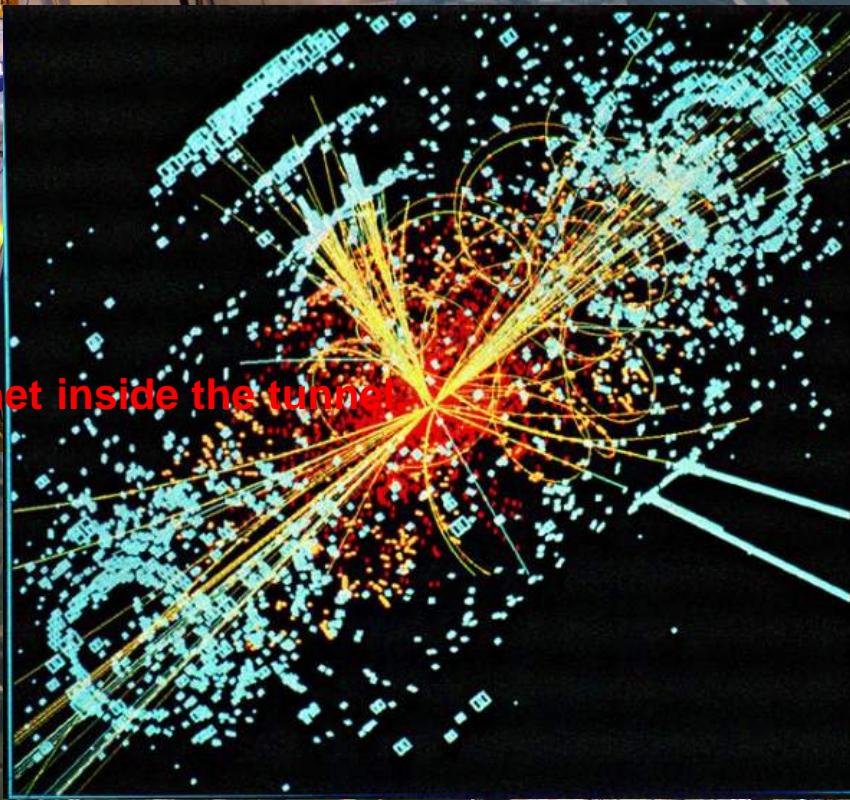
## Enhancement-mode $\text{In}_x\text{Ga}_{1-x}\text{As}$ MOSFETs



# Large Hadron Collider (LHC) Experiment



View of the LHC cryo-magnet inside the tunnel.



Aerial view of CERN and the surrounding region of Switzerland and France.



View of the ATLAS detector.